COMPUTATIONAL FLUID DYNAMICS MODELING WITH EXPERIMENTAL VALIDATION OF THE COMPLEX SPATIO-TEMPORAL PHENOMENA IN SLURRY BUBBLE COLUMN REACTORS FOR FISCHER-TROPSCH SYNTHESIS

by

Omar M. Basha

B.S. Chemical Engineering, Texas A&M University at Qatar, 2010
M.S. Chemical Engineering, Texas A&M University at Qatar, 2012

Submitted to the Graduate Faculty of
The Swanson School of Engineering in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Chemical Engineering

University of Pittsburgh

2016
This dissertation was presented

by

Omar M. Basha

It was defended on

November 4th, 2016

and approved by

Shiao-Hung Chiang, Ph.D., Professor Emeritus, Department of Chemical and Petroleum Engineering

George Klinzing, Ph.D., Professor, Department of Chemical and Petroleum Engineering

Ipsita Banerjee, Ph.D., Associate Professor, Department of Chemical and Petroleum Engineering

Patrick Smolinski, Ph.D., Associate Professor, Department of Mechanical Engineering and Materials Science

Isaac K. Gamwo, Ph.D., Senior Research Chemical Engineer, U.S. Department of Energy

Dissertation Director: Badie I. Morsi, Ph.D., Professor, Department of Chemical and Petroleum Engineering
A multiphase Eulerian, three-dimensional, computational fluid dynamics (CFD) model was developed and implemented in ANSYS, Fluent v14.5 to predict the local hydrodynamics and the overall performance of Slurry Bubble Column Reactors (SBCRs) for Fischer Tropsch (F-T) synthesis [1, 2]. The CFD model predictions were validated against the experimental gas holdup profiles obtained under ambient conditions by Yu and Kim [3] for air-water-glass beads system and by Chen et al. [4] for N₂-Drakeol-glass beads system. The model predictions were also validated against the overall gas holdup data for He/N₂ mixtures, as surrogates for H₂/CO, measured in a molten F-T reactor wax containing iron catalyst, under operating conditions typical to those of F-T synthesis in our pilot-scale SBCR, available in the Reactor and Process Engineering Laboratory (RAPEL) at the University of Pittsburgh. These validations, carried out in the absence of F-T reactions, showed that the inclusion of the RNG k-ε turbulence model, coupled with the gas-liquid drag model by Wen-Yu [5], the liquid-solid drag model by Schiller -Naumann [6] and the lift coefficient by Tomiyama et al. [7], along with our empirical mass transfer coefficients correlation into the CFD model, led to the most accurate predictions of the experimental data mentioned above.

The validated CFD model was then used to predict the effects of internals and spargers design on the local hydrodynamics in our pilot-scale (0.3-m ID, 3-m height) SBCR and the effects of internals on the local hydrodynamics in a larger-scale conceptual SBCR (1-m ID, 10-m height), in
the absence of F-T reactions. Moreover, the kinetic expressions for F-T and WGS reactions measured for iron catalyst provided by the National Institute for Clean-and-Low-Carbon Energy (NICE), China were incorporated into the validated CFD model and the subsequent model was then used to predict the local hydrodynamics and the overall performance of our pilot-scale SBCR and those of the commercial-scale (5.8-m ID, 30-height) SBCR by NICE. The simulation results are described in the following:

- In the absence of F-T reactions, the effect of parallel internals on the local hydrodynamics (gas holdup, liquid and gas velocity vectors, and mixing intensities) were predicted in the pilot-scale SBCR reactor, provided with a 6-arms spider gas sparger, using the CFD model. The simulation results showed that the presence of internals increased the gas holdup, the gas and liquid velocities and the turbulence intensities, and led to more even gas holdup radial distribution in the reactor. Also, larger liquid recirculation cells were present in the upper part of the reactor around the internals after 40 s, while smaller and faster liquid recirculation cells were present in the vicinity of the sparger.

- In the absence of F-T reactions, the effects of the gas sparger types and orifice orientations on the gas holdup, Sauter mean bubble diameter, axial concentration profiles, mean axial velocity profiles and flow structure were predicted in the pilot-scale SBCR, including no internals, using the CFD model. Three spargers (a 6-arms spider and a concentric ring sparger, both with upward- and downward-facing orifices, and a perforated plate) were used. The simulation results showed that the spargers with downward-facing orifices were more effective in solids dispersion and exhibited larger Sauter bubble diameters when compared with those of upward-facing orifices. The 6-arms spider spargers resulted in smaller Sauter bubble diameters when compared with those of the concentric ring spargers. For the spider spargers, faster and smaller
liquid recirculation cells appeared in the vicinity of the spargers, whereas, larger and slower liquid recirculation cells appeared after about 0.36-m measured from the bottom flange. For the concentric ring and perforated plate spargers, however, slower and larger liquid recirculation cells were present throughout the reactor starting at the top of the distributor.

- In the absence of F-T reactions, the effects of internals configuration (3 parallel and 4 bundled) on the gas holdup and liquid axial velocity were predicted in the large-scale conceptual SBCR using the CFD model. A concentric-ring sparger, consisting of 3 concentric-rings with 333, 167 and 111 identical (7-mm ID) orifices was used. The simulation results showed that using parallel internals led to faster and larger liquid recirculations at a much earlier time when compared with those using bundled internals. Liquid recirculations were stronger when using 1-bundled or 3-bundled internals than those when using a 4-bundled or 5-bundled internals; and the liquid backmixing profiles were governed by the clearance between the internals and the reactor’s wall. Also, using bundled internals exhibited smoother radial gas holdup profiles, with lower local gas holdup values, when compared with those using parallel internals.

- In the presence of F-T and WGS reaction kinetics with iron catalyst, the gas holdup, the Sauter mean bubble diameter and the performance (CO and H₂ conversions, and C₅⁺ products yield) of the pilot-scale SBCR, provided with one-bundled internals (one, 2.5-inch pipe at the center surrounded by six, 1.75-inch pipes in a hexagonal pattern) and a 6-arms spider sparger, were predicted using the CFD model. The simulations were carried out using catalyst concentrations of 5, 10 and 15 vol.% and H₂/CO ratios of 1, 1.5 and 2, at a pressure of 20.5 bar, a temperature of 443 K, and a superficial gas velocity of 0.24 m/s. The simulation results showed that the gas holdup and Sauter mean bubble diameter axial profiles in the presence of F-T reactions were different from those predicted in the absence of F-T chemical reactions. Also, the CO and H₂
conversions increased with increasing catalyst concentration; and our pilot-scale SBCR can produce a maximum yield of 1.87 tons/day of C₅⁺ products using a H₂/CO ratio of 2/1 and a catalyst concentration of 15 vol%.

- In the presence of F-T and WGS reaction kinetics with iron catalyst, the overall performances of the NICE commercial-scale F-T SBCR, provided with 604 bundled internals and a 12 concentric-ring spargers, were also predicted using the CFD model. The simulations were carried out at four superficial gas velocities of 0.12, 0.24, 0.3 and 0.4 m/s using a catalyst concentration of 10 vol%, a pressure of 29 bar, and a temperature of 528 K. Under these conditions, the simulation results showed that the CO conversions were 48%, 59%, 58% and 55%; the H₂ conversions were 36%, 51%, 56% and 54%; and the C₅⁺ products yields were 275, 576, 627 and 654 ton/day at the superficial gas velocities of 0.12, 0.24, 0.3 and 0.4 m/s, respectively.

Thus, our CFD model built and validated in this study for 3-phase non-reactive and reactive systems could be used to optimize the SBCR design and/or troubleshoot any problems associated with the internal reactor operation.
DESCRIPTORS

Absorption
Bubble size
Computational Fluid Dynamics
Dynamic Gas Disengagement
Fischer-Tropsch
Gas Holdup
Gas-Liquid Interfacial Area
Hydrodynamics
Multiphase Flow
Multiphase Modelling

Multiphase Reactors
Mass Transfer
Reactor Design
Reactor Modeling
Sauter Mean Bubble Diameter
Slurry Bubble Column Reactor
Statistical Experimental Design
Syngas
Volumetric Mass transfer Coefficient
TABLE OF CONTENTS

DESCRIPTORS ........................................................................................................... VIII

TABLE OF CONTENTS ............................................................................................... IX

LIST OF TABLES ......................................................................................................... XIV

LIST OF FIGURES ....................................................................................................... XVII

NOMENCLATURE ....................................................................................................... XXIV

ACKNOWLEDGEMENT ............................................................................................... XXX

1.0 INTRODUCTION ................................................................................................. 1

2.0 LITERATURE REVIEW ....................................................................................... 9

2.1 KINETIC STUDIES OF FISCHER-TROPSCH SYNTHESIS ............................... 9

2.2 HYDRODYNAMIC STUDIES IN F-T SBCR ..................................................... 13

2.2.1 Overall Gas Holdup ......................................................................................... 14

2.2.2 Radial Distribution of Gas Holdup ................................................................. 20

2.2.3 Sauter Mean Gas Bubbles Diameter ............................................................. 22

2.2.4 Bubble Dynamics ............................................................................................ 25

2.2.5 Bubble Rise Velocity ....................................................................................... 28

2.3 MASS TRANSFER STUDIES IN F-T SBCR ................................................... 30

2.4 HEAT TRANSFER STUDIES IN F-T SBCR ................................................... 37

2.4.1 Previous Studies Investigating Effect of Internals on BCR and SBCR
Performance .................................................................................................................. 37

2.5 MODELING OF SBCRS FOR F-T SYNTHESIS ............................................ 42

2.5.1 Axial Dispersion Models ................................................................................. 43
2.5.2 Multiple Cell Circulation Models .......................................................... 51
2.5.3 Computational Fluid Dynamics (CFD) Models ........................................ 56
     2.5.3.1 Commonly used drag coefficient models for two-phase and three-phase systems .......................................................... 64

3.0 RESEARCH OBJECTIVE ............................................................................. 68

4.0 CFD MODEL FORMULATION ..................................................................... 70

4.1 SOLID PHASE REPRESENTATION ............................................................. 72
4.2 TURBULENCE MODEL ............................................................................ 74
4.3 MOMENTUM EXCHANGE TERMS AND INTERPHASE COEFFICIENT CORRELATIONS ........................................................................ 75
4.4 BUBBLES REPRESENTATION ................................................................... 77
     4.4.1 Bubble Induced Turbulence ............................................................... 78
     4.4.2 Bubble Population Balance ............................................................... 79
4.5 KINETICS AND MASS TRANSFER .......................................................... 82
4.6 SOLUTION METHOD AND BOUNDARY CONDITIONS ............................. 83

5.0 CFD MODEL VALIDATION ......................................................................... 86

5.1 TESTING OF CFD MODEL USING AQUEOUS AIR-WATER-GLASS BEADS DATA BY YU AND KIM [3] ............................................................. 86
5.2 VALIDATION OF OUR CFD MODEL USING ORGANIC N2-DRAKEOL-GLASS BEADS DATA BY CHEN ET AL. [4] ........................................ 91
5.3 VALIDATION AGAINST OUR EXPERIMENTAL DATA OBTAINED FOR N2-F-T REACTOR WAX-IRON-BASED CATALYST SYSTEM ............... 93
     5.3.1 Experimental Setup ........................................................................... 93
     5.3.2 Gas-Liquid-Solid System and Operating Conditions Used ............... 100
          5.3.2.1 Gas Phase .................................................................................. 100
          5.3.2.2 Liquid Phase ............................................................................ 100
          5.3.2.3 Solid Phase ............................................................................. 104
5.3.2.4 Operating Conditions Used ................................................................. 104
5.3.3 Hydrodynamic and Mass Transfer Parameters in the Pilot Scale SBCR under F-T Conditions ........................................................................................................ 106
  5.3.3.1 Gas Holdup ............................................................................................... 106
  5.3.3.2 Sauter Mean Bubble Diameter .............................................................. 112
  5.3.3.3 Volumetric Mass Transfer Coefficients ............................................... 116
5.3.4 Geometry and Numerical Meshing of the Pilot-Scale SBCR ............... 120
5.3.5 Comparison between the CFD model predictions and our experimental data ....................................................................................................................... 123

6.0 CFD MODEL PREDICTIONS OF THE HYDRODYNAMICS INSIDE A SBCR ......................................................................................................................... 126

6.1 EFFECT OF THE GAS SPARGER TYPE ON THE LOCAL HYDRODYNAMICS IN THE PILOT-SCALE SBCR ................................................................. 126
  6.1.1 Effect of Sparger Design on the Gas Holdup Inside the Pilot-Scale SBCR . 130
  6.1.2 Effect of Sparger Design on the Liquid Recirculations inside the SBCR .... 137
  6.1.3 Effect of Sparger Design on the Liquid Turbulence Intensity inside the SBCR ....................................................................................................................... 141
  6.1.4 Effect of Sparger Orifices Orientation on the Local Hydrodynamics in the SBCR ................................................................................................................... 145
  6.1.5 Sensitivity Analysis of the Model Parameters ........................................... 154

6.2 EFFECTS OF INTERNALS ON THE LOCAL HYDRODYNAMICS IN SBCRS ......................................................................................................................... 157
  6.2.1 Effect of Internals in the Pilot-Scale Reactor on the Liquid Backmixing, Gas Holdup and Local Turbulence Intensity ...................................................... 158
  6.2.2 Effect of Parallel Internal Configurations on the Liquid Backmixing and Gas Holdup ......................................................................................................... 165
  6.2.3 Effect of Bundled Internal Configurations on the Gas Holdup and Liquid Backmixing in the Conceptual Reactor ......................................................... 170

6.3 CFD MODEL PREDICTIONS OF PERFORMANCE OF A PILOT- AND LARGE- SCALE SBCRS FOR F-T SYNTHESIS ......................................................... 177
6.3.1 Prediction of the Pilot-Scale SBCR Performance ............................................ 179

6.3.2 Effect of Incorporating Kinetics on the Local Hydrodynamics in the Pilot-
Scale SBCR .............................................................................................................. 182

6.3.3 Prediction of the Industrial-Scale SBCR Performance ................................. 187

7.0 CONCLUDING REMARKS ............................................................................... 190

APPENDIX A: LITERATURE REVIEW TABLES ............................................... 199

APPENDIX B: EXPERIMENTAL PROCEDURES AND CALCULATION
METHODS .................................................................................................................. 261

B.1 EXPERIMENTAL PROCEDURES ..................................................................... 261

B.1.1 \( \varepsilon_G \) Measurement .................................................................................. 261

B.1.2 \( d_{32} \) Measurement .................................................................................. 262

B.1.3 \( k_{La} \) Measurement .................................................................................. 262

B.2 CALCULATIONS .............................................................................................. 264

B.2.1 Peng-Robinson EOS ..................................................................................... 264

B.2.2 Equilibrium Solubility, \( C^* \) ............................................................... 266

B.2.3 Gas Holdup, \( \varepsilon_G \) ................................................................................... 266

B.2.4 Gas Bubbles Size (\( d_b \)) and the Sauter Mean Bubble Diameter (\( d_{32} \)) .... 268

B.2.5 Volumetric Liquid-Side Mass Transfer Coefficient, \( k_{La} \) ......................... 271

APPENDIX C: EFFECT OF OPERATING CONDITIONS ON THE GAS BUBBLES
DISTRIBUTION ........................................................................................................ 272

C.1 EFFECT OF PRESSURE ON GAS BUBBLES DISTRIBUTION ......................... 273

C.2 EFFECT OF SOLID CONCENTRATION ............................................................ 275

C.3 EFFECT OF TEMPERATURE .............................................................................. 277

C.4 EFFECT OF SUPERFICIAL GAS VELOCITY .................................................... 280

C.5 EFFECT OF GAS DENSITY ................................................................................ 281

APPENDIX D: COMPARISON WITH LITERATURE GAS HOLDUP AND SAUTER
BUBBLE DIAMETER DATA ...................................................................................... 283
APPENDIX E: CORRELATIONS OF THE HYDRODYNAMIC AND MASS TRANSFER PARAMETERS ......................................................... 291

E.1 OVERALL GAS HOLDUP CORRELATION ........................................ 291
E.2 SAUTER MEAN DIAMETER OF GAS BUBBLES CORRELATION ........ 293
E.3 HOLDUP OF LARGE GAS BUBBLES CORRELATION ................. 294
E.4 DIAMETER OF LARGE GAS BUBBLES CORRELATION ............. 295
E.5 VOLUMETRIC MASS TRANSFER COEFFICIENT CORRELATION .... 295
E.6 NOVEL APPROACH AND CORRELATION FOR BUBBLE SIZE DISTRIBUTION IN THE SBCR OPERATING IN THE CHURN-TURBULENT FLOW REGIME .............................................................. 297

REFERENCES .................................................................................. 311
LIST OF TABLES

Table 1-1: Commercial F-T plants, catalysts and reactor technologies [12, 32]..........................6
Table 2-1: Operating conditions used in the correlations for comparison purposes......................18
Table 2-2: Correlations for the physicochemical properties of the liquid phase [126]...............18
Table 2-3: Experimental work for measuring radial gas holdups in three phase reactors ..........21
Table 2-4: Summary of reported effects of operating conditions on the hydrodynamic mass transfer parameters........................................................................................................35
Table 2-5: Different turbulence models available in the literature [275].................................61
Table 4-1: Momentum interphase terms used in our model.................................................76
Table 4-2: Interphase coefficient expressions used in our model........................................77
Table 5-1: Experimental conditions by Yu and Kim [3] used for selecting of our CFD model parameters..................................................................................................................86
Table 5-2: Model equations for the three k-ε turbulence models used.................................88
Table 5-3: Absolute average relative errors (AARE) for different turbulence and drag G-L and L-S models against experimental data by Yu and Kim [3]........................................89
Table 5-4: Experimental details by Chen et al. [4]..................................................................92
Table 5-5: Comparison between average relative errors (ARE) and absolute average relative errors (AARE) between experimental results and CFD predictions.............................92
Table 5-6: Characteristics of the SBCR..................................................................................94
Table 5-7: Thermodynamic properties of the gases used.....................................................100
Table 5-8: Correlations for predicting the physicochemical properties of the reactor wax .......102
Table 5-9: Size distribution of the solid particles used.......................................................104
Table 5-10: Experimental conditions....................................................................................105
Table 6-1: Description of the spargers investigated in this work .................................................. 128
Table 6-2: Model performance against the radial gas holdup experimental data of ...................... 155
Table 6-3: Model performance against overall gas holdup data measured in our lab ............... 156
Table 6-4: Details of parallel internal configurations used in this study .................................... 166
Table 6-5: Details of bundled internal configurations used in this study ................................. 170
Table 6-6: F-T Catalyst and kinetics provided by NICE ................................................................. 177
Table 6-7: Syngas composition used in this investigation .............................................................. 177
Table 6-8: Design data for the pilot-scale and industrial-scale SBCRs ........................................ 179
Table A-1: Kinetics studies for the F-T synthesis on iron catalyst ............................................ 200
Table A-2: Kinetics studies for the WGS reaction on iron catalyst ............................................ 207
Table A-3: Kinetics studies for the Fischer-Tropsch synthesis on cobalt-based catalyst .......... 210
Table A-4: Literature data on the hydrodynamics and mass transfer in SBCRs using F-T liquids ........................................................ ........................................ 213
Table A-5: Gas holdup correlations for three-phase reactors available in literature ............ 214
Table A-6: Bubbles diameter correlations available in the literature ...................................... 221
Table A-7: Bubbles rise velocity correlations available in the literature ................................. 224
Table A-8: Gas-Liquid mass transfer correlations applicable to SBCRs ..................................... 227
Table A-9: Heat transfer correlations applicable to SBCRs ........................................................ 232
Table A-10: Liquid-phase axial dispersion coefficient models ..................................................... 236
Table A-11: Liquid-phase radial dispersion coefficient investigations ..................................... 239
Table A-12: Solid-phase dispersion coefficient models .............................................................. 240
Table A-13: Literature F-T SBCR empirical models [46, 126] .................................................. 241
Table A-14: Summary of multiple cell circulation models [285] ............................................. 244
Table A-15: CFD modeling of three-phase reactors ................................................................. 246
Table A-16: Commonly used gas-liquid drag models .............................................................. 255
Table A-17: Commonly used liquid-solid and gas-solid drag models .................................... 257
Table D-1: Gas holdup data sets used in the comparison in Figure D-1.................................287
Table D-2: Sauter bubble diameter data sets used in the comparison in Figure D-2.................290
Table E-1: Comparison among predictions of the gas holdup correlations ..........................292
Table E-2: Comparison among predictions of the gas bubbles Sauter mean diameter correlations .........................................................................................................................294
Table E-3: Comparison among predictions of the large gas bubbles holdup correlations.........294
Table E-4: Comparison among predictions of the large gas bubble diameter correlations .......295
Table E-5: Comparison among predictions of $k_{L\alpha}$ correlations....................................296
Table E-6: Forces involved in the overall energy balance for the gas bubble [272, 323, 336, 351, 372, 647] ........................................................................................................................295
LIST OF FIGURES

Figure 1-1: Overview of XTL process ...........................................................................................................2
Figure 1-2: Commercial F-T activities worldwide as of 2016 [12, 31, 36, 37] ................................. 3
Figure 1-3: Different F-T reactor technologies ..........................................................................................8
Figure 2-1: Comparison among F-T rate expressions at various H₂/CO ratios over Iron catalysts (T = 528 K and P = 3 MPa) ...........................................................................................................11
Figure 2-2: Comparison among F-T rate expressions at various H₂/CO ratios over Cobalt catalysts (T = 528 K and P = 3 MPa) ...........................................................................................................12
Figure 2-3: Comparison among WGS kinetic rate expressions at various H₂/CO ratios (T = 528 K and P = 3 MPa) .........................................................................................................................13
Figure 2-4: Comparison among literature gas holdup correlations at various (a) superficial gas velocities, (b) Catalyst particle diameters, (c) Solid loadings and (d) h_c/d_c values ........................................19
Figure 2-5: Comparison of various bubble diameter velocity correlations .............................................24
Figure 2-6: Comparison among various bubble rise velocity correlations .............................................29
Figure 2-7: Concentration profiles for mass transfer into a slurry with catalytic particles [46] ...31
Figure 2-8: Comparison among three-phase correlations for k_La at various (a) superficial gas velocities, (b) Catalyst particle diameters, (c) Solid loadings and (d) h_c/d_c values ........................................34
Figure 2-9: Comparison among the liquid axial dispersion models at various .................................50
Figure 2-10: Circulation cell depiction of the continuous-phase circulation patterns in BCRs and SBCRs: (a) Zehner [280, 281], (b) Groen et Al. [290], (c) Joshi And Sharma [256] ..................55
Figure 2-11: Overview of CFD process ......................................................................................................56
Figure 2-12: Comparison of various (a) Liquid-Solid and (b) Gas-Liquid drag correlation ............67
Figure 4-1: Schematic of the model components and their couplings ................................................70
Figure 5-1: Evaluation of various G-L and L-S drag model combinations using the standard k-ε ((a) to (c)) and the RNG k-ε ((d) to (f)) turbulence models against experimental data by Yu and Kim [3] .................................................................90
Figure 5-2: Geometry sketch and mesh of the column used by Chen et al. [4] ..................................92
Figure 5-3: Comparison between our CFD model predictions and the experimental radial gas holdup data by Chen et al. [4].............................................................................................................93
Figure 5-4: Mechanical Specifications of the SBCR ........................................................................97
Figure 5-5: Schematic of the Experimental Setup ..........................................................................98
Figure 5-6: Photographs of the SBCR and Gas Sparger .................................................................99
Figure 5-7: Wax composition in weight fraction .............................................................................101
Figure 5-8: Effect of temperature on the density (a), viscosity (b), surface tension (c) and vapor pressure (d) of the molten reactor wax .................................................................................103
Figure 5-9: CCSD experimental design matrix [8, 151, 365] .........................................................105
Figure 5-10: Effect of solids concentration on $\varepsilon_G$ in F-T reactor wax ..................................108
Figure 5-11: Effect of temperature on $\varepsilon_G$ in F-T reactor wax at 0-5 vol. % solid concentrations ...........................................................................................................................................108
Figure 5-12: Effect of temperature on $\varepsilon_G$ in F-T reactor wax at 10 vol. % solid concentrations 109
Figure 5-13: Effect of temperature on $\varepsilon_G$ in F-T reactor wax at 15 vol. % solid concentrations 109
Figure 5-14: Effect of pressure on $\varepsilon_G$ in F-T reactor wax .......................................................110
Figure 5-15: Effect of superficial gas velocity on $\varepsilon_G$ in F-T reactor wax ..................................110
Figure 5-16: Effect of gas density on $\varepsilon_G$ in F-T reactor wax ..................................................111
Figure 5-17: Effect of solids concentration on $d_{32}$ in F-T reactor wax .......................................113
Figure 5-18: Effect of temperature on $d_{32}$ in F-T reactor wax at 0 – 5 vol. % solid concentrations .................................................................................................................................................113
Figure 5-19: Effect of temperature on $d_{32}$ in F-T reactor wax at 10 vol. % solid concentrations .................................................................................................................................................114
Figure 5-20: Effect of temperature on $d_{32}$ in F-T reactor wax at 15 vol. % solid concentrations .................................................................................................................................................114
Figure 5-21: Effect of Pressure on $d_{32}$ in F-T reactor wax ..........................................................115
Figure 5-22: Effect of superficial gas velocity on $d_{32}$ in F-T reactor wax ....................................115
Figure 5-23: Effect of temperature on $k_{La}$ in F-T reactor wax at 0 – 5 vol. % solid concentrations .................................................................117

Figure 5-24: Effect of temperature on $k_{La}$ in F-T reactor wax at 10 vol. % solid concentrations .................................................................117

Figure 5-25: Effect of solids concentration on $k_{La}$ in F-T reactor wax .................................118

Figure 5-26: Effect of pressure on $k_{La}$ in F-T reactor wax ....................................................118

Figure 5-27: Effect of superficial gas velocity on $k_{La}$ in F-T reactor wax ................................119

Figure 5-28: (a) Picture and (b) Constructed geometry of the sparger used in this study ........120

Figure 5-29: Mesh Independence analysis ..............................................................................121

Figure 5-30: Geometry and mesh details of the numerical structure employed in our simulations: (a) Cross section view, (b) Side view in sparger vicinity, (c) Side view of whole column .......122

Figure 5-31: Time averaged CFD model validation vs. gas holdup data as a function of (a) temperature and (b) superficial gas velocity.................................................................124

Figure 5-32: Effect of mass transfer coefficients on our CFD model predictions of the gas holdup data under different operating conditions .................................................................125

Figure 6-1: (a) Picture and (b) Constructed geometry of the spider sparger used in this study .128

Figure 6-2: Geometry and mesh details of the spider sparger: (a) Cross-section view, ............128

Figure 6-3: Geometry and mesh details of the concentric-rings sparger: (a) Built geometry, ....129

Figure 6-4: Geometry and mesh details of perforated plate: (a) Cross-section view, ............129

Figure 6-5: Snapshots of gas holdup contours at different times for the spider sparger.........131

Figure 6-6: Snapshots of gas holdup contours at different times for the concentric-rings sparger .................................................................................................................................132

Figure 6-7: Snapshots of gas holdup contours at different times for the perforated plate .......133

Figure 6-8: Comparison of time averaged radial profiles of gas holdup at H/D = 0.5 for the three gas spargers used ..............................................................................................134

Figure 6-9: Comparison of time averaged radial profiles of gas holdup at H/D = 1 for the three gas spargers used ..............................................................................................134

Figure 6-10: Comparison of time averaged radial profiles of gas holdup at H/D = 2 for the three gas spargers used ..............................................................................................135
Figure 6-11: Comparison of time averaged radial profiles of gas holdup at H/D = 3 for the three gas spargers used.................................................................135

Figure 6-12: Comparison of time averaged radial profiles of gas holdup at H/D = 5 for the three gas spargers used.................................................................136

Figure 6-13: Comparison of time averaged radial profiles of gas holdup at H/D = 7 for the three gas spargers used.................................................................136

Figure 6-14: Snapshots of liquid velocity vectors at different times for the spider sparger .......138

Figure 6-15: Snapshots of liquid velocity vectors at different times for the concentric-rings sparger ...........................................................................................................139

Figure 6-16: Snapshots of liquid velocity vectors at different times for the perforated plate.....140

Figure 6-17: Snapshots of local turbulence intensity contours at different times for the spider sparger..................................................................................................................142

Figure 6-18: Snapshots of local turbulence intensity contours at different times for the concentric-rings sparger ..................................................................................................................143

Figure 6-19: Snapshots of local turbulence intensity contours at different times for the perforated plate ..................................................................................................................144

Figure 6-20: Effect of temperature on Eofr0.5 under the experimental conditions ..................146

Figure 6-21: Effect of sparger type and nozzles orientation on the gas holdup at different superficial gas velocities ..................................................................................................149

Figure 6-22: Effect of sparger type and nozzles orientation on the Sauter bubble diameter at different superficial gas velocities ..................................................................................................149

Figure 6-23: Comparison of axial solid loadings for different sparger nozzles orientations at u_g = 0.1 m/s .......................................................................................................150

Figure 6-24: Comparison of axial solid loadings for different sparger nozzles orientations at u_g = 0.2 m/s .......................................................................................................150

Figure 6-25: Comparison of axial solid loadings for different sparger nozzles orientations at u_g = 0.3 m/s .......................................................................................................151

Figure 6-26: Mean axial liquid velocity profiles at H/D = 1 for different gas spargers at u_g = 0.2 m/s .......................................................................................................152

Figure 6-27: Mean axial liquid velocity profiles at H/D = 3 for different gas spargers at u_g = 0.2 m/s .......................................................................................................153
Figure 6-28: Mean axial liquid velocity profiles at H/D = 6 for different gas spargers at $u_g = 0.2$ m/s ......................................................... 153

Figure 6-29: Geometry and mesh structure used in this section: Cross sectional view (a) and view in the vicinity of the sparger (b) ................................................................. 159

Figure 6-30: Snapshots of gas holdup contours at different times ........................................... 160

Figure 6-31: Snapshots of turbulence intensity contours at different times ..................... 162

Figure 6-32: Snapshots of liquid velocity vectors at different times ........................................ 163

Figure 6-33: Steady state Gas holdup (a), Local turbulence intensity (b) and liquid velocity vectors (c) of the pilot-scale reactor with vertically extended internals ........................................ 164

Figure 6-34: Liquid axial velocity cross-sectional contours at different heights for the parallel internals configurations at 30 s ................................................................. 164

Figure 6-35: Liquid axial velocity cross-sectional contours at different heights for the parallel internals configurations at 300 s ........................................................................ 167

Figure 6-36: Gas holdup cross-sectional contours at different heights for the parallel internals configurations at 30 s ................................................................. 168

Figure 6-37: Gas holdup cross-sectional contours at different heights for the parallel internals configurations at 300 s ........................................................................ 169

Figure 6-38: Liquid axial velocity cross-sectional contours at different heights for the bundled internals configurations at 30 and 300 s (1-m ID, 10-m high SBCR) .................................................................. 171

Figure 6-39: Liquid axial velocity cross-sectional contours at different heights for the bundled internals configurations at 30 and 300 s (1-m ID, 10-m high SBCR) .................................................................. 172

Figure 6-40: Gas holdup cross-sectional contours at different heights for the bundled internals configurations at 30 s (1-m ID, 10-m high SBCR) .................................................................. 173

Figure 6-41: Gas holdup cross-sectional contours at different heights for the bundled internals configurations at 300 s (1-m ID, 10-m high SBCR) .................................................................. 174

Figure 6-42: Axial Sauter mean bubble diameter for different internals configurations .......... 175

Figure 6-43: Effect of number of internal pipes and internals CSA coverage on the gas holdup .................................................................................................................... 176

Figure 6-44: Effect of number of internal pipes and internals CSA coverage on the liquid backflow fraction ........................................................................................................... 176

Figure 6-45: CFD model predictions of CO conversion for different H$_2$/CO ratios at different catalyst concentrations for F-T synthesis in the pilot-scale SBCR .............................................. 180
Figure 6-46: CFD model predictions of H₂ conversion for different H₂/CO ratios at different catalyst concentrations for F-T synthesis in the pilot-scale SBCR ........................................ 181

Figure 6-47: CFD model predictions of the C₅+ products yield for different H₂/CO ratios at different catalyst concentrations for F-T synthesis in the pilot-scale SBCR .......................... 181

Figure 6-48: Effect of coupling kinetics on the average Sauter mean bubble diameter in the .... 183

Figure 6-49: Effect of incorporating kinetics in the CFD model on the average gas holdup in the pilot-scale SBCR .......................................................... 184

Figure 6-50: Effect of incorporating kinetics in the CFD model on the gas holdup contours with and without chemical reaction at t = 60 s in the pilot-scale SBCR .............................. 185

Figure 6-51: Effect of incorporating kinetics in the CFD model on the liquid recirculation patterns with and without chemical reaction at t = 60 s in the pilot-scale SBCR ...................... 186

Figure 6-52: Geometry and mesh details of the industrial scale SBCR: (a) Cross-sectional view, (b) mesh structure ................................................................. 187

Figure 6-53: CFD model predictions of the CO conversion for different superficial gas velocities for F-T synthesis in the industrial-scale SBCR ..................................................... 188

Figure 6-54: CFD model predictions of H₂ conversion for different superficial gas velocities for F-T synthesis in the industrial-scale SBCR .......................................................... 189

Figure 6-55: CFD model predictions of the C₅+ products yield for different superficial gas velocities for F-T synthesis in the industrial-scale SBCR ................................. 189

Figure B-1: Dynamic Gas Disengagement in SBCR [619] ..................................................... 270

Figure C-1: Effect of pressure on bubble volume fraction ...................................................... 274

Figure C-2: Effect of pressure on bubble relative frequency .................................................. 275

Figure C-3: Effect of solid concentration on bubble relative frequency ................................. 276

Figure C-4: Effect of solid concentration on bubble relative frequency ................................. 277

Figure C-5: Effect of temperature on bubble volume fraction .............................................. 278

Figure C-6: Effect of temperature on bubble relative frequency ........................................... 279

Figure C-7: Temperature on the slurry density (a) and viscosity (b) at different solid concentrations ................................................................................. 279

Figure C-8: Effect of superficial gas velocity on bubble volume fraction .............................. 280

Figure C-9: Effect of superficial gas velocity on bubble relative frequency ............................ 281
Figure C-10: Effect of gas density on bubble volume fraction ..................................................282
Figure C-11: Effect of gas density on bubble relative frequency ........................................282
Figure D-1: Comparison of measured gas holdup data with published data sets in the literature (Details provided in Table 7) ..................................................................................286
Figure D-2: Comparison of measured Sauter bubble diameter data with published data sets in the literature ................................................................................................................289
Figure E-1: Comparison between experimental data and predicted gas holdup values using Equation (E-1) ..........................................................................................................................293
Figure E-2: Comparison between experimental data and predicted $k_{La}$ values using ........296
Figure E-3: Pressure drop change with time as obtained from three DGD experiments ........300
Figure E-4: Bubbles volume fraction distributions from the DGD under different operating conditions ............................................................................................................................304
Figure E-5: Bubbles relative frequency distributions from the DGD under different operating conditions ............................................................................................................................305
Figure E-6: Comparison between experimental and predicted values of the mean bubble diameter .................................................................................................................................308
Figure E-7: Comparison between experimental and predicted values of the bubble size variance .................................................................................................................................309
Figure E-8: Comparison between experimental and predicted values of the Sauter bubble diameter using Equation (E-21) .................................................................................................310
NOMENCLATURE

\( a \)  Interfacial area

\( A_b \)  Heat exchange surface, bed side (m\(^2\))

\( A_f \)  Relative free cross-sectional area

\( A_m \)  log mean of \( A_b \) and \( A_u \) (m\(^2\))

\( A_u \)  Heat exchange surface, heat transfer medium side (m\(^2\))

\( C^* \)  Equilibrium concentration (solubility) in the liquid phase (mol·m\(^{-3}\))

\( C_D \)  Drag Coefficient

\( C_L \)  Concentration in the liquid phase (mol·m\(^{-3}\))

\( C_s \)  Concentration of solid particles in the slurry phase (wt.\%)

\( C_{s,0} \)  Solid Concentration at the bottom of the reactor (kg·m\(^{-3}\))

\( C_P \)  Concentration of solid particles in the slurry phase (kg·m\(^{-3}\))

\( C_V \)  Volumetric concentration of solid particles in the slurry phase (vol.\%)

\( d_C \)  Column diameter (m)

\( d_o \)  Sparger orifice diameter (m)

\( d_p \)  Particle diameter (m)

\( d_R \)  Diameter of internal pipe (m)

\( d_t \)  Tube/Column diameter (m)

\( d_{32} \)  Sauter mean bubble diameter (m)

\( D_{AB} \)  Diffusivity of phase A into B
\( D_{ea} \)  Effective diffusivity in the axial direction
\( D_{ra} \)  Effective diffusivity in the radial direction
\( D_{rl} \)  Radial dispersion coefficient in SBCR
\( D_{zl} \)  Axial dispersion coefficient in SBCR
\( Eö \)  Eötvös number
\( f \)  Friction factor
\( F_c \)  Particle collision force (N)
\( F_D \)  Drag force (N)
\( F_k \)  Interphase momentum exchange (N\cdot s)
\( F_{lm} \)  Suspension inertial force (N)
\( F_L \)  Lift force (N)
\( F_P \)  Continuous phase pressure gradient force (N)
\( Fr \)  Froude number
\( F_{VM} \)  Virtual mass force (N)
\( g \)  Gravitational acceleration, m/s\(^2\)
\( G \)  Mass flow rate (kg/m\(^2\)\cdot s)
\( Ga \)  Galileo number
\( h \)  Reactor height (m)
\( h_C \)  Column height (m)
\( h_{tot} \)  Mean total enthalpy (kJ/mol)
\( \Delta H \)  Enthalpy (kJ/mol)
\( J_k \)  Flux
\( k \)  Turbulent kinetic energy (J/mol)
\( k_L a \) Volumetric liquid side mass transfer coefficient (1/s)

\( k_{WGS} \) WGS reaction rate constant (units depend on rate expression)

\( K_L \) Thermal conductivity (W/m·K)

\( l \) Packing height (m)

\( l_e \) Characteristic length scale of the eddies

\( M_W \) Molecular weight (kg·kmol\(^{-1}\))

\( n_R \) Number of internals

\( P \) Pressure (Pa)

\( P_s \) Saturation vapor pressure (Pa)

\( Pe \) Peclet number

\( P_m \) Specific energy of dissipation per unit mass (J/kg)

\( Pr \) Prandtl number

\( P_V \) Liquid-phase vapor pressure, bar

\( r \) Reaction rate (mol·kg\(^{-1}\)catalyst·s\(^{-1}\))

\( R \) Reaction term (mol·m\(^{-3}\)·s\(^{-1}\))

\( Re \) Reynolds number

\( S \) Particle surface area per unit volume (m\(^2\)/m\(^3\))

\( Sc \) Schmidt number

\( Sh \) Sherwood number

\( t \) Time (s)

\( t_R \) Tube pitch

\( T \) Temperature (K)

\( u_b \) Gas bubble rise velocity (m·s\(^{-1}\))

\( u_G \) Superficial gas velocity (m·s\(^{-1}\))
Overall heat transfer coefficient (kJ/m$^2$\cdot s\cdot °C)

Linear flow velocity (m/s)

Radial momentum transfer coefficient (m$^2$/s)

Kinematic slurry viscosity (m$^2$/s)

Eulerian control volume fixed in space and time

Weight fraction of the primary liquid in the mixture (See Behkish et al. [8])

Mole fraction of gas component, -

**Greek Letters**

Heat transfer coefficient on the bed side (kJ/m$^2$\cdot s\cdot °C)

Phase volume fraction

Heat transfer coefficient, heat transfer medium side (kJ/m$^2$\cdot s\cdot °C)

Gas sparger coefficient (See Behkish et al. [9])

Turbulence dissipation (J/kg\cdot s)

Gas holdup

Liquid holdup

Kinematic viscosity (m$^2$/s)

Coefficient of bulk viscosity

Dimensionless radial position at maximum downward liquid velocity

Effective axial coefficient of thermal conductivity

Static contribution of effective thermal conductivity (kJ/m$^2$\cdot s\cdot °C)

Coefficient of thermal conductivity of fluid (kJ/m$^2$\cdot s\cdot °C)

Coefficient of thermal conductivity of packed bed with flowing fluid (kJ/m$^2$\cdot s\cdot °C)
\( \lambda^0_p \) Coefficient of thermal conductivity of packed bed with stagnant fluid (kJ/m\(^2\cdot\)s\(^\circ\)C)

\( \lambda_{ra} \) Effective radial coefficient of thermal conductivity

\( \lambda_s \) Coefficient of thermal conductivity of packing material (kJ/m\(^2\cdot\)s\(^\circ\)C)

\( \mu \) Viscosity kg/m\cdot s

\( \mu_b \) Relative apparent bed viscosity

\( \mu_T \) Turbulent or eddy viscosity

\( u \) Local velocity of the dispersed phase

\( \xi \) Dimensionless radial position

\( \pi \) 3.14

\( \rho \) Density (kg/m\(^3\))

\( \sigma \) Surface tension (N/m)

\( \tau \) Viscous stress tensor (Pa)

\( \tau_{rz} \) Reynolds shear stress

\( \phi \) Body source per unit mass

**Subscripts**

- \( g \text{ or } G \) Gas
- \( k \) Phase
- \( l \) Liquid
- \( s \) Solid
- \( w \) Wall

**Acronyms**
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADM</td>
<td>Axial-Dispersion Model</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>CSA</td>
<td>Cross Sectional Area</td>
</tr>
<tr>
<td>CTL</td>
<td>Coal to Liquid</td>
</tr>
<tr>
<td>F-T</td>
<td>Fischer Tropsch</td>
</tr>
<tr>
<td>GTL</td>
<td>Gas to Liquid</td>
</tr>
<tr>
<td>L-H</td>
<td>Langmuir-Hinshelwood</td>
</tr>
<tr>
<td>MCM</td>
<td>Mixing-Cell Model</td>
</tr>
<tr>
<td>SDM</td>
<td>Sedimentation-Dispersion Model</td>
</tr>
<tr>
<td>WGS</td>
<td>Water Gas Shift</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENT

First and foremost, I want to thank my advisor Dr. Badie I. Morsi, who has been a tremendous mentor and inspiration for me, and to whom I will always be deeply grateful for his advice and guidance, both academically and personally. I would like to thank Dr. George Klinzing for encouraging my research and for his help and support throughout the past few years. I would also like to thank my committee members, Dr. Shiao-Hung Chiang, Dr. Ipsita Banerjee, Dr. Isaac Gamwo and Dr. Patrick Smolinski for serving on my committee and for their comments and suggestions.

Thanks to all the students, members and staff of the Reactor and Process Engineering Laboratory and the Department of Chemical and Petroleum Engineering at the University of Pittsburgh. I would like to acknowledge Dr. Laurent Sehabiague for his help and support in performing the experimental part of my thesis and for his guidance when I first arrived at the lab. Also, I want to acknowledge the long term, not only financial, support provided by The National Institute of Clean-and-Low-Carbon Energy (NICE).

Finally, I would like to thank my family, to whom I will always be indebted.
1.0 INTRODUCTION

Fischer-Tropsch (F-T) synthesis provides a pathway for converting carbon containing natural resources, such as natural gas, coal, heavy residue, biomass, municipal waste, etc., into liquid fuels and high value chemicals. Initially called “Synthol,” the F-T synthesis was developed in the 1920’s in Germany at the Kaiser Wilhelm Institute by two Germans, Franz Fischer and Hans Tropsch [10-14], with the intent of producing synthetic hydrocarbons based on the 1902 discovery by Sabatier and Senderens [15] that methane can be produced from H\textsubscript{2} and CO in the presence of nickel catalyst.

The overall F-T process involves three main steps: syngas generation, F-T catalytic reactions and product upgrading, as shown in Figure 1-1. Syngas generation involves converting the carbonaceous feedstock into a H\textsubscript{2}-CO mixture (synthesis gas, known as syngas) via reactions with steam and optionally air or oxygen. Solid feedstocks, such as coal and biomass, are converted in a gasifier, of which various types have been already in industrial applications [16-19]. Different gasification processes and technologies have also been discussed in the literature [13, 20-30]. Natural gas, on the other hand, is converted to syngas in a reformer using either partial oxidation (POX), steam methane reforming (SMR) or auto-thermal reforming (ATR).
Current worldwide commercial activities are summarized in Figure 1-2. As of 2016, the global commercial F-T capacity is 402,500 barrels per day (bpd), with an additional 216,000 bpd under construction. Although numerous planned F-T activities and plants have been put on hold or delayed due to the 2014 slump in oil prices [31, 32], there remains a significant and increased interest in GTL and CTL commercialization, once the oil market stabilizes [33-35].
Figure 1-2: Commercial F-T activities worldwide as of 2016 [12, 31, 36, 37]
In F-T synthesis, the syngas reacts in the presence of a heterogeneous catalyst to produce a wide range of hydrocarbon products, primarily linear alkanes and alkenes. Although many metals have been identified to catalyze the F-T reactions, only iron (Fe) and cobalt (Co) have been used in industrial applications [18, 30]. Iron catalyst is cheap and has a high water-gas-shift (WGS) activity, however, it is prone to severe attrition and the water produced during the reaction appeared to decrease its activity [12, 38]. Cobalt-based catalyst, on the other hand, has higher activity than iron catalyst since it is not strongly inhibited by water. It also has longer life than iron catalyst as it is more resistant to attrition. Cobalt-based catalyst, however, is more expensive and has no WGS activity [12, 39].

During Cobalt catalyzed F-T reaction, the oxygen from CO dissociation is converted to H$_2$O, as shown in Equation (1-1). Conversely, Iron catalyst has a high affinity for the WGS reaction as shown in Equation (1-2), resulting in the conversion of a significant portion of the oxygen from CO dissociation into CO$_2$.

\[ F - T: \quad CO + 2H_2 \rightarrow \text{-CH}_2\text{-} + H_2O \tag{1-1} \]

\[ \text{WGS:} \quad CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{1-2} \]

Thus, the extent of the WGS reaction has to be closely considered as it affects the H$_2$/CO ratio in the F-T process.

In the case of gas-to-liquid (GTL) applications, the produced syngas is highly rich in H$_2$ and any additional H$_2$ via the WGS reaction is undesirable. In contrast, carbon-rich feedstocks, such as coal or biomass, produce a CO-rich syngas; and would therefore require an extent of WGS in the F-T reactor. Hence, industrial GTL plants have conventionally used cobalt-based catalysts, such as the Shell (Pearl) and the Sasol (Oryx) plants in Qatar, whereas the coal-to-liquid (CTL)
plants usually use iron-based catalysts, such as the Sasol Synfuels complex in Secunda, South Africa and the planned CTL plants in China [30, 32, 40].

The F-T process configuration could ultimately dictate the type of the catalyst to be used for GTL or CTL applications. For instance, if the process is configured for recycling CO₂ or CO₂-rich tailgas to the methane reformer, this will lower the H₂/CO ratio and will allow the use of iron catalyst in GTL applications. Similarly, if the process is configured for a sour shift of the syngas from the gasifier over Cu/ZnO catalyst, followed by an acid gas (CO₂ and H₂S) removal, this will allow the use of cobalt in CTL applications. Various process configurations for Anything-to-Liquid (XTL) plants can be found elsewhere [12, 21, 32, 41-45].

Depending on the reaction temperature, the F-T process is referred to as low temperature F-T (LTFT) or high temperature F-T (HTFT). The temperature of the LTFT ranges from 180 to 260 °C and the syncrude produced is wax consisting mostly of long chain hydrocarbons, while the temperature of the HTFT process is between 290 and 360 °C and the products are mostly short chain hydrocarbons and gases. Therefore, the final products of the LTFT process consist mostly of diesel fuel, while gasoline production has been the focus of the HTFT [11]. The LTFT syncrude product is easy to upgrade by a hydroprocessing step and a fractionation step to obtain naphtha and middle distillate, whereas the HTFT syncrude requires more complex refinery facilities [11]. It should be noted that recent R&D and large-scale commercial efforts have been focused on the LTFT due to the current drive for using more diesel engines than gasoline engines, the excellent quality of sulfur-free F-T diesel, and perhaps the mild conditions of the process.

Reactor technologies used for commercial applications of the F-T synthesis are summarized in Table 1-1 and depicted in Figure 1-3. The HTFT reactors include fixed fluidized-bed reactors (FFBRs) and circulating fluidized-bed reactors (CFBRs), whereas multi-tubular
fixed-bed reactors (FBRs) and slurry bubble column reactors (SBCRs) are used for the LTFT process. Also, LTFT micro-channel reactors for small-scale applications have been recently receiving increasing attention, even though, no commercial applications are yet available.

Table 1-1: Commercial F-T plants, catalysts and reactor technologies [12, 32]

<table>
<thead>
<tr>
<th>F-T Plant</th>
<th>Country</th>
<th>Date of Operation</th>
<th>Reactor Technology</th>
<th>Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTL</td>
<td>Germany</td>
<td>1935-1962</td>
<td>LTFT FB</td>
<td>Co/ThO₂/kieselguhr (100:18:100) before 1938 Co/ThO₂/MgO/kieselguhr (100:5:8:200) after 1938</td>
</tr>
<tr>
<td>Hydrocol GTL</td>
<td>USA</td>
<td>1951-1957</td>
<td>HTFT FFB</td>
<td>Fused Fe₃O₄/Al₂O₃/K₂O (97:2.5:0.5) Later replaced by natural magnetite with 0.5% K₂O</td>
</tr>
<tr>
<td>Sasol I CTL/GTL</td>
<td>South Africa</td>
<td>1955-present</td>
<td>HTFT CFB LTFT FB LTFT SBCR</td>
<td>Magnetite with 0.5% K₂O (same as Hydrocol GTL) Precipitated Fe/SiO₂/K₂O/Cu (100:25:5:5) Precipitated Fe/SiO₂/K₂O/Cu (100:25:5:5)</td>
</tr>
<tr>
<td>Sasol Synfuels CTL</td>
<td>South Africa</td>
<td>1980-present</td>
<td>HTFT FFB</td>
<td>Fused Fe (similar to Sasol I HTFT CFB catalyst)</td>
</tr>
<tr>
<td>PetroSA GTL</td>
<td>South Africa</td>
<td>1992-present</td>
<td>HTFT CFB LTFT SBCR</td>
<td>Fused Fe (same as Sasol Synfuels) Co based catalyst</td>
</tr>
<tr>
<td>Shell Bintulu</td>
<td>Malaysia</td>
<td>1993-present</td>
<td>LTFT FB</td>
<td>Co/Zr/SiO₂</td>
</tr>
<tr>
<td>Sasol Oryx GTL</td>
<td>Qatar</td>
<td>2007-present</td>
<td>LTFT SBCR</td>
<td>Co/Pt/Al₂O₃</td>
</tr>
<tr>
<td>Shell Pearl GTL</td>
<td>Qatar</td>
<td>2011-present</td>
<td>LTFT FB</td>
<td>Co/Zr/SiO₂</td>
</tr>
<tr>
<td>Escravos GTL</td>
<td>Nigeria</td>
<td>2014-present</td>
<td>LTFT SBCR</td>
<td>Co/Pt/Al₂O₃</td>
</tr>
</tbody>
</table>

In multi-tubular FBRs, the syngas flows through small diameter tubes packed with catalyst at small voidage, resulting in a high pressure drop and an increased operating cost. These reactors have comparatively complex heat transfer characteristics and their maximum production capacity
is limited by the amount of heat which can be removed. Hot spots would ultimately result in carbon deposits on the catalyst surfaces and serious plugging of the reactor tubes. These types of reactors, however, have been used to carry out LTFT by both Germany during WWII and Sasol since 1950’s as well as by Shell at the Bintulu GTL (Malaysia) and more recently at the Pearl GTL (Qatar) [12, 20, 32, 46, 47].

SBCRs, on the other hand, have a simpler design and allow for much higher heat removal efficiencies than multi-tubular FBRs due to the presence of a large volume of the liquid-phase. Its advantages include a much greater flexibility than FBRs and its capital cost is 20 - 40% lower than that of a multitubular FBRs [48]. However, the high mechanical shear on the catalyst resulting in particles attrition and the lack of a reliable system for the fine particles separation from the liquid products, have delayed commercial deployment of SBCRs until the 1990’s. Conversely, microchannel reactors have a stationary catalyst bed combined with enhanced heat and mass transfer characteristics. Also, they are typically aimed at exploiting a different market than conventional reactors where their small size is an advantage.

The proper design and scaleup of SBCRs for LTFT synthesis require, among other, precise knowledge of the kinetics, hydrodynamics, mass transfer, heat transfer in F-T synthesis. In the following, a comprehensive literature review of the current state-of-knowledge of the mechanisms, kinetics, hydrodynamics, mass transfer, heat transfer and mathematical as well as computational fluid dynamics (CFD) modeling of LTFT synthesis in SBCRs is provided.
**Multitubular Fixed Bed:**
Gas passes through catalyst packed tubes
- LTFT: 180—260 °C
- $\alpha = 0.70 - 0.75$
- Products: Petrol and chemicals
- Catalysts: Fused Fe, K —promoted

**Slurry Bubble Column:**
Bubbles rise through liquid containing fine suspended solids
- LTFT: 180—260 °C
- $\alpha = 0.85 - 0.92$
- Products: Wax, diesel, naphtha
- Catalysts: Supported Co or precipitated Fe

**Circulating Fluidized Bed:**
Small solid particles suspended in upward flowing gas
- HTFT: 320—350 °C
- $\alpha = 0.70 - 0.75$
- Products: Petrol and chemicals
- Catalysts: Fused Fe, K —promoted

**Microchannel Reactor:**
Packed channels with highly active catalyst
- Catalysts: Supported Cobalt
- Cross flow channels for cooling

*Figure 1-3: Different F-T reactor technologies*
2.0 LITERATURE REVIEW

2.1 KINETIC STUDIES OF FISCHER-TROPSCH SYNTHESIS

The complexity of the F-T reaction mechanism and the numerous species involved are major obstacles to fully describe the kinetics of the F-T synthesis. In order to simplify the task, many empirical overall reaction rate equations have been developed and are available in the literature. Latest studies, however, have focused on developing comprehensive kinetics based on the Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach, since the variety of the products obtained from the F-T synthesis can only be explained and modeled by detailed kinetic models, which include every elementary reaction [49]. The reaction rates available in the literature for the iron and cobalt-based catalysts are presented in the following.

Iron catalyst has a high WGS activity and therefore the rate of the WGS reaction along with that of the F-T must be taken into account for simulation purposes. Since the 1950’s, numerous studies of the kinetics of the F-T on iron catalyst, conducted mostly in fixed-bed and slurry reactors, led to very different kinetic rate expressions as can be seen in Tables A-8-1 and A-8-2 (Appendix A), for F-T and WGS reactions, respectively. Only recently, however, comprehensive kinetic models, able to predict both the syngas consumption rate and products distribution, have been proposed [49-55]. The differences among the rate equations may arise from the diversity of the catalysts, reactors (mass transfer not always negligible) and the operating conditions used in these studies. As a matter of fact, when choosing one of those expressions for
modeling purposes, one has to select the correlations which have been developed within the conditions closest to the simulated ones.

Iron catalyst activity was found to increase with the partial pressure of $H_2$ and decrease with the partial pressure of $H_2O$ [56, 57], suggesting a strong competition between CO and $H_2O$ for the adsorption onto the active catalyst sites. It was therefore suggested that the F-T reaction rate over iron catalysts is inhibited by water as well as CO$_2$, as reflected by the kinetic equations by Anderson [58], Huff and Satterfield [59] and Ledakowicz et al. [60]. In 2006, however, Botes et al. [61] conducted kinetic studies on a potassium-promoted precipitated iron catalyst at Sasol and concluded that neither water nor CO$_2$ had any significant influence on the chemical reaction kinetics. Also, in 2010, Zhou et al. [62], confirmed the findings and the proposed rate equation by Botes et al. [61].

Review articles on cobalt-catalyzed F-T kinetics are available in the literature [63, 64], whereas Zennaro et al. [65] and Das et al. [66] presented in a tabulated format the explicit rate equations, which were suggested for cobalt catalyst. Of these, the LHHW type rate equations proposed by Outi et al. [67], Sarup and Wojciechowski [68] and Yates and Satterfield [69] had been frequently cited in the literature [70]. Table A-3 (Appendix A) shows the kinetic rate expressions available in the literature for the F-T cobalt-based catalysts.

Thus, the main difference between the kinetics of cobalt-based catalysts and those of iron catalysts lies in the former’s inactivity towards the WGS reaction since $H_2O$ is not adsorbed on the catalyst active sites. As a result, the WGS reaction can be neglected when modeling the kinetics of F-T synthesis using cobalt-based catalysts. It seems that the kinetic models for cobalt are consistent with a mechanism where CO dissociation occurs before any interaction with $H_2$, whereas those for iron are consistent with a mechanism of hydrogen-assisted CO dissociation.
Actually, recent results from the DFT calculations lend some support to these implications [71]. It was reported that direct CO dissociation is facile over open, high reactivity surfaces, such as corrugated or stepped cobalt surfaces, however, H₂ involvement in CO dissociation seems to be required on low reactivity surfaces, such as carbided iron, which is the predominant active phase under iron catalyzed F-T synthesis conditions [72, 73]. Figures 2-1, 2-2 and 2-3 compare various F-T and WGS rate expressions by different authors at various H₂/CO ratios; and as expected, different expressions provide different values.

![Figure 2-1: Comparison among F-T rate expressions at various H₂/CO ratios over Iron catalysts (T = 528 K and P = 3 MPa)](image-url)
Figure 2-2: Comparison among F-T rate expressions at various H$_2$/CO ratios over Cobalt catalysts (T = 528 K and P = 3 MPa)
2.2 HYDRODYNAMIC STUDIES IN F-T SBCR

Although numerous experimental studies on the hydrodynamic and mass transfer parameters in SBCRs are available, only few, as shown in Table A-4 (Appendix A), covered conditions similar to those encountered in industrial F-T SBCRs ($P > 25$ bar, $T > 450$ K, $u_G > 0.15$ m/s, $C_V > 10$
vol.%, mixture of hydrocarbons as the liquid-phase, $H_2$ and CO mixture as the gas-phase, micron sized Fe or Co-based on typical catalyst support as a solid-phase). It should be mentioned that the hydrodynamics and mass transfer in SBCRs have been consistently shown to depend on the reactor size as well as operating conditions [74], and accordingly, using such available data in the literature, which were obtained in small reactor diameters (< 0.15 m) under ambient conditions or with a single gas for designing commercial-scale SBCRs, with inside diameters reaching several meters and operating in the churn-turbulent flow regime, could be risky.

2.2.1 Overall Gas Holdup

The gas holdup represents the volume fraction of the gas-phase in the reactor. Deckwer et al. [75] measured the gas holdup for $N_2$ in a paraffin wax in the presence of up to 16 wt.% of alumina particles at 416 and 543 K. However, their experiments were carried out in small columns of 0.04 and 0.1 m ID at low superficial gas velocities, $u_G < 0.04$ m/s and pressures, $P < 11$ bar. The gas holdup for $N_2$ in paraffin wax was investigated by Bukur et al. [76] who used iron oxide and silica as solid phases. Their data were measured in a small column of 0.05 m ID at low ranges of gas velocities and at low pressure (~ 1 bar). Krishna et al. [77] reported gas holdup data obtained in a relatively large column of 0.38 m ID with a three-phase system consisting of air, paraffin oil and silica particles and covered ranges of solid concentrations and gas velocities typical to those of industrial F-T reactor, nevertheless, their experiments were conducted at atmospheric pressure and ambient temperature. Vandu et al. [78] measured the gas holdup of air in a paraffin oil in the presence of alumina particles, however, they used a small SBCR of 0.1 m ID operating at atmospheric pressure and ambient temperature. Woo et al. [79] obtained gas holdup data while carrying out F-T synthesis over alumina-supported cobalt catalyst in a small SBCR of 0.05 m ID.
They reported that optimal conditions were reached when using gas velocities in the range of 0.068-0.1 m/s and catalyst concentration of 15 wt.%. It should be emphasized, however, that higher gas flow rates and solid loading would be expected in large-scale SBCRs in order to increase the reactor productivity. Behkish et al. [8, 80] measured the gas holdup for H₂, CO, N₂, CH₄ and He in Isopar-M (an iso-paraffinic liquid mixture of C₁₀ – C₁₆) in the presence of alumina particles under high pressures (up to 30 bar), temperatures (up to 473 K), gas velocities (up to 0.39 m/s) and solid concentrations (up to 36 vol.%). While typical F-T operating conditions were covered, these authors did not use gas mixtures which would mimic the syngas. Furthermore, although Isopar-M could be used as a startup liquid for an F-T reactor, its composition varies greatly from the molten reactor wax which would be present in the SBCR once steady-state operating conditions are reached. More recently, Sehabiague et al. [81] have measured gas holdup data for N₂ and He, in C₁₂-C₁₃, paraffins mixture, light F-T cut, and heavy F-T cut in a 0.3 m ID SBCR under high pressure (up to 30 bar), temperature (up to 500 K) in the presence of Alumina, Puralox Alumina, and iron oxide particles (up to 20 vol.%) at varying superficial gas velocities (up to 0.27 m/s).

The effects of various operating variables on the gas holdup have been extensively investigated in the literature; and the parameters believed to impact the gas holdup are the superficial gas velocity, liquid density, liquid surface tension, liquid viscosity, and liquid vapor pressure. Hikita et al. [82] concluded that the effects of nozzle diameter, column diameter and liquid height on the gas holdup could be neglected. Akita et al. [83] showed that the effect of liquid superficial velocity on the gas holdup could be neglected at values < 0.044 m/s. The gas holdup has been shown to increase with increasing the superficial gas velocity [46], which affects the flow regime in the reactor. The following power law expression best describes the relationship between gas holdup and superficial gas velocity.
\[\varepsilon_G \propto u_G^n\]  

The value of \(n\) is dependent on the flow regime. In the homogenous flow regime, the value of \(n\) is in the range of 0.7 - 1.2 [84, 85], exhibiting an almost linear relationship between the gas holdup and the superficial gas velocity. The value of the gas holdup changes at the transition regime and as a result the value of “n” increases, enhancing the nonlinear dependency on the superficial gas velocity. The value of “n” then drops to 0.4 - 0.7 in the heterogeneous flow regime [84-87]. This change of the value of “n” was attributed to the variation of the system physical properties and the operating variables during the regime transition. Other studies have also reported that the effect of surface tension become more significant at low superficial gas velocities (< 0.05 m/s) [87-89].

The dependence of gas holdup on the pressure has been widely investigated and most of studies concluded that increasing pressure increases the gas holdup in SBCRs [90-92]. This dependency was attributed to the effect of increasing gas density (gas momentum) as the pressure increases. Increasing pressure is believed to reduce coalescence between the gas bubbles, and thus increases the number of small rigid gas bubbles, which translates into a high gas holdup [89, 93, 94].

The gas holdup was reported to increase with liquid viscosity and surface tension, and in some instances was reported to increase and decrease with increasing liquid density [93, 95-103]. The effect of viscosity was attributed to the rise of more bubbles coalescence in more viscous liquids. The effect of surface tension was attributed to the cohesive forces between the liquid molecules, which make it harder for the smaller bubbles to either coalesce or breakup [102, 104]. The gas holdup was found to be higher in organic liquids when compared with that in water. Moreover, for organic mixtures, the gas holdup was found to reach a maximum at a certain composition of the mixture.
The dependence of gas holdup on temperature was related primarily to the effect of temperature on the liquid physical properties. High temperatures, such as F-T synthesis, will reduce the liquid density, viscosity and surface tension, which in turn, will affect the gas holdup [105].

Increasing the solid particles density was reported to decrease the gas holdup [106-114]. The effect of solid particles size on the gas holdup was dependent on the wettability of the particles [76, 89, 103]. For non-wetting particles, the gas holdup was found to increase with the particle size, whereas the opposite was observed for wetting particles [76, 103, 106-114]. The effect of solid particles wettability on the gas holdup, however, was not clear as the values were reported to increase and also decrease [76, 103].

The reactor geometry has a strong effect on the gas holdup, depending on the location within the reactor. At the bottom of the SBCR, the gas holdup is influenced by the sparger design, whereas the values in the bulk and near the top of the reactor exhibit different dependencies [102, 115, 116]. Typically, slug flow and large gas bubbles would not occur at large reactor inside diameters (> 0.15 m) [83, 85, 102, 117-119]. In reactors with small inside diameters, slug flow and large gas bubbles would occur, decreasing the gas holdup. Similarly, the effect of reactor height, usually represented in terms of height to diameter ratio was found to be negligible for \( h_c/d_c \) values > 6 [102, 117, 120]. In addition, sparger design greatly influences the gas holdup as it affects the size and distribution of the initial bubbles generated at the bottom of the reactor [83, 94, 121-125].

There are numerous gas holdup correlations available in literature as highlighted by Behkish [9]. Many of these correlations were developed for aqueous and highly ionic systems at ambient conditions in laboratory-scale reactors, which brings into question their ability in predicting the gas holdup in industrial large-scale reactors operating under F-T conditions. Table
A-5 (Appendix A) summarizes the gas holdup correlations available in literature for three-phase reactors.

In order to graphically show the difference among these correlations, the data given in Table 2-1 were used to predict the effects of superficial gas velocity, catalyst particle diameter, solid loading and \( h_c/d_c \) on the overall gas holdup as depicted in Figure 2-4. As can be seen in this figure, there is a wide variation among the predicted values, especially at high superficial gas velocities. Also, with the exception of the correlations by Behkish et al. [9] and Sehabiague et al. [81], most correlations do not account for the effect of particle diameter, catalyst loading and \( h_c/d_c \) on the overall gas holdup.

Table 2-1: Operating conditions used in the correlations for comparison purposes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>3 MPa</td>
</tr>
<tr>
<td>Temperature</td>
<td>500 K</td>
</tr>
<tr>
<td>( u_G )</td>
<td>0.05 - 0.45 m/s</td>
</tr>
<tr>
<td>( u_L )</td>
<td>0.01 m/s</td>
</tr>
<tr>
<td>( C_v )</td>
<td>5-35 vol.%</td>
</tr>
<tr>
<td>( d_p )</td>
<td>40-520 micron</td>
</tr>
<tr>
<td>( h_c )</td>
<td>50 m</td>
</tr>
<tr>
<td>( h_c/d_c )</td>
<td>2.5-20</td>
</tr>
</tbody>
</table>

Liquid and Solid physical properties are taken from Sehabiague and Morsi [126]

Table 2-2: Correlations for the physicochemical properties of the liquid phase [126]

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
<th>(2-2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_L = 978.05 - 0.5403T )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mu_L = \exp \left( \frac{2504.2}{T} - 4.3371 \right) )</td>
<td>(2-3)</td>
<td></td>
</tr>
<tr>
<td>( \sigma_L = \frac{1.367 \times 10^{-4}T^2 - 0.1915T + 80.486}{1000} )</td>
<td>(2-4)</td>
<td></td>
</tr>
<tr>
<td>( \log_{10}(P_v) = -\frac{50951}{T^2} - \frac{1694.1}{T} + 3.146 )</td>
<td>(2-5)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2-4: Comparison among literature gas holdup correlations at various (a) superficial gas velocities, (b) Catalyst particle diameters, (c) Solid loadings and (d) $h_c/d_c$ values.
2.2.2 Radial Distribution of Gas Holdup

The radial profile of the gas holdup in two-phase flows has been measured and reported in the literature [127-134]. Literature experiments for measuring the radial gas holdup distribution are given in Table 2-3. The exact experimental measurements have proven to be complex and time consuming, even though numerous tomographic and velocimetric techniques had been developed over the past three decades. The radial distribution of the gas holdup is generally modeled with a power law [134] (Equations (2-6) and (2-7)), based on experimental findings using Computed Tomography (CT) measurements [135, 136].

\[
\varepsilon_G(\xi) = \bar{\varepsilon}_G\left(\frac{m + 2}{m}\right)(1 - c\xi^m)
\]  

(2-6)

Where \( \bar{\varepsilon}_G \) is related to the cross-sectional average holdup by the following equation:

\[
\bar{\varepsilon}_G = \bar{\varepsilon}_G\left(\frac{m + 2 - 2c}{m}\right)
\]  

(2-7)

The value of the parameter ‘m’ is high for a flat gas holdup distribution (corresponding to bubbly flow regime) and decreases for the more parabolic profile prevalent in the churn-turbulent flow regime [134, 137]. This number is typically > 5 for a flat holdup profile, which exists in the bubbly-flow regime and is lower (~2) for the churn-turbulent flow regime. While the parameter c allows for a non-zero holdup at the wall, which was observed from CT measurements [138, 139]. The above equations have been validated by other authors to fit the experimental radial holdup profiles [140, 141].

For industrial reactors, however, it is important to obtain a few cross-sectional measurements of the gas holdup throughout the column. It is often overlooked that a single line averaged holdup, even across the centerline of the column, is not representative of the cross-
sectional mean value. Nevertheless, a line averaged gas holdup along several radial positions can be used to obtain a cross-sectional mean, provided that the holdup distribution is assumed axisymmetric. If such an assumption can be made, the radial variation of the gas holdup and hence the cross-sectional mean can be obtained by making use of the Abel integral and its inversion (Equation (2-8)) [135, 137].

$$
\varepsilon_G(x, R) = 2 \int_0^{\sqrt{(R^2-x^2)}} f\left(\sqrt{(R^2-x^2)}, R\right) dy = 2 \int_0^R \frac{f(r,R)r}{\sqrt{r^2-x^2}} dr \tag{2-8}
$$

Where $f(r, R)$ is a function of the radial position, which is not zero within the circle of radius R.

### Table 2-3: Experimental work for measuring radial gas holdups in three phase reactors

<table>
<thead>
<tr>
<th>Reactor dimensions</th>
<th>Phase properties</th>
<th>Operating conditions</th>
<th>Reference</th>
</tr>
</thead>
</table>
| $d_c = 0.1 \text{ m}$; $h_c = 0.8 \text{ m}$ | Glass beads/ Air/Water  
  • $d_p$: 0.12 – 0.47 mm  
  • $\rho_s$: 2500 kg/m$^3$ |  
  • Solid loading: 12.5 – 50%  
  • $u_G = 0.01 \text{ m/s}$ | Rigby [142] |
| $d_c = 0.12 \text{ m}$; $h_c = 2 \text{ m}$ | Glass beads / Air/ Water  
  • $d_p$: 2.2 mm  
  • $\rho_s$: 2500 kg/m$^3$ |  
  • 30 kg solid loading  
  • $u_L = 0.05 \text{ m/s}$  
  • $u_G = 0.02 - 0.14 \text{ m/s}$ | Marooka [143] |
| $d_c = 0.254 \text{ m}$; $h_c = 2.5 \text{ m}$ | Glass beads / Air/ Water  
  • $d_p$: 2.3 mm  
  • $\rho_s$: 2500 kg/m$^3$ |  
  • 30 kg solid loading  
  • $u_L = 0.06 \text{ m/s}$  
  • $u_G = 0.01 - 0.14 \text{ m/s}$ | Yu and Kim [3] |
| $d_c = 0.102 \text{ m}$; $h_c = 1.05 \text{ m}$ | Alumina particles /Air/Water  
  • $d_p$: 75 $\mu$m |  
  • Solid loading: 0 – 25%  
  • $u_G = 0.02 - 0.13 \text{ m/s}$ | Wu [144] |
2.2.3 Sauter Mean Gas Bubbles Diameter

Behkish et al. [8, 80] measured the Sauter mean gas bubble diameter ($d_{32}$) for H$_2$, CO, N$_2$, CH$_4$ and He in Isopar-M (an isoparaffinic liquid mixture of C$_{10}$ – C$_{16}$) in the presence of alumina particles under high pressures (up to 30 bar), temperatures (up to 473 K), gas velocities (up to 0.39 m/s) and solid concentrations (up to 36 vol.%). While the experiments by these authors were conducted under typical F-T operating conditions, they did not use gas mixtures, mimicking the syngas; and the composition of their Isopar-M is different than that of the molten wax produced in the F-T SBCRs. More recently, Sehabiague et al. [81] have measured the Sauter mean gas bubble diameter ($d_{32}$) for N$_2$ and He, in C$_{12}$-C$_{13}$, paraffins mixture, light F-T cut, heavy F-T cut in a 0.3 m ID SBCR under high pressure (up to 30 bar), temperature (up to 500 K) and in the presence of Alumina, Puralox Alumina, and Iron oxide particles (up to 20 vol.%) at various superficial gas velocities (up to 0.27 m/s).

SBCRs are customarily operated in the churn-turbulent flow regime, which is believed to be the best mode of operation of such reactors [78, 145]. In this regime, large and small size gas bubbles were found to co-exist [145-147]. The large gas bubbles, with typical rise velocities in the order of 1.5 m/s, usually rise straight up through the reactor and disengage without any recirculation. The small bubbles, on the other hand, may experience recirculation and backmixing due to their low rise velocities.

Modeling of the gas bubbles behavior in SBCRs has received significant attention due to its effect on solid distribution and reactants conversion, Table A-6 (Appendix A) highlights commonly referenced bubble diameter correlations available in the literature, whereas Figure 2-5 depicts the behavior various correlations at various superficial gas velocities; and as can be observed, different values and trends of the bubble sizes are predicted.
In the bubbly flow regime, the gas-phase behavior can be adequately modeled assuming a uniform gas bubbles size distribution [148, 149]. On the other hand, in the Churn-turbulent flow regime, the two-class modeling approach introduced by Krishna [145, 147] was implemented by Rados [150], Sehabiague [151], and Maretto [152], among others. It assumes a generalized two-phase model, in which a dilute- and a dense-phase are identified. The dilute-phase which is dominated by large gas bubbles is virtually in plug flow, while the dense-phase experiences turbulent backmixing. The main disadvantage of this approach is that the cross flow interactions between the two-bubble classes usually are either neglected in steady state models or assumed to occur infinitely fast to quickly homogenize the composition of both classes in the transient and startup models [153, 154]. This approach gives rise to inaccuracies and deviations since it is only concerned with the limiting cases, while the actual extent of the interaction between the large and small gas bubbles would occur somewhere in the middle, which would create some differences in species concentration [136]. Moreover, intra-phase backmixing has either been accounted for using perfect mixing or by assuming plug flow [155], however, non-ideal flow models, accounting for a finite degree of backmixing, are believed to be more realistic.

It should be mentioned that the two-bubble class model in conjunction with the axial dispersion model has been accepted and used to model bubbles behavior in SBCRs [151, 152, 154-159]. In this model, the churn turbulent flow regime was assumed where large bubbles rise straight up through the reactor without recirculation, while small bubbles with lower rise velocity were entrained in the liquid and as such they followed the liquid-phase backmixing behavior.

There are two basic categories of non-ideal flow models, axial dispersion models and multi-cell models. Moreover, Iliuta [160] proposed a core annulus, multi-compartment model, which is a modified multi-cell approach that divides the reactor into compartments based on the
bubble size, and individually models the chemistry, thermodynamics and thermal effects of each compartment, while accounting for the thermo-physical interaction between the compartments.

Although many of the earlier SBCR models assumed no solids concentration gradient throughout the reactor, Kato [150] showed a gradient in the longitudinal concentration of solid particles, which was a function of the liquid micro- and macro-mixing. Therefore, the axial profile of the solids concentration is not flat and is highly dependent on the slurry properties and the operating conditions.

Figure 2-5: Comparison of various bubble diameter velocity correlations
2.2.4 Bubble Dynamics

Gas–liquid–solid systems have been applied extensively in industry for physical, chemical, petrochemical and biochemical processing [136, 161-163]. Current worldwide commercial activities in converting natural gas to fuels and chemicals, or gas-to-liquids technology use slurry bubble column reactors with column sizes considerably larger than those commonly considered in research investigations and in previous industrial applications [164]. Such commercial activities have prompted further fundamental research interest in fluid and bubble dynamics, transport phenomena, and the effects of high temperature and pressure conditions.

In gas–liquid–solid systems, bubble dynamics plays a key role in dictating the transport phenomena and ultimately affects the overall rates of reactions. It has been recognized that the bubble wake, when it is present, is an important factor governing the system hydrodynamics [135]. In general, consideration of the flow associated with the bubble wake near the bubble base, whether laminar or turbulent, is essential to characterize the complete behavior of the rising bubble, including its motion. Conversely, examining the shape, rise velocity, and motion of a bubble can provide an indirect understanding of the dynamics of the liquid–solid flow around the bubble. Most of the three-phase processes with considerable commercial interest are conducted under high pressure and high temperature, for example, methanol synthesis (at $P = 5.5$ MPa and $T = 260$ °C), resin hydro-treating (at $P = 5.5–21$ MPa and $T = 300–425$ °C), Fischer–Tropsch synthesis (at $P = 1.5–5.0$ MPa and $T = 250$ °C), and benzene hydrogenation (at $P = 5.0$ MPa and $T = 180$ °C) [165-170]. Fundamental study of bubble dynamics in these gas–liquid–solid fluidization systems, particularly under high-pressure and high-temperature conditions, is thus crucial.
Generally, bubble-induced turbulence and shear induced turbulence are two sources of liquid phase turbulence in bubble columns. However, the dominating mechanism of the liquid phase turbulence is still not clear in such bubbly flows.

In a three-phase fluidization system, bubble size variation is intimately related to bubble–particle collisions. The collisions can yield two different consequences: the particle is ejected from the bubble surface, or the particle penetrates the bubble leading to either bubble breakage or non-breakage. Bubble–particle collisions generate perturbations on the bubble surface. After the bubble–particle collision, three factors become crucial in determining the breakage characteristics of the bubble [171]:

1. Shear stress, which depends on the liquid velocity gradient and the relative bubble–particle impact speed, and tends to break the bubble;
2. Surface tension force, which tends to stabilize the bubble and causes it to recover the bubble’s original shape;
3. Viscous force, which slows the growth rate of the surface perturbation, and tends to stabilize the bubble.

There are three criteria that are required for particle penetration through a bubble. These criteria were developed by neglecting the shear effects due to the liquid flow [4]. The particle will penetrate the bubble when any of the following three criteria is satisfied. The three criteria are given as follows:

1. The acceleration of the particle is downward;
2. The particle velocity relative to the bubble is downward;
3. The particle penetration depth is larger than the deformed bubble height.
When none of these criteria are satisfied, the particle will be ejected from the bubble surface upon contact with the bubble.

The bubble dynamics is controlled by the size and distribution of the gas bubbles present in the reactor. The bubble size controls the gas-liquid interfacial area and subsequently it influences the overall rate of reactions occurring in the reactor during commercial processes. The formation of gas bubble at the injection point is subject to the buoyancy forces due to the difference in density between the gas and liquid phases, and the surface tension forces that govern the stability of the gas bubble from the orifice and throughout the liquid/slurry phase. The behavior of the gas bubbles depends, among others, on the hydrodynamic flow regime. If a bubbly flow regime governs in the reactor, the bubbles will be narrowly distributed and low bubble-bubble interactions could be expected. In fact a uniform bubble size distribution is generally characteristics of the homogeneous bubbly flow regime. As the superficial gas velocity is increased, the high frequency of gas bubble interactions leads to coalescence and breakup and the reactor is found to be operating in the churn turbulent flow regime, and a distinguishable bimodal bubble size distribution can be observed. Consequently, bubbles in this regime can be arbitrary classified into “small”, and “large”. These bubbles appear to behave differently as the large gas bubbles rise rapidly in the reactor in a plug flow mode and create backmixing, and the small gas bubbles are entrained and re-circulate with the liquid/slurry. In the churn turbulent flow regime, bubble breakup and coalescence can occur at any moment after the formation of the gas bubble at the orifice, thus the bubble size distribution will depend on the balance between coalescence and breakup.
2.2.5 Bubble Rise Velocity

The behavior of the rising gas bubbles can be described using the rise velocity, shape and motion of the bubbles, which are related to the physical properties of the surrounding medium (solid loading, liquid viscosity and density) as well as the interfacial properties of the bubbles. The bubble rise velocity primarily depends on the bubble size for small gas bubbles and on the liquid surface tension and viscosity for large bubbles. Most studies investigating the bubble rise velocity were mainly conducted in water-based systems under ambient conditions, which bring into question the confidence in applicability to a realistic F-T SBCR conditions.

Table A-7 (Appendix A) summarizes the bubble rise velocity correlations available in literature for use in bubble columns and SBCRs modeling, whereas Figure 2-6 compares the behavior of different correlations at various superficial gas velocities. Krishna et al. [172] studied the effect of pressure on the rise velocity and found that the gas density has no noticeable effect on the bubble rise velocity. Their work, however, was conducted within a very narrow pressure range. Lin et al. [173, 174] measured the rise velocities of a single bubble of a known size in Paratherm NF heat transfer fluid under a wide range of pressures ranging from 0.1 to 14.9 MPa at three temperature 300, 320 and 350 K. They showed that the rise velocity was independent of temperature and decreased with increasing pressure. They attributed this behavior to the pressure-temperature effects on the liquids physical properties. Lou et al. [135] developed a mechanistic first principle-based correlations to predict the initial bubble size in slurries at high pressure and temperature conditions by accounting for the various competing forces at the bubble distribution source. In their model, the bubbles were assumed to be formed in two stages, expansion and detachment. During the expansion stage, the bubble initially expands with its base attached to the source nozzle; and the detachment stage occurs when the bubble’s base moves away while
remaining connected to the nozzle through the neck. The bubble was assumed to be spherical during the entire formation process.

The volume of the gas bubbles can be determined using the balance of all the forces, if either of the instantaneous gas flow or the instantaneous gas velocity through the orifice is known, as has been discussed by Behkish [89].

![Comparison among various bubble rise velocity correlations](image-url)

**Figure 2-6:** Comparison among various bubble rise velocity correlations
2.3 MASS TRANSFER STUDIES IN F-T SBCR

In F-T SBCRs, the reactants have to diffuse through the liquid produced in order to reach the catalyst active sites before the chemical reaction can take place. Figure 2-7 shows the mass transfer process in gas-liquid-solid systems, where the reaction takes place inside the pores of the solid catalyst. As can be seen, the reactants in the gas-phase have to travel from the bulk gas-phase to the gas-liquid interface and then through the liquid bulk. Once in the liquid bulk, the reactants start to mix before transferring to the external surface of the catalyst (solid) particles. After reaching the catalyst surface, the reactants have to diffuse inside the catalyst pores until they collide with an active site, where the chemical reaction can take place based on the kinetic conditions of the system. Once the products are formed, they start diffusing all the way back from the active sites to the catalyst surface, through the liquid bulk, to the gas-liquid interface, before diffusing into the gas-phase.

Since the diameter of the catalyst particles frequently used in SBCRs is very small (micron size), the interfacial area between the liquid and the catalyst surface is considerably large, and as such, the mass transfer resistance between the liquid and solid phases could be neglected. Additionally, the mass transfer resistance due to mixing of the reactants in the bulk liquid could also be neglected, if the reactor is operating in the churn-turbulent flow regime, as it provides effective mixings conditions. Furthermore, since the majority of F-T products have negligible vapor pressure, the resistance to transfer of the reactants from the bulk gas-phase to the gas-liquid interface could be neglected. Thus, the two remaining resistances which have to be considered are the reaction kinetic and the liquid-film resistances.

Generally, mass transfer between the phases can be represented using Fick’s law as shown in Equation (2-9), where $D_{AB}$ is the diffusivity of component A into component B. Vermeer and
Krishna [175], however, argued in favor of using Maxwell-Stephan’s equation for representing a multicomponent mixture close to the saturation, as shown in Equation (2-10).

\[
\frac{\partial C}{\partial t} = -D_{AB} \frac{\partial^2 C}{\partial x^2} \quad (2-9)
\]

\[-\frac{\phi}{RT} \nabla \cdot \mu_i = \sum_{j=1}^{n} \frac{c_j N_i - c_i N_j}{c_j D_{ij}} + \frac{N_i}{D_i}, \quad i = 1, 2, \ldots n \quad (2-10)
\]

The mass transfer through the liquid-film can be described by a steady-state mass transfer flux according to the two-film theory as shown in Equation (2-11).

\[J_L = k_L \alpha (C^* - C_L) \quad (2-11)\]

Where \(C^*\) is the concentration at the gas-liquid interface, \(C_L\) is the concentration in the liquid bulk and \(k_L\) is the liquid-side mass transfer coefficient, which is often represented as a function of the gas-liquid diffusivity and the liquid film thickness by Equation (2-12).
\[ k_L = \frac{D_{AB}}{\delta} \]  

The volumetric liquid-side mass transfer coefficient \( (k_L a) \) is the product of the liquid-side mass transfer coefficient \( (k_L) \) and the gas-liquid interfacial area \( (a) \). The gas-liquid interfacial area is the area of interface between the gas bubbles and the liquid-phase, which represents the surface through which mass transfer takes place. This area can be determined from the knowledge of the gas holdup and a characteristic length for the gas bubbles assuming the bubbles to be of a specific shape.

The effects of mass transfer on three-phase reactor performance have been extensively investigated in the literature [80, 81, 176-179]. Earlier studies on the mass transfer focused on the significance of hydrogen mass transfer compared to the overall reaction resistance. This was due to the fact that F-T kinetics over iron catalyst were reported to be first order with respect to hydrogen. The principal mass transfer resistance occurs in the slurry-phase of the reactor and the extent of the effect of gas-liquid mass transfer on the reactor performance has been argued. Satterfield and Huff [180] concluded that the hydrogen mass transfer was the limiting step for reactor productivity, whereas Deckwer [75] showed that the mass transfer resistance was small compared to the kinetics resistance. Inga and Morsi [181] and Sehabiague and Morsi [81, 177] reported that F-T SBCRs operating under a kinetically-controlled regime at low catalyst concentrations could move to a mass transfer-controlled regime at high catalyst concentrations, where the reactor performance quickly declines. Nonetheless, it is generally agreed that the mass transfer strongly depends on the bubble size, where smaller gas bubbles result in a greater gas-liquid interfacial area, which improves the overall mass transfer.

The volumetric mass transfer coefficients, derived from the inlet and outlet concentrations of absorption experiments, were influenced by the dispersion in both phases. [74] Since the
dispersion is strongly dependent on the column size and geometry, the developed equations for the calculating the volumetric mass transfer coefficients appear to include geometric parameters, such as the column diameter and sparger characteristics. Behkish et al. [8, 80] measured the volumetric mass transfer coefficients \( (k_La) \) for \( \text{H}_2, \text{CO}, \text{N}_2, \text{CH}_4 \) and \( \text{He} \) in Isopar-M (an isoparaffinic liquid mixture of \( \text{C}_{10} – \text{C}_{16} \)) in the presence of alumina particles under high pressures (up to 30 bar), temperatures (up to 473 K), gas velocities (up to 0.39 m/s) and solid concentrations (up to 36 vol.%). While the experiments by these authors were conducted under typical F-T operating conditions, they did not use gas mixtures, mimicking the syngas; and the composition of their Isopar-M was greatly different than that of the molten wax produced in the SBCR. More recently, Sehabiague et al. [81] have measured the volumetric mass transfer coefficients for \( \text{N}_2 \) and \( \text{He} \), in \( \text{C}_{12}-\text{C}_{13} \), paraffins mixture, light F-T cut, heavy F-T cut in a 0.3 m ID SBCR under high pressure (up to 30 bar), temperature (up to 500 K) in the presence of Alumina, Puralox Alumina, Iron oxide particles (up to 20 vol.%) at various superficial gas velocities (up to 0.27 m/s).

Table A-8 (Appendix A) summarizes the few available literature studies and correlations for \( k_La \) in SBCRs. It should be mentioned, however, that numerous \( k_La \) correlations in BCRs are available in the literature as highlighted by Behkish. [89] Moreover, Figure 2-8 shows the effects of superficial gas velocity, catalyst particle diameter, solid loading and \( h_c/d_c \) on \( k_La \) using the conditions provided Table 2-1. As can be in this figure, there is a wide variation in the predicted \( k_La \) values especially at higher superficial gas velocities, which is similar to the behavior shown by gas holdup correlations presented in Figure 2-4, it should be noted that most of the correlations presented in Table A-8 do not account for the effect of particle diameter, catalyst loading and \( h_c/d_c \) on \( k_La \).
Figure 2-8: Comparison among three-phase correlations for $k_{L\alpha}$ at various (a) superficial gas velocities, (b) Catalyst particle diameters, (c) Solid loadings and (d) $h_c/d_c$ values.
Table 2-4 summarizes the effects of various parameters on the hydrodynamics and mass transfer parameters in SBCRs based on the preceding literature review.

**Table 2-4: Summary of reported effects of operating conditions on the hydrodynamic mass transfer parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas density [74, 80, 89, 90, 105, 121, 174, 182-184]</td>
<td>Denser gas leads to higher gas holdups and smaller gas bubbles.</td>
</tr>
<tr>
<td>Gas molecular weight [90]</td>
<td>Same effect as gas density; higher molecular weights results in higher gas holdups and smaller gas bubbles</td>
</tr>
</tbody>
</table>
| Liquid density [83, 99, 105, 107, 118, 121, 183-188] | • Effect is unclear, both an increase and decrease of the gas holdup has been reported.  
  • Volumetric mass transfer coefficient decreases with decreasing liquid density. |
| Liquid viscosity [82, 83, 99, 101, 105, 107, 118, 183, 184, 186, 188, 189] | Increasing liquid viscosity:  
  • Increases gas bubbles size  
  • Decreases gas holdup and mass transfer coefficients |
| Liquid surface tension [82, 83, 90, 105, 187, 188, 190-193] | Increasing liquid surface tension:  
  • Decreases gas holdup  
  • Results in the formation of large gas bubbles  
  • Decreases the volumetric mass transfer coefficients |
| Solid density [194]            | Increasing solid density decreases gas holdup.                         |
| Particle Diameter [106, 194, 195] | Increasing particle diameter:  
  • Increases gas holdup for non-wettable particles  
  • Decrease/No effect on gas holdup for wettable particles |
| Wettability [194]              | In general, have no clear effect on the gas holdup. Although some reported it to increase or decrease the gas holdup. |
| Temperature [183, 184, 188, 193, 196, 197] | Increasing temperature:  
  • Decreases liquid surface tension; Decreases liquid viscosity  
  • Increases gas holdup; Increases gas diffusivity;  
  Increases volumetric mass transfer coefficients |
### Table 2-4 (continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure [80, 185, 198-200]</td>
<td>Increasing pressure:</td>
</tr>
<tr>
<td></td>
<td>• Increases gas density and gas momentum; Increases gas holdup</td>
</tr>
<tr>
<td></td>
<td>• Increases volumetric mass transfer coefficients</td>
</tr>
<tr>
<td>Superficial gas velocity [75,</td>
<td>Increases superficial gas velocity:</td>
</tr>
<tr>
<td>82, 83, 90, 105, 183, 184, 186-</td>
<td>• Increases gas holdup; Increases volumetric mass transfer coefficients</td>
</tr>
<tr>
<td>188, 196]</td>
<td></td>
</tr>
<tr>
<td>Liquid velocity [76, 106, 195,</td>
<td>Increasing liquid velocity decreases the gas holdup in the absence and</td>
</tr>
<tr>
<td>201, 202]</td>
<td>presence of solid particles</td>
</tr>
<tr>
<td>Solid loading [8, 76, 103, 106,</td>
<td>Increasing solid loading:</td>
</tr>
<tr>
<td>107, 203]</td>
<td>• Decreases the gas holdup, despite some studies reported otherwise.</td>
</tr>
<tr>
<td></td>
<td>• Increases slurry viscosity</td>
</tr>
<tr>
<td></td>
<td>• Decreases the volumetric mass transfer coefficients</td>
</tr>
<tr>
<td></td>
<td>• Leads to the formation of large gas bubbles</td>
</tr>
<tr>
<td></td>
<td>• Increases the rate of bubble coalescence</td>
</tr>
<tr>
<td></td>
<td>• Increases the volumetric mass transfer coefficient at low solid</td>
</tr>
<tr>
<td></td>
<td>concentrations</td>
</tr>
<tr>
<td>Column Diameter [83, 85, 102,</td>
<td>Strong effect for small column diameters &lt; 0.15 m, no effect for</td>
</tr>
<tr>
<td>118, 119, 204, 205]</td>
<td>larger diameters.</td>
</tr>
<tr>
<td>Column Height/Diameter ratio</td>
<td>No effect on gas holdup for ratios &gt; 6</td>
</tr>
<tr>
<td>[90, 120, 204, 206]</td>
<td></td>
</tr>
<tr>
<td>Gas distributor [102, 190]</td>
<td>• Increasing the size of the openings decreases the gas holdup due</td>
</tr>
<tr>
<td></td>
<td>to the formation of large gas bubbles.</td>
</tr>
<tr>
<td></td>
<td>• Has minimal effect on the gas bubbles size and gas holdup for</td>
</tr>
<tr>
<td></td>
<td>orifice diameters 0.001-0.002 m.</td>
</tr>
<tr>
<td>Internal design [4, 207-215]</td>
<td>Some effect on increasing gas holdup has been reported;</td>
</tr>
<tr>
<td></td>
<td>most variations lie within the range of experimental error;</td>
</tr>
<tr>
<td></td>
<td>and no major effect was reported when internals represent the</td>
</tr>
<tr>
<td></td>
<td>&lt;15-20 % of reactor volume.</td>
</tr>
</tbody>
</table>
2.4 HEAT TRANSFER STUDIES IN F-T SBCR

One of the main advantages of SBCRs is the ease of heat removal and the uniform temperature distribution within the reactor, which makes modeling of the heat transfer a simple task. The effect of the slurry physical properties on the heat transfer is indisputable and thus the presence of water produced in F-T synthesis and its effect on the slurry properties should in turn affect the heat transfer behavior. A generalized heat balance on the SBCR can be written as:

\[
\frac{\partial}{\partial z} \left[ \rho_{sl} C_{p_{sl}} (1 - \varepsilon_G) D_L \frac{\partial T}{\partial z} \right] - \frac{\partial \left( \rho_{sl} C_{p_{sl}} u_{sl} T \right)}{\partial z} - U_{Heat} (T - T_{cool}) + (1 - \varepsilon_G) (-\Delta H_{FT} r_{FT}) = 0
\] (2-13)

Although interphase heat exchange is not important because the inlet gas is typically preheated by the outlet gas before entering the reactor [166, 216], the continuous contact among the phases and the degree of mixing are important to allow for a uniform temperature gradient and almost isothermal operation.

In SBCRs, the intimate contact among the phases allows for an almost uniform temperature and near isothermal operation. Most of studies on the heat transfer in multiphase reactors have been focused on the determination of the effects of operating variables on the heat transfer coefficients. Table A-9 (Appendix A) summarizes the heat transfer coefficient correlations available in the literature for BCRs and SBCRs.

2.4.1 Previous Studies Investigating Effect of Internals on BCR and SBCR Performance

The vicinity of the gas sparger is highly chaotic and generally well-mixed. Krishna et al. [110] listed the typical conditions for an industrial F-T SBCR, including the heat removal by means of
cooling pipes, which are essential for controlling temperature in the highly exothermic F-T reactor [217-219]. The fact is the effect of internals on the performance of SBCRs has received little attention as of today. In addition, there is no convincing guidance on the design of internals in SBCRs. However, there have been numerous investigations on the effect of internals in BCRs, which will be discussed below.

Hulet et al. [220] reviewed the heat transfer studies in BCRs and recommended that more work involving columns with internals needs to be conducted to develop reliable models for predicting large-scale unit performance. Kölbel and Ralek [221] suggested the insertion of honeycombed cross section vertical shafts inside the column, with cooling pipes located in corners or around the shafts. They claimed this design would eliminate unfavorable backmixing, which can reduce desirable selectivities as it reduces the residence time in the BCR to that in an ideal stirred tank reactor.

Korte [222] studied heat transfer from horizontal and vertical tube bundles with an embedded heat transfer probe in BCRs of 0.19 and 0.45 m diameter and concluded that the heat transfer coefficient is very sensitive to the configuration and density of the bundle. He showed that even with high viscosity liquids, which enhance bubble coalescence, the presence of internals may inhibit any decrease of the heat transfer values by enhancing the bubble break-up rate. He also developed the following correlation:

\[
St = 0.139 \left[ \left( Re_G Fr_G Pr_L^{2.26} \right)^{1/3} \right]^{0.84} A_f^{0.2} \left( \frac{E_R}{d_R} \right)^{0.14} \left( \frac{H_L}{\mu_{lw}} \right)^{0.3} 
\]

(2-14)

Where:

\[
A_f = \frac{(d_c^2 - n_R d_R^2)}{d_c^2} 
\]

(2-15)
From a fundamental standpoint, it is expected that similar to the heat transfer coefficients, the mass transfer coefficients are altered by the presence of internals; and accordingly mass transfer correlations and models developed in columns without internals need to be revisited. Bernemann [223] used a flywheel anemometer and found the axial component of the liquid-phase velocity to be higher in a column with internals than in a column without internals, irrespective of the gas velocity used. However, in the radial profile, the inversion point (stationary liquid velocity) between the upward and downward liquid velocities was maintained at about the same dimensionless radius of ~ 0.7.

Saxena et al. [207] investigated the effect of internal tubes in 0.305 m diameter column, representing 1.9, 2.7 and 14.3% of the total column cross-sectional area operating with an air-water-glass beads system. The gas holdup was found to be higher for 37 tubes than for 7 tubes. They reported the overall gas holdup as a macroscopic value, with no mention of the radial profile and accordingly the effect of internals on the liquid recirculation could not be assessed using their data. Similarly, Pradhan et al. [224] studied six different volume fractions of straight tube internals ranging from 10.8 to 19.3% and helical coil internals ranging from 2.6 to 3.9% of the reactor cross-sectional area, within a 0.102 m diameter column, and found that the gas holdup increased with increasing the internals volume fraction. Moreover, helical coil internals provided higher gas holdup than vertical tubes, which was attributed to the fact that vertical inter-tubes gaps allow large bubbles to escape, decreasing the gas holdup, while in the helical coils, smaller gaps were present.

Chen et al. [4] studied the effect of internals covering ~ 5% of the total column cross-sectional area, using gamma ray Computed Tomography (CT) and Computer Automated Radioactive Particle Tracking (CARPT). They studied gas holdup, liquid recirculation, and turbulent parameters in a 0.46 m diameter column. Their data showed that the presence of internals
have no significant effect on the liquid recirculation velocity, while gas holdup increased by ~ 10% at the center of the column and less towards the wall region. Also, the turbulent stresses and eddy diffusivities were lower when the internals were added.

Modeling BCRs with internals was attempted by Forret et al. [213], who developed a 2-D model to predict the effect of internals on the liquid mixing by accounting for an axial dispersion coefficient \( D_{ax,2-D} \), a radial dispersion coefficient \( D_{rad,2-D} \), and a radially dependent axial velocity profile. They reported that the presence of internals decreased the liquid fluctuation velocity and enhanced the large-scale liquid recirculation based on their liquid tracer experiments.

Larachi et al. [225] carried out CFD simulations for the flow behavior in a column without internals and with four different internal arrangements. The occupied cross-sectional areas ranged between 2 and 16.2%; and the core-annulus flow was predicted by the simulation of the uniform internals configurations, which confirmed the results highlighted earlier by Bernemann [223, 226]. However, for non-uniform internals, a complex flow behavior was detected. Youssef et al. [227] reviewed experimental efforts investigating the effect of internals in BCRs and the following summary of the effects of horizontal and vertical arrangements of internals in BCRs was given [228]:

1. Sectionalizing bubble columns via perforated trays leads to an increase of the gas holdup; and a similar increase of the gas holdup was observed when utilizing horizontal tubes instead [114];

2. Blass and Cornelius [229] reported a decrease in the bubble coalescence upon the addition of horizontal sectionalizing plates ranging from 1.1% to 46% of open cross-sectional area in a 3-phase system (0.14 m diameter). Kemoun et al. [230] used ~ 5% open cross-sectional
area sieve trays in an air-water system (0.19 m diameter) and claimed that the trays induce bubble coalescence and present an obstacle to the formation of uniform bubbles;

3. Horizontal internals in bubble columns tend to reduce the overall backmixing, so that the benefits of reactor operation as an ideal cascade can be approached [231-235];

4. Other authors [229, 236] reported an increase of the backflow ratio with increasing the perforated plate open free area, making the overall reactor behavior approach similar to that of a mixed stirred vessel. While other studies [233, 237] showed that decreasing the open free area reduced the liquid recirculation and increased the pressure drop;

5. The mass transfer coefficients were found to increase upon sectionalization with perforated trays [238], and to decrease with the addition of more horizontal tube rows [234];

6. Saxena et al. [113] and Pradhan et al. [224] reported that vertical internals inhibit bubble coalescence and enhance bubble breakup; however, O’Dowd et al. [208] found an increase in bubble size with the insertion of the vertical baffles;

7. Intuitively, longitudinal tube internals tend to decrease the area available for flow, resulting in an increase in gas holdup when compared with that in empty reactors [210, 239]. The same applies when helical coils are used [224].

8. The gap size between internals is important in the longitudinal funneling of liquid flow, as it governs the size of the large-scale eddies. This gap length is also responsible for decreasing the liquid kinetic turbulent energy [225].

9. The large-scale liquid recirculation increased when vertical tube internals covered a large cross-sectional area (~22%) [213], while a less covered cross-sectional area (5%) did not affect the liquid recirculation; [4]
10. Forret et al. [213] proposed a 2-D model that seemed to provide good prediction for large BCRs with and without vertical tube internals; and

11. Vertical tubes increased the heat transfer coefficient more than horizontal internals did [240]. The axial dispersion coefficient also increased, especially in the bubbly flow regime, where it was a strong function of the gas velocity at the bottom of the column. This distribution was largely affected by the presence of internals [214].

### 2.5 MODELING OF SBCRS FOR F-T SYNTHESIS

Recent efforts have been focused on simulating F-T in SBCRs, with the aim of understanding the complex hydrodynamics and their effects on the reactor performance. Empirical 1-D models have been proposed for F-T SBCRs [126, 150, 241], which provide valuable information and predictions of the overall reactor performance. Multidimensional effects were accounted for using dispersion coefficients which cannot be calculated from first principles, but were empirically obtained for each system in question. However, the flow structures and internal recirculation zones in the SBCR were ignored in the 1-D models.

Earlier studies mainly focused on experimentally examining the macroscopic fluid dynamic behavior of three-phase fluidized beds and developing empirical correlations, however, with increasing computer power, the use of CFD has gained considerable attention. Over the past decade, significant advances have been made in numerical modeling of gas-solid and gas-liquid flow systems. However, understanding of the three-phase flows is still limited because of the complex phenomena underlying interactions among the phases, including the particle-bubble interaction and the liquid interstitial effect during particle-particle collision. Recently, several CFD
models have been reported to simulate three-phase fluidization behavior [242-244]. The following literature review indicates that modeling effort of SBCRs can be grouped as (1) Axial dispersion models (ADM); (2) multiple cell circulation models (MCCM); and (3) CFD models. Details are given in the following.

### 2.5.1 Axial Dispersion Models

The most common approach for modeling liquid mixing in bubble columns is the 1-D axial dispersion model (ADM), in which all mechanisms leading to liquid-phase macro-mixing are lumped into a single axial dispersion coefficient. Due to its simplicity and ease of use, the 1-D axial dispersion model has been widely implemented, however, its validity in describing multiphase flows with large degrees of backmixing, such as those present in bubble and slurry bubble columns has been scrutinized [245, 246], with investigators going as far as advising against the use of the ADM for multiphase systems [247, 248]. Hatton and Lightfoot [248] assessed the problem of dispersion and mass transfer from a generalized dispersion framework and showed that simplistic 1-D dispersion models were incapable of describing the dispersion in multiphase systems. Myers et al. [249] presented a detailed analysis of the shortcomings of the ADM in bubble columns by comparing it to a two region phenomenological model designated as the slug and cell model, which represents the gas-rich and gas-lean parts of the column. Their model accounted for the different mechanisms governing the upwards and downwards mixing within the bubble column, which was in contrast to the gradient transport nature of the ADM, predicting a symmetric rate of transport with the mean liquid velocity. Nonetheless, despite the arguments against the use of ADMs, they remain widely popular due to their ease of implementation in complex systems,
and the fact that numerous correlations were developed for gas, liquid and solid dispersion coefficients in multiphase flows as shown in Tables A-8-10 to A-8-12 (Appendix A).

It should be emphasized that these dispersion coefficient correlations vary considerably in complexity as well as details; and different correlations could predict an order of magnitude difference as reported by Rice and Littlefield. [250]. Also, a major drawback of the ADM is that most of the experiments were conducted using air-water systems at ambient conditions; and the experimental data points obtained in the churn-turbulent flow regime were limited when compared with those in the bubbly flow regime [251].

The determination of liquid-phase dispersion coefficients is based on a tracer injection method, followed by analysis of the mean and the variance of the system response curves. Electrolytes, dyes, and heat are normally applied as a tracer, which can be injected in a steady-state or an unsteady-state method; and it has been verified that both methods provide same results [86]. In the steady-state method, a tracer is injected at the exit or in another convenient point in the reactor, the axial concentration profile is measured upward in the liquid bulk, and the dispersion coefficients are then evaluated from this profile. In the unsteady-state method, a variable flow of a tracer is injected, usually at the reactor inlet and samples are then taken at the exit.

Most of the liquid-phase dispersion coefficient ($D_L$) correlations are function of the superficial gas velocity and column diameter and in some cases, liquid properties are accounted for. The majority of these correlations are empirical; however, attempts at theoretical or semi-theoretical derivations of the axial dispersion coefficients, based on several theories and approaches, were made [252]. Baird and Rice [253] assumed the validity of the Kolmogorov theory of isotropic turbulence [254] and used dimensional analysis to show that the liquid-phase axial dispersion coefficient can be expressed as:
\[ D_L = K_r l_e^{1/3} P_m^{1/3} \]  

(2-16)

Where \( l_e \) is the characteristic length of the eddies, which are primarily responsible for eddy diffusion effects, \( P_m \) is the specific energy dissipation per unit mass which can be expressed as \( u_g g \) for bubble columns. Assuming the characteristic length is equivalent to the column diameter, Equation (2-16) can be rewritten as shown in Table A-10. This correlation is one of the most widely used to predict the liquid-phase backmixing in bubble columns.

Several investigators also correlated the axial liquid-phase dispersion coefficient in terms of the liquid circulation velocity [255, 256]. Joshi and Sharma [256] assumed the existence of axially symmetric steady multiple circulation cells in the bubble columns and used an energy balance to derive an expression for the average liquid circulation velocity. The liquid-phase axial dispersion coefficient was then directly correlated with the liquid recirculation velocity as shown in Equation (2-17).

\[ D_L = 0.31 d_c^{1.5} u_{lc}^{1.5} ; \quad \text{Where} \quad u_{lc} = 1.4 \left[ d_r g \left( u_G - \varepsilon_g \right) \right] \]  

(2-17)

This correlation showed good agreement with the experimental data [256] in small column diameters, however, its applicability to large column diameters is questionable as the existence of these multiple cells in a time averaged sense has not been experimentally investigated or correlated. Similarly, Zehner [255] develop an alternative model assuming the stationary eddies are layered transversely above each other, and showed the validity of the following commonly used relationship by McHenry and Wilhelm [257]:

\[ Pe = \frac{u_{lc} d_c}{D_L} \]  

(2-18)

He then derived the following expression for the liquid-phase axial dispersion coefficient, which is similar to that by Baird and Rice [253] as:
\[ D_L = 0.5 f^{1/3} d_c^{1/3} (u_c g)^{1/3} \]  

(2-19)

Where \( f \) is the friction factor, which was empirically correlated to be 0.398.

Figure 2-9 compares the predictions of the liquid axial dispersion coefficient by different models; and as can be seen most of the models exhibit similar trends with various column diameters, whereas there is a large discrepancy among the predictions at different superficial gas velocities.

Generally, the radial dispersion in BCRs has been lumped with the axial dispersion coefficient and the latter has been widely used and almost exclusively as an indication of mixing in such reactors. As a matter of fact, while considerable information exists on axial dispersion of fluids in bubble columns, radial mixing has been almost completely ignored. The few measurements cited by Deckwer [137] suggested that the radial dispersion coefficient is always less than one-tenth of the value of the axial dispersion coefficient.

Based on the assumptions that the velocities and holdups of individual phases are uniform in the radial and axial directions, and the axial (\( D_{zl} \)) as well as the radial (\( D_{rl} \)) dispersion coefficients were assumed to be constant throughout the fluidized bed, and the two-dimensional unsteady-state dispersion model can be expressed as:

\[
\frac{\partial (\varepsilon C)}{\partial t} + \frac{\partial (\varepsilon u_z C)}{\partial z} + \frac{1}{r} \frac{\partial (r \varepsilon u_r C)}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r \varepsilon D_{rl} \frac{\partial C}{\partial r} \right] + \frac{\partial}{\partial z} \left[ \varepsilon D_{zl} \frac{\partial C}{\partial z} \right]
\]  

(2-20)

Equation (2-20) is usually reduced to the axial dispersion (1-D) model, since the radial dispersion coefficient (\( D_{rl} \)) is often assumed to be negligible when compared with the axial dispersion coefficient.

Table A-13 (Appendix A) shows a summary of the ADM models in three-phase reactors available in the literature; and as can be seen in all models, three distinct phases (gas-phase, liquid-phase and solid-phase) are used. In most of these models, the gas-phase is described in terms of
‘large’ and ‘small’ bubbles [56, 150, 153, 241, 258, 259] and in other studies, a single-bubble model is assumed [157, 260, 261]. The solid-phase dispersed in the liquid-phase is referred to as the “slurry-phase”.

The solid (catalyst) concentration in the reactor is often assumed constant, and in several models, the Sedimentation-Dispersion Model (SDM) is used to estimate the catalyst concentration profile. Also, the syngas consumption is not always considered or is estimated using a linear relationship between the gas consumption and the syngas conversion; and in several models, an overall mass balance on the gas-phase is formulated in order to simulate the effect of syngas consumption [151, 158, 262-267].

Early models treated the gas-phase as plug-flow, while the slurry-phase is often assumed to be perfectly-mixed [247, 248, 253, 268-270]. This latter assumption is inappropriate for simulating small-scale reactors, however, it could be viable for large-scale ones since the liquid-phase backmixing and the dispersion coefficients were reported to increase with reactor diameter [253]. Recent models have introduced the dispersion coefficients in the mass balance equations when using the ADM for the gas and slurry phases [46, 150, 265]. Rados et al. [265] showed that utilizing the ADM to model backmixing in the F-T SBCR is more versatile than the combination of ideal reactor models, such as plug-flow and perfectly-mixed. Nonetheless, for large-scale F-T reactors, considering the gas-phase moves in a plug-flow and the slurry-phase moves as perfectly-mixed appeared to give the closest results to those obtained from the ADM [265].

Visual observations and photographic methods revealed the coexistence of distinctly two classes of gas bubbles (small and large) in Bubble Column Reactors (BCRs) operating in the churn-turbulent (heterogeneous) flow-regime [8, 175, 178, 185, 271]. This finding led to the separation of the gas-phase into two distinct classes, large gas bubbles and small gas bubbles. The large gas
bubbles class is often modeled as plug-flow while the small gas bubbles class is assumed to be perfectly-mixed, similar to the slurry-phase. This is an adequate assumption, since in large-scale F-T SBCRs operating in the churn-turbulent flow regime, the fast-rising large gas bubbles induce strong circulations and create backmixing or re-circulation zones wherein the small gas-bubbles are entrained [145, 175].

Few models employed the ADM for the large and small gas bubble classes as well as for the slurry-phase. de Swart and Krishna [153] used the ADM and 1st order reaction kinetics with respect to H₂ to simulate the F-T SBCR. These authors estimated the gas consumption using a simple linear relationship for the syngas conversion. Rados et al. [150] also used the ADM for both classes, however, they introduced a gas bubbles term to account for the interactions among gas bubbles of different classes. Moreover, they assumed that the magnitude of the interaction is proportional to a dimensionless cross-flow coefficient and the slip velocity between the two interacting classes of gas bubbles; however, they only provided a guessed value for this coefficient corresponding to moderate interactions between the small and large gas bubbles. In addition, these authors included the change of gas holdup and gas velocity due to the syngas consumption and in their derivation, they considered all of the variables as space-dependent of the mass balances.

Thus, it is obvious that the reactor model developed by Rados et al. [150] is quite different from the earlier models which assumed constant parameters along the reactor height or used a linear relationship between the syngas conversion and the gas velocity to represent the gas consumption. However, like de Swart and Krishna [153], Rados et al. [150] used 1st order reaction kinetics with respect to H₂ in order to simulate the F-T reaction and assumed the catalyst to be uniformly distributed. Iliuta et al. [160] introduced a pseudo 2-dimensional model based on the two-class bubbles model and the ADM by separating the reactor radially into a core region and an
annulus region; and they included the gas bubbles interactions term previously introduced by Rados et al. [150]. They considered the WGS reaction and used detailed kinetics for the F-T reaction. They also estimated the gas consumption from the overall mass balance, and the gas-phase and liquid-phase concentrations from the vapor-liquid-equilibria (VLE). Although the empirical reactor model by Iliuta et al. [160] appears to be the most complete to date, it requires the knowledge of many parameters which are not readily available, especially for high-pressure, high-temperature reactors operating with organic liquids, such as F-T synthesis. Obviously, this could be a disadvantage, since the estimation of so many unknown parameters may compound the errors, leading to significant uncertainties in the reactor model predictions.
Figure 2-9: Comparison among the liquid axial dispersion models at various
(a) column diameters for $u_g = 0.25$ m/s, (b) gas velocities for $d_c = 3.5$ m
### 2.5.2 Multiple Cell Circulation Models

Multiple cell circulation models (MCCM) were very popular in early modeling attempts aimed at understanding the hydrodynamics of bubble and slurry bubble column reactors. These models are based on the idea that the flow instability can be described mathematically using flow disturbances in the dispersed-phase, which can be accounted for in the mass balance as follows:

\[
\frac{\partial (\varepsilon + \delta \varepsilon)}{\partial t} + \nabla \cdot [(\varepsilon + \delta \varepsilon)(v + \delta v)] = 0
\]  
(2-21)

Mixing of the liquid-phase is attributed to various phenomena, such as turbulent vortices, liquid entrainment in the wakes of rising bubbles, liquid circulation and radial exchange flows. Generally, liquid mixing in bubble columns and SBCRs is a resultant of three major contributing mechanisms [140, 272-276]: (1) global convective circulation of the liquid-phase induced by the non-uniform radial gas holdup distribution [277]; (2) turbulent diffusion due to the presence of large and small eddies generated by the rising bubbles [135]; and (3) molecular diffusion is negligible when compared with the other diffusion mechanisms.

In SBCRs operating in the churn-turbulent flow regime, the gas flow generates significant backmixing in the slurry-phase (dense-phase). This backmixing of the dense-phase is caused by the gas-induced eddies, which derive their energy from the large fast-rising bubbles. The maximum size of eddies, for reactors with \(h_c/d_c > 1\) is limited by the column diameter \(d_c\) [135]. The induced circulation patterns have a strong impact on the mass transfer and productivity and are especially vital in eliminating the concentration gradients within the SBCRs. Therefore, the design of SBCRs will require consideration of the liquid-phase backmixing. In BCRs operating in the churn-turbulent flow regime, the large gas bubbles tend to concentrate in the middle of the column,
the liquid-phase is drawn upwards in the central region and when the bubbles disengage at the top, the liquid returns down the column in the wall region.

Despite the availability of ample experimental data on the liquid-phase backmixing in the literature for different column diameters and superficial gas velocities, it is somewhat difficult to compare the results due to the differences in the reactor dimensions and the physicochemical properties of the liquids used. Generally, the circulations consist of an upward flow region where the liquid-rich of entrained gas bubbles moves upward and a compensating region where a liquid-poor of gas bubbles moves downward [278]. The liquid circulations are driven by the buoyancy of the gas-phase as it rises and drags the liquid. The bubbles-driven circulations can occur with or without net superficial liquid motion, but it requires a net upward motion of the gas.

Although the liquid circulation is desirable for some applications, such as gas lift, thermosyphon devices, or in the downcomers of distillation columns, it is undesirable in BCRs or SBCRs, because it decreases the gas retention time and causes liquid backmixing, which decrease the gas-liquid mass transfer. For instance, the widely used simplification that the flow is uniform across any horizontal cross-sectional area of the BCR or SBCR consistently predicts greater gas holdup and better mass transfer values than those actually observed [278, 279]. Also, the assumption that large gas bubbles are completely backmixed [279] may not be true for columns with significant \( h_c/d_c \) ratios, wherein many liquid circulations are prevailing. The liquid circulation phenomenon, has been claimed by many authors to be analogous to the natural convection [161, 280-284]. Yet, this analogy is inaccurate, because in natural convection, the mixing of streams with different densities eliminates the driving force by producing a stream with intermediate density, which cannot regroup spontaneously into low- and high-density streams. However, if a bubble-rich and a bubble-lean streams are mixed to produce one stream of intermediate bubble content, this stream
can regroup (due to buoyancy forces) to reform bubble-rich and bubble-poor streams. Therefore, circulation in bubble columns does not permanently eliminate the driving forces of bubble-induced circulations as it does in natural convection.

Millies and Mewes [285] argued that the liquid recirculation in bubble columns is a turbulence-induced flow instability due to the disturbance or non-uniformity of the gas distribution profile, and hence they used the MCCM similar to that by Joshi and Sharma [256] to calculate the flow fields in their bubble column. This effect was firstly reported by De Nevers [278], who stated that the liquid circulation pattern is induced by density differences caused by the uneven distribution of the bubbly-phase across the cross-sectional area of the BC. In the central area of the BC, however, the local gas holdup values are greater than those close to the wall, resulting in liquid up-flow in the central region and liquid down-flow along the wall.

When there are no baffles or internals, the length of the circulation cell will depend on the difference between the gas and slurry viscosities and densities in the SBCRs. It is typically smaller for low viscosity liquids, such as water, and much larger for high viscosity systems, such as F-T slurries [278]. This makes the use of water-based empirical models, representing circulation or turbulence parameters, inaccurate for representing the F-T SBCRs. When the gas velocity inside the column is increased, the bubble flow ceases to be uniform and strong circulation was observed within the gas-slurry mixed phase and the column operated in the circulation flow regime [139, 140]. This circulation is once again due to the existence of a bubble-rich phase near the center of the column and a bubble-lean phase near the wall of the column, which creates a difference in buoyancy forces.

The 1-D circulation models are based on solving the one-dimensional continuity and momentum balance equations, which are simplified versions of the two-fluid model equations
These models are typically applicable to the middle of the SBCR with an $h_c/d_c > 5$, where experimental evidence shows the presence of 1-D profiles [277]. The model equations for the conservation of momentum are:

$$\frac{1}{r} \frac{d}{dr} \left( r \tau_{rz} \right) = \frac{dp}{dz} + \rho_l \left( 1 - \varepsilon_g(r) \right) g$$

(2-22)

$$- \frac{dp}{dz} = \frac{2 \tau_{rz}}{R} + \rho_l \left( 1 - \bar{\varepsilon}_g \right) g$$

(2-23)

Where $\varepsilon_g$ is the gas holdup and $\tau_{rz}$ is the Reynolds shear stress.

The Reynolds shear stress distribution is commonly described using the following procedure by Rice and Geary [141]:

$$\tau_{rz}(\xi) = \frac{\rho_l g d_c}{2} \left( \frac{2 \bar{\varepsilon}_G}{m \lambda^2} \right) \xi \left[ 1 - \left( \frac{\xi}{\lambda} \right)^m \right] \quad \xi \leq \lambda$$

$$\tau_{rz}^*(\xi) = \frac{\rho_l g d_c}{2} \left( \frac{\bar{\varepsilon}_G}{\lambda^2} \right) \xi \left[ \frac{\lambda^2 - \xi^2}{\xi} \right] \quad \xi \geq \lambda$$

(2-24)

The solution of the above model requires the knowledge of the gas holdup profile and a closure model for the Reynolds shear stress. Several variations of the above 1-D circulation model as shown in Figure 2-10 have been discussed in the literature [139-141, 286-288]. The variations of these models are mostly due to the boundary conditions and the Reynolds shear stress turbulence models used. Table A-14 (Appendix A) provides a summary of the various MCCM published in the literature.

Generally, the 1-D circulation model has been proven to be successful in studying liquid circulation in BCRs and SBCRs [289]. Kumar et al. [139] compared the existing variations of the 1-D circulation model to study liquid recirculation in BCRs; and they concluded that there is a lack of literature correlations for eddy viscosity and mixing length to predict the 1-D liquid velocity profiles under a wide range of operating conditions. They correlated a mixing length profile from
the experimental measurements of the Reynolds shear stress and liquid velocity gradient and showed that the mixing length in a 0.19 m diameter column can be used along with the measured holdup profile to predict recirculation in large diameter columns, up to 0.30 m. Their model was validated for gas velocities ranging from 0.02 – 0.12 m/s. The use of the power law expression was later introduced to predict the radial gas holdup profiles, as discussed in Section 2.2.2. The above system of equation is usually solved using numerical integration and details of the solutions can be found elsewhere [243, 285, 288, 290].

![Circulation cell depiction of the continuous-phase circulation patterns in BCRs and SBCRs: (a) Zehner [280, 281], (b) Groen et Al. [291], (c) Joshi And Sharma [256].](image-url)
2.5.3 Computational Fluid Dynamics (CFD) Models

CFD modeling of multiphase systems can be successful, if the calculations are carefully validated. A general overview of a CFD model development is shown in Figure 2-11. It is typically composed of three main stages: pre-processing, solver development, and post processing. Pre-processing involves the development of the geometry to be investigated and defining the meshing procedure over which the model will be solved. Solver development describes all activities related to defining model structures, properties, parameters, boundary and initial conditions, and solution methods. Once the model is solved for a specific case, the raw data is then post processed to generate analyzable figures and graphics.

The two most commonly used CFD approaches [292] are the Eulerian-Eulerian or Multi-fluid Eulerian approach [293] and the Eulerian-Lagrangian approach [294]. The Eulerian-Eulerian approach assumes that the dispersed and continuous phases are interpenetrating continua, and a set of Navier-Stokes equations is solved for each of the phases. The coupling between the motion of

Figure 2-11: Overview of CFD process

The two most commonly used CFD approaches [292] are the Eulerian-Eulerian or Multi-fluid Eulerian approach [293] and the Eulerian-Lagrangian approach [294]. The Eulerian-Eulerian approach assumes that the dispersed and continuous phases are interpenetrating continua, and a set of Navier-Stokes equations is solved for each of the phases. The coupling between the motion of
of the dispersed and continuous phases is achieved by implementing momentum exchange terms into the respective phase’s momentum balance equations, which are based on drag consideration. On the other hand, the Eulerian-Lagrangian approach assumes that the dispersed-phase consists of representative particles transported with the continuous-phase and a set of Navier-Stokes equations, which include coupling between the continuous and dispersed phases, is solved only for the continuous-phase, whereas the dispersed-phase particles are tracked by solving the individual motion equations for each particles. Table A-15 (Appendix A) shows a summary of the CFD modeling efforts in three-phase reactors using 2-D and 3-D Multi-fluid Eulerian and Eulerian-Lagrangian models. In general, the Eulerian-Lagrangian model is best suited for fundamental studies, such as bubble-bubble and bubble-liquid interactions and its applications are limited only to cases where the gas superficial velocities are low and the phase holdups are small. Thus, this model is not viable when the dispersed-phase occupies a large volume fraction of the reactor, such as in many industrial applications. As a result, the Multi-fluid Eulerian approach is typically preferred for modeling large-scale applications, including SBCRs, which often operate in the churn-turbulent flow regime [295], where gas holdup values are high. Additional simplifications, such as 2-D Cartesian with axisymmetry and isothermal flow, are usually implemented in order to lower the computational cost [201, 243, 244, 293, 294, 296-302]. Details of the various modeling approaches can be found elsewhere [242, 275, 298, 303-308].

The momentum balance equation in the Multi-fluid Eulerian approach is:

$$\frac{\partial (\alpha_k \rho_k u_k)}{\partial t} + \nabla \cdot (\alpha_k \rho_k u_k u_k) = -\alpha_k \nabla p - \nabla \cdot (\alpha_k \tau_k) + \alpha_k \rho_k g + F_D + F_G$$  \hspace{1cm} (2-25)

In the Eulerian-Lagrangian approach, the force balance equation used to track individual particles is:
Among the above forces, Becker [309] and Oey et al. [310] reported that the drag force ($F_D$) is the most critical, whereas the other forces only have a minor or “tuning” effect.

The drag force between any two phases can be written as:

$$F_D = \frac{1}{2} C_D \pi r_d^2 \rho_c \left| u_s \right| u_s$$  \hspace{1cm} (2-27)

Where, $C_D$ is the drag coefficient.

The CFD modeling of multiphase reactors strongly depends on the closure drag model; and the effects of using different drag coefficient correlations on the modeling results have been reported in literature [302, 311, 312]. The most commonly used drag coefficients for two-phase and three-phase systems are given in Section 2.5.3.1.

In most CFD reactor modeling, the simulation domain is typically restricted to the reactor and the general flow within the feed, whereas spargers and cooling pipes are not accounted for. Furthermore, although the inlet volumetric flow rates are known, the velocity distribution is not specified. The most widely used practice is to use the knowledge of fully developed flow in pipes to specify the inlet velocity distribution. Therefore, for laminar flow through a cylindrical inlet pipe, one can specify a parabolic velocity profile as a boundary condition at the inlet, however, if the feed pipes have complex shapes, which is typical of bubble columns and SBCRS, it is necessary to develop an additional model, which include appropriate boundary conditions. The outlet is the surface of the solution domain through which the flow exits. Usually the outlet boundary condition implies that the gradients normal to the outlet boundary are zeros for all the variables, except pressure. In order to predict the effects of turbulence, CFD models primarily concentrate on the methods which make use of turbulence models. These methods have been specifically developed
to account for the effects of turbulence without recourse to a prohibitively fine mesh and direct numerical simulation.

Generally, liquid mixing in SBCRs is a resultant of three major contributing mechanisms [140, 272-276]: (1) global convective circulation of the liquid-phase induced by the non-uniform radial gas holdup distribution [277]; (2) turbulent diffusion due to the presence of large and small eddies generated by the rising bubbles [135]; and (3) molecular diffusion is negligible when compared with the other diffusion mechanisms.

Scaling laws are an important tool for describing turbulence. Most of the conclusions and observations regarding turbulence are based on the order of magnitude estimates, which follow from logical applications of scaling laws and dimensional analysis. Generally, the turbulent length scale is a physical quantity related to the size of the large eddies, containing the energy in the turbulent flow. A variety of length scales (eddy sizes) exists within the turbulent flow, wherein the size of the largest eddies are typically denoted by \( L \), and those of the smallest eddies are denoted by \( \eta \). The largest eddies in the flow account for most of the momentum and energy transport, and their size is only constrained by the physical boundaries of the flow. Thus, \( L \) is referred to as the integral length scale. The size of the smallest eddies \( (\eta) \), on the other hand, is determined by the viscosity. Therefore, the effect of viscosity increases with decreasing length scales. The smallest length scales are those where the kinetic energy is dissipated into heat. The turbulence eddies are visualized as molecules, constantly colliding and exchanging momentum and obeying laws similar to the kinetic theory of gases. Most models of Reynolds stress, using an eddy viscosity hypothesis based on an analogy between the molecular and turbulent motions, are described as follows:

\[
-\rho u_i u_j = \mu_T \left( \frac{\partial u_i}{\partial x_i} + \frac{\partial u_j}{\partial x_j} \right) - \frac{2}{3} \delta_{ij} \left( \mu_T \frac{\partial u_k}{\partial x_k} + \rho k \right)
\] (2-28)
Where $\mu_T$ is the turbulent or eddy viscosity, which unlike molecular viscosity, is not a fluid property, but depends on the local state of flow or turbulence; $\mu_T$ is a scalar quantity, which varies significantly within the flow domain; and $k$ is the turbulent kinetic energy.

Although there are numerous turbulence models as outlined in Table 2-5, the most widely used is the two-equation, $k$-$\varepsilon$, model; in which the turbulence viscosity is related to $k$ and $\varepsilon$ by the following equation:

$$\mu_T = \frac{C_\mu \rho k^2}{\varepsilon}$$  \hspace{1cm} (2-29)

Where $C_\mu$ is an empirical coefficient; and the modified form of the transport equation for the $k$-$\varepsilon$ model becomes:

$$\frac{\partial p k}{\partial t} + \frac{\partial (\rho u_i k)}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \frac{\mu_T}{\sigma_k} \frac{\partial k}{\partial x_i} \right) + G - \rho \varepsilon$$  \hspace{1cm} (2-30)

$$\frac{\partial \rho \varepsilon}{\partial t} + \frac{\partial (\rho u_i \varepsilon)}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \frac{\mu_T}{\sigma_k} \frac{\partial \varepsilon}{\partial x_i} \right) + \varepsilon \left( C_1 G - C_2 \rho \varepsilon \right)$$  \hspace{1cm} (2-31)

Where $G$ is the turbulence generation term expressed as:

$$G = \frac{1}{2} \mu_T [ \nabla \bar{u} + (\nabla \bar{u})^T ]^2$$  \hspace{1cm} (2-32)

The values of the empirical parameters in the above turbulence equations are obtained using experimental data and can be found in the literature.
<table>
<thead>
<tr>
<th>Model</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero-equation models (Mixing length model)</td>
<td>• Cost-effective</td>
<td>• Applicable to very limited number of flows</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• $v_T \to 0$ as $\partial U / \partial y = 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Lack of transport of turbulent scales.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Estimation of mixing lengths is difficult.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Cannot be used as a turbulence model.</td>
</tr>
<tr>
<td>One-equation model (k-algebraic model)</td>
<td>• Cost-effective model</td>
<td>• Applicable to limited number of flows</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• The use of an algebraic equation to represent length scale is too restrictive.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Transport of the length scale is not accounted for.</td>
</tr>
<tr>
<td>Reynolds Stress Model (RSM)</td>
<td>• Most general model</td>
<td>• Solves for seven additional PDE’s, increased computational load</td>
</tr>
<tr>
<td></td>
<td>• Can well predict many complex flow scenarios such as non-circular ducts and curved flows</td>
<td>• Not good for round jets and flows involving significant curvature, swirl, sudden acceleration, separation and low Re regions.</td>
</tr>
<tr>
<td>Two-equation models (k-$\varepsilon$: standard, RNG, realizable)</td>
<td>• Can predict velocity and length scales with transport equations.</td>
<td>• Limited to an eddy viscosity assumption.</td>
</tr>
<tr>
<td></td>
<td>• Good results for numerous flow applications.</td>
<td>• Turbulent viscosity is assumed to be isotropic.</td>
</tr>
<tr>
<td></td>
<td>• Robust economically and easy to implement.</td>
<td>• Convection and diffusion of the shear stress are neglected.</td>
</tr>
<tr>
<td>Standard k-$\varepsilon$</td>
<td>• Very widely used and heavily validated.</td>
<td>• Performs poorly in certain scenarios same as RSM.</td>
</tr>
<tr>
<td>RNG k-$\varepsilon$</td>
<td>• Enhancement of the standard k-$\varepsilon$ model primarily to improve prediction of swirling flows and flow separation.</td>
<td>• Not as stable as the standard k-$\varepsilon$ model, not suitable for round jets.</td>
</tr>
<tr>
<td>Realizable k-$\varepsilon$</td>
<td>• Enhancement of the standard k-$\varepsilon$ model to handle both swirling flows and round jets.</td>
<td>• Can be very unstable and susceptible to divergence.</td>
</tr>
</tbody>
</table>
Grevskott [243] modeled water-TiO$_2$ nanoparticles as a single pseudo-homogenous-phase, assuming that the nanoparticles are sufficiently small to behave as liquid molecules, and accordingly the water and solid particles were assumed to have the same local velocity. The momentum and continuity equations were then solved using a 3-D, two-fluid Eulerian model with per phase $k$-$\varepsilon$ turbulence in order to investigate the local holdups and velocities of the phases. Fan et al. [294, 313] developed a 2-D Eulerian-Lagrangian model for three-phase systems using: (1) the averaged Navier-Stokes equation for the liquid-phase (Euler), (2) the volume of fluid (VOF) method for the gas-phase, and (3) the discrete particle method (DEM) for the solid-phase (Lagrange). Their simulations, however, were limited to 100 solid particles, and they investigated the behavior of a single-bubble rise. A similar approach was used by Zhang and Ahmadi [298].

Mitra-Majumdar et al. [244] used a 2-D axisymmetric model with a modified drag coefficient model between the liquid and gas phases to represent the effect of gas bubbles, and another modified drag coefficient model between liquid and solid phases to simulate the effect of solid particles. Matonis et al. [297] applied the kinetic theory of granular flow (KTGF) for the solid-phase and the $k$-$\varepsilon$ turbulence model for the continuous-phase. Schallenberg et al. [299] accounted for the interphase momentum between the two dispersed phases (gas and solid) and extended the $k$-$\varepsilon$ turbulence model to account for the bubble induced turbulence. Panneerselvam et al. [293] used the multi-fluid Eulerian model to investigate the gas holdup and axial solid velocity patterns in three-phase fluidized beds. They used the closure law for modeling the liquid turbulence as well as the interphase momentum exchange and the $k$-$\varepsilon$ turbulence for modeling the turbulence induced by the phases. They also used the constant viscosity model for calculating the solid pressure term, instead of using the kinetic theory of granular flow.
Matos et al. [301] used an axisymmetric two-fluid Eulerian approach for modeling a three-phase slurry reactor for petroleum hydrodesulfurization. They combined the solid and liquid phases into a pseudo-liquid-phase and assumed that the difference between the densities of the catalyst and the slurry-phase was so small that the catalyst did not settle, and that the fluid velocity was so small that a 2-D axisymmetric model was justified. They used friction terms to couple the momentum balance of the gas-phase and the pseudo-liquid-phase; the overall mass balance to couple both phases; the $k$-$\varepsilon$ turbulence model to describe the behavior of the continuous-phase; and the axial velocities at the entrance of the reactor were set using the experimental results by Torvik and Svendsen [314]. They also added simplified hydro-desulfurization kinetics to the mass balance. They then investigated the radial variations of the gas and liquid holdups and the results were validated against the experimental values reported by Grienberger and Hofmann [315] for a two-phase, air-water system. They also, investigated the effects of the grid size and simulation time on the kinetic results.

Troshko and Zdravistch [316] employed a two-fluid Eulerian approach to model a three-phase SBCR for F-T synthesis. They used a population balance model to predict the bubble size distribution throughout the reactor and a turbulence was described using the two-equation RNG $k$-$\varepsilon$ turbulence model. They used the interphase drag exchange coefficient by Ishii and Mishima [272] and incorporated the heterogeneous and homogenous kinetic reaction rates by Yates and Satterfield [317], representing a simplified F-T synthesis. They predicted the time-averaged Sauter mean bubble diameter at different elevations from the inlet of the SBCR, the gas holdup at different catalyst concentration, and the axial variation of the time-averaged Sauter mean bubble diameter along the reactor axis at different catalyst concentrations. Their results were then validated against the experimental data by Kulkarni et al. [318] for air-water bubble columns at standard
atmospheric conditions. Moreover, they also modeled the effect of the syngas inlet velocity on its conversion and reactor productivity; however, these results were not validated against any experimental data.

It should be emphasized that around half of the CFD multi-phase modeling efforts shown in Table A-15 (Appendix A) have not been experimentally validated and that, except for the work by Matos et al. [301], almost all experimental validations were conducted using small-scale air-water-solid systems at ambient pressures and temperatures, which brings into question the validity of extrapolating the conclusions to large-scale industrial reactors, operating under high pressures and temperatures with organic liquids and slurries, such as F-T synthesis.

2.5.3.1 Commonly used drag coefficient models for two-phase and three-phase systems

While there is extensive work on two-phase flow systems, studies investigating three-phase hydrodynamics are rather limited. Tables A-8-16 and A-8-17 (Appendix A) show the gas-liquid and solid-fluid drag coefficient models, respectively, which are commonly used in CFD modeling of multiphase flows. In general, the drag coefficient (CD), is a function of the bubble (or particle) Reynolds Number and the void fraction. Table A-16 (Appendix A) shows the gas-liquid drag coefficient correlations obtained using experiments in two-phase systems by Clift et al. [171], Ishii and Zuber [319], Kurose et al. [320], Lain et al. [321] and in three-phase systems by Grevskott et al. [243] and Tomiyama et al. [322]. Also, the model by Mei and Klausner [323] was based on a derivation for spherical bubble in an unbounded shear flow and the model by Snyder et al. [324] was based on the statistical analysis of small bubbles in isotropic turbulence. The solid loading used by Grevskott et al. [243] was 7 – 20 wt.% and the solid holdup used by Tsuchiya et al. [325] was up to 57 vol.%. Moreover, Figure 2-12 (b) compares a few gas-liquid drag correlations, and
as can be seen most correlations predict very similar values for the drag coefficient at varying bubble Reynolds numbers. It should be noted that all the gas-liquid drag coefficient correlations presented in Table A-16 (Appendix A) were developed under ambient conditions.

Table A-17 (Appendix A) shows the gas-solid and liquid-solid drag coefficient correlations; and as can be seen all correlations were derived from experimental data, except those by Ma and Ahmadi [326] who used thermodynamic derivation for multiphase turbulent flows; Gidaspow [242] who used theoretical derivation; and Zhang and Van der Heyden [327] who used numerical simulation for gas-solid flows. This difference among the correlations is primarily due to the nature of the experiments conducted or to the assumptions made to develop these correlations. For instance, the model by Ishii and Zuber [319] assumes the slip velocity is independent of the gas bubble diameter, while that by Schiller and Nauman [6] does not account for the bubble deformation effects. This in fact, limits these models applicability beyond the systems used in their development. Figure 2-12 (a), compares various liquid-solid drag correlations at various particle Reynolds numbers, and unlike the gas-liquid drag correlations, the liquid solid drag coefficients appear to vary greatly at similar values of the Reynolds Number which amplifies the confusion about the selection of solid-liquid and/or gas-solid drag coefficient models for CFD modeling of SBCRs.

Thus, the gas-liquid and liquid solid drag models available were obtained mostly using air-water or air-water-glass beads flows under ambient conditions, which again bring into question their applicability for modeling large-scale industrial SBCRs, operating with organic media under high pressures and temperatures. Moreover, Zhang and Ahmadi [298] and more recently Hamidipour et al. [292] underscored the need for better and more representative drag correlations for their CFD modeling of the hydrodynamics in three-phase reactors. In addition, in some CFD
modeling efforts, the gas-liquid drag coefficients were justified by lumping the liquid and solid phases into one pseudo-homogenous phase (slurry), assuming the particle-liquid slip velocity is too small, which reduces the gas-liquid-solid system to a two-phase system [158, 292, 294, 298, 301, 302]. This is definitely a gross oversimplification of the three-phase flow since the gas-liquid drag coefficients were used instead of gas-slurry drag coefficients. Therefore, there is a great need to develop pertinent and applicable drag coefficient correlations for modeling SBCRs.
Figure 2-12: Comparison of various (a) Liquid-Solid and (b) Gas-Liquid drag correlation
3.0 RESEARCH OBJECTIVE

Modeling of 3-phase Slurry Bubble Column Reactors (SBCRs) requires, among others, detailed description of the hydrodynamics, reaction kinetics and mass as well as heat transfer parameters. Over the past 20 years, our research group has been measuring macroscopic values of these parameters in a pilot-scale (0.3-m ID and 3-m height) hot SBCR, available in our Reactor and process Engineering Laboratory (RAPEL) at the University of Pittsburgh. These data were used as input in 1-D and 2-D steady-state empirical reactor models which were incorporated into a working simulator in our laboratory [301, 328]. These empirical models, however, are incapable of predicting the local hydrodynamic or mass transfer values, flow patterns, radial velocities, species distribution or solid concentration profiles, which makes it difficult to interpret the hydrodynamic behavior and overall performance of SBCRs. Computational Fluid Dynamics (CFD), which could provide such data, have been recently used in modeling SBCRs, as 2-D and 3-D CFD multiphase systems are available in the literature. Many CFD modeling frameworks, however, have not been properly validated since, except for the work by Matos et al. (2009) [301], almost all validations were carried out with data obtained in small-scale reactors for air-water-solid systems at ambient conditions. Therefore, the predictions of the current CFD models cannot offer any proper interpretation of the complex hydrodynamic behavior of large-scale SBCRs operating at high-pressures and high-temperatures, and often provided with cooling internals.

68
The overall objective of this study is to develop a more comprehensive CFD model in ANSYS for LTFT synthesis in SBCRs. This three-phase model is based on the principles of conservation of mass and momentum in turbulent flow, and includes many complexities, such as gas-liquid-solid contacts, momentum exchange, solid-phase representation, bubble induced turbulence, bubble population balance, and actual reaction kinetics and gas-liquid mass transfer data for F-T synthesis. The CFD model is used to predict the volume fractions, species distribution and velocity profiles for the three phases in space and time. These predictions are validated against actual experimental hydrodynamic data available in the literature and those obtained for F-T synthesis in our pilot-scale SBCR. Upon successful validation, the CFD model is used to thoroughly investigate the effects of the three main spatio-temporal complexities, namely gas sparger design, cooling internals layout, and reaction kinetics, on the hydrodynamic and overall behavior of SBCRs for F-T synthesis.

In order to achieve this objective, the following tasks are proposed:

Task 1: Develop a three-phase CFD model for the slurry bubble column reactor.

Task 2: Validate the CFD model predictions against our experimental data and those available in the literature for multi-phase systems.

Task 3: Use the CFD model to investigate the effects of spargers on the local hydrodynamics in the pilot-scale SBCR:

Task 4: Use the CFD model to predict the effects of internals on the local hydrodynamics in the pilot-scale and a conceptual large-scale SBCRs

Task 5: Incorporate the F-T reaction kinetics into the CFD model and use it to predict the performance as well as the local hydrodynamics in the pilot-scale and a commercial-scale F-T SBCRs.
The 3-D transient model built in the present study is based on the Eulerian multi-fluid approach for the three phases (gas-liquid-solid). The model equations are based on the ensemble averaging of the local instantaneous equations for a single-phase flow [274, 329]. The complete mathematical model is based on an a multi-Eulerian approach and consists of three main components: (i) the core hydrodynamics model consisting of the Navier-Stokes equations; (ii) the multiple-fluid model based on an analog of Boussinesq approximation to represent the natural convection; and (iii) the population balance equations to describe the size distribution of the dispersed gas-phase. A schematic diagram of the model components and their couplings is given in Figure 4-1.

Figure 4-1: Schematic of the model components and their couplings
The mass and momentum conservation equations are:

$$\frac{\partial \left( \rho_k \alpha_k \right)}{\partial t} + \nabla \left( \rho_k \alpha_k \bar{u}_k \right) = \dot{m}_{kn}$$  \hspace{1cm} (4-1)

$$\frac{\partial \left( \rho_k \alpha_k \bar{u}_k \right)}{\partial t} + \nabla \left( \rho_k \alpha_k \bar{u}_k \bar{u}_k \right) = -\alpha_k \cdot \nabla p_f + \nabla (\alpha_k \bar{\tau}_k) + \alpha_k \rho_k g + \bar{u}_{kn} \dot{m}_{kn} + \bar{M}_k$$  \hspace{1cm} (4-2)

Where \( k \) indicates the phase (G for gas, L for liquid and S for solid); \( \bar{u}_k = (u, v, w) \) is the velocity of phase \( k \); \( \dot{m}_{kn} \) is the mass transfer rate between phases \( k \) and \( n \); \( \bar{u}_{kn} \) is the relative velocity between phases \( k \) and \( n \); \( \alpha \) is the volume fraction of each phase; \( \bar{M}_k \) is the overall interfacial momentum, \( p_f \) is the fluid pressure; and \( \tau \) is the stress tensor.

The stress tensor \( \bar{\tau}_k \) is represented as:

$$\bar{\tau}_{k=G,L} = \alpha_k \mu_{k,\text{eff}} \left( \nabla \bar{u}_k + \left( \nabla \bar{u}_k \right)^T - \frac{2}{3} I \left( \nabla \cdot \bar{u}_k \right) \right)$$  \hspace{1cm} (4-3)

\( \mu_{\text{eff}} \) is the effective viscosity, which is typically the sum of molecular and turbulent viscosities.

For the liquid-phase, the effective viscosity, which accounts for the three contributions (1) molecular viscosity, \( \mu_{L,M} \), (2) shear induced turbulence viscosity, \( \mu_{L,T} \) and (3) additional term due to the bubble induced turbulence, \( \mu_{L,B} \) is represented as:

$$\mu_{\text{eff}} = \mu_{L,M} + \mu_{L,T} + \mu_{L,B}.$$  \hspace{1cm} (4-4)

The turbulent viscosity is expressed as:

$$\mu_{L,T} = C_{\mu,B} \rho_L \left( \frac{k^2}{\epsilon} \right), \hspace{1cm} \text{with} \hspace{1cm} C_{\mu,B} = 0.6$$  \hspace{1cm} (4-5)

For the gas-phase, the effective viscosity is represented as the sum of the molecular viscosity \( \mu_{G,M} \) and the turbulence induced viscosity:

$$\mu_{\text{eff}} = \mu_{G,M} + \mu_{G,T}.$$  \hspace{1cm} (4-6)

Where the turbulence induced viscosity for the gas-phase is represented as:
\[ \mu_{G,T} = \frac{\rho_L}{\rho_G} (\mu_{L,T}) \] (4-7)

### 4.1 SOLID PHASE REPRESENTATION

For the solid-phase, the effect of particle-particle interactions will be accounted for by introducing additional terms to the stress tensor. The kinetic theory of granular flow (KTGF) is be used to represent the solids behavior in the system. The stress tensor for the solid-phase is represented as:

\[ \tau_s = \alpha_s \mu_s (\nabla \bar{u}_s + (\nabla \bar{u}_s)^T) - p_s \bar{I} + \alpha_s \mu_s \left( \lambda_s - \frac{2}{3} \right) \bar{I} (\nabla \cdot \bar{u}_s) \] (4-8)

\( \lambda_s \), is the solids bulk viscosity, which describes the resistance of the particle suspension against compression; and is expressed as:

\[ \lambda_s = \frac{4}{3} \alpha_s^2 \rho_s d_p g_0 (1 + e_p) \sqrt{\frac{\theta}{\pi}} \] (4-9)

\( P_s \), is the solids pressure, which represents the normal solid-phase forces due to particle-particle interactions; and is expressed as: [330]

\[ P_s = \rho_s \alpha_s \theta + 2 g_0 \rho_s \alpha_s^2 \theta (1 + e_p) \] (4-10)

The first term in the right-hand-side of the solid pressure equation represents the kinetic contribution, which accounts for the momentum transferred through the system by particles moving across imaginary shear layers in the flow. The second term represents the collisional contribution, which represents the momentum transferred by direct collisions.

\( e_p \), is the restitution coefficient, which represents the ratio of normal relative velocity after and before the collision, and it is taken as 0.9 as proposed by Ding and Gidaspow [331].
$g_0$, is the radial distribution function, which accounts for the increase in the probability of collisions when the particle density increases; and is expressed as [171, 331]:

$$
g_0 = 0.6 \left[ 1 - \left( \frac{\alpha_s}{\alpha_{s,\text{max}}} \right)^{1/3} \right]^{-1}
$$

(4-11)

Where $\alpha_{s,\text{max}} = 0.62$, and beyond this value, the radial distribution function goes to infinity.

$\Theta$, represents the granular temperature, which is a measure of the kinetic energy contained in the fluctuating velocity for the solid particles and it is defined using the algebraic model by Ding and Gidaspow, [331] which helps minimize the computational load by avoiding to solve an additional differential equation along with its closure models:

$$
\theta = \frac{d_p^2}{30(1 - e_p)} (\mathbf{v}_s + (\mathbf{v}_s)^T)
$$

(4-12)

$\mu_s$, represents the solids shear viscosity, which is an elastic force, arising from the solid-phase the response to shear, compression and extension stresses exerted on it by the continuous liquid-phase. It should not be confused with the viscous forces, which arise during the fluid flow, as fluid viscosities are proportional to the rate of deformation over time, whereas the solid viscosity is proportional to the amount of shear deformation. The following model by Gidaspow [242] is used to describe the solid-phase viscosity as follows:

$$
\mu_s = \frac{4}{5} \alpha_s^2 \rho_s d_p g_0 (1 + e_p) \sqrt{\theta \pi} \left[ \frac{2 \sqrt{\pi}}{96} \rho_s d_p \sqrt{\theta} \right] \left[ 1 + \frac{4}{5} \alpha_s g_0 (1 + e_p) \right]^2
$$

(4-13)
4.2 TURBULENCE MODEL

As the mass and momentum balances are obtained through the ensemble averaging formulations, the terms $u_k$ and $u_k'$ represent the mean and fluctuating components of the velocity, thus the unclosed terms in the stress Equation (4-3) should be modeled. It is decided to use the RNG $k$-$\varepsilon$ turbulence model after a comparison between various $k$-$\varepsilon$ turbulence schemes was conducted [332]. The turbulent kinetic energy ($k$) and the turbulent energy dissipation ($\varepsilon$) are calculated based on the following governing equations, respectively:

$$\frac{\partial (\rho k)}{\partial t} + \mathbf{V}(\rho K \mathbf{u}) = \nabla (P r_{eff,k} \mu_{eff} \nabla k) + G_k + G_b - \rho \varepsilon - Y_M + S_k \quad (4-14)$$

$$\frac{\partial (\rho \varepsilon)}{\partial t} + \mathbf{V}(\rho \varepsilon \mathbf{u}) = \nabla (P r_{eff,\varepsilon} \mu_{eff} \nabla \varepsilon) + C_{\varepsilon 1} \frac{\varepsilon}{k} (G_k + C_{\varepsilon 3} G_b) - C_{\varepsilon 2} \rho \frac{\varepsilon^2}{k} - R_{\varepsilon} + S_{\varepsilon} \quad (4-15)$$

Where $G_k$ represents the generation of turbulence kinetic energy due to the mean velocity gradients; $G_b$ is the generation of turbulence kinetic energy due to buoyancy; $Y_M$ is the contribution of the fluctuating dilatation in compressible turbulence to the overall dissipation rate; $C_{\varepsilon 1}$, $C_{\varepsilon 2}$, $C_{\varepsilon 2}$ are constants set as 1.44, 1.92 and 0.09, respectively. $P r_{eff,k}$ and $P r_{eff,\varepsilon}$ are the inverse effective Prandtl numbers for $k$ and $\varepsilon$, respectively derived analytically using the RNG theory. In addition, $S_k$ and $S_{\varepsilon}$ are user-defined source term. The equations used to calculate some of the above parameters are:

$$G_k = \mu_t \left( \frac{\partial \mathbf{U}_i}{\partial x_j} + \frac{\partial \mathbf{U}_j}{\partial x_i} \right) \frac{\partial \mathbf{U}_i}{\partial x_j} - \frac{2}{3} \frac{\partial \mathbf{U}_k}{\partial x_k} \left( 3 \mu_t \frac{\partial \mathbf{U}_k}{\partial x_k} + \rho k \right) \quad (4-16)$$

$$G_b = \begin{cases} \frac{\mu_t}{\rho \sigma_p} \frac{\partial p}{\partial x_i} & \text{full buoyancy model} \\ \frac{\mu_t}{\rho \sigma_p} \rho \beta g_i \frac{\partial T}{\partial x_i} & \text{Boussinesq buoyance model} \end{cases} \quad (4-17)$$
\[ \left( \frac{Pr_{eff}^{-1} - 1.3929}{\alpha_0 - 1.3929} \right)^{0.6321} \cdot \left( \frac{Pr_{eff}^{-1} + 2.3929}{\alpha_0 + 2.3929} \right)^{0.3679} = \frac{\mu_{mol}}{\mu_{eff}}, \quad \alpha_0 = 1 \] (4-18)

Where \( \alpha_0 = 1 \), ( \( \mu_{mol} \) ) is the molecular viscosity. In the high Reynolds number limit where \( \left( \frac{\mu_{mol}}{\mu_{eff}} \ll 1 \right) \), and \( Pr_{eff,e}^{-1} = Pr_{eff,k}^{-1} \approx 1.393 \) [333].

### 4.3 MOBILEMUM EXCHANGE TERMS AND INTERPHASE COEFFICIENT CORRELATIONS

The momentum exchange term in the momentum balance Equation (4-2), which describes the interface forces between the phases has been described as follows:

\[ \vec{M}_k = \vec{M}_D + \vec{M}_L + \vec{M}_VM + \vec{M}_W + \vec{M}_{TD} \] (4-19)

The right hand terms of Equation (4-19) represent the interphase drag, lift, virtual mass, wall force, and turbulence dispersion, respectively. A brief description of each of the momentum (force per unit volume), in addition to the expression used to describe them in this model is presented in Table 4-1. The terms for the various coefficients used in these terms are presented in Table 4-2.
<table>
<thead>
<tr>
<th>Force Term</th>
<th>Equation used in model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drag</td>
<td>( \vec{M}<em>{D,G} = \vec{M}</em>{D,G-L} + \vec{M}<em>{D,G-S} ), ( \vec{M}</em>{D,L} = \vec{M}<em>{D,L-G} + \vec{M}</em>{D,L-S} ), ( \vec{M}<em>{D,S} = \vec{M}</em>{D,S-G} + \vec{M}_{D,S-L} )</td>
<td>Clift et al. [171] Schallenberg et al. [299]</td>
</tr>
<tr>
<td></td>
<td>( G - L: \vec{M}<em>{D,G-L} = \frac{3}{4} C</em>{D,G-L} \alpha_G \alpha_L \rho_L</td>
<td>\vec{u}_G - \vec{u}_L</td>
</tr>
<tr>
<td></td>
<td>( S - L: \vec{M}<em>{D,G-L} = \frac{3}{4} C</em>{D,S-L} \alpha_S \alpha_L \rho_L</td>
<td>\vec{u}_S - \vec{u}_L</td>
</tr>
<tr>
<td></td>
<td>( S - G: \vec{M}<em>{D,G-S} = \frac{3}{4} C</em>{D,S-G} \alpha_S \rho_G</td>
<td>\vec{u}_S - \vec{u}_G</td>
</tr>
<tr>
<td>Lift</td>
<td>( \vec{M}_{L,L} = \alpha_G \rho_L \sum (\vec{u}_G - \vec{u}_L) \times (\nabla \times \vec{u}_L) )</td>
<td>Drew et al. [334, 335]</td>
</tr>
<tr>
<td>Virtual Mass.</td>
<td>( \vec{M}_{VM} = \alpha_G \rho_L \sum \left( \frac{D \vec{u}_G}{Dt} - \frac{D \vec{u}<em>L}{Dt} \right) ), ( C</em>{VM} = 0.5 )</td>
<td>Auton et al. [336]</td>
</tr>
</tbody>
</table>
| Lateral     | \( \vec{M}_W = \left\{ \begin{align*} \alpha_G \rho_L \frac{(\vec{u}_G - \vec{u}_L)}{D_S} \max \left( 0, C_{w1} + C_{w2} \frac{D_S}{y_w} \right) n_w \quad y_w < \left( \frac{C_{w2}}{C_{w1}} \right) D_S \\
0 \end{align*} \right. \) \( y_w: \) distance from wall, \( n_w: \) vector normal to wall, \( C_{w1} = -0.0064, C_{w2} = 0.0166 \) | Antal et al. [337] Krepper et al. [338] |
| Turbulence dispersion | \( M_{TD} = C_{TD} \rho_L k \nabla \alpha_G \) \( C_{TD} = 0.2 \) | Bertodano [339] Burns et al. [340] |
### Table 4-2: Interphase coefficient expressions used in our model

<table>
<thead>
<tr>
<th>Term</th>
<th>Model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas-Liquid Drag</strong></td>
<td>$C_{D,G-L} = \begin{cases} \left(\frac{24}{Re_b}\right)(1 + 0.1Re_b^{0.75}) &amp; N_\mu &lt; 36\sqrt{2}\frac{(1 + 0.1Re_b^{0.75})}{Re_b^2} \ \frac{2}{3}\sqrt{E\ddot{o}<em>b} &amp; N</em>\mu \geq 36\sqrt{2}\frac{(1 + 0.1Re_b^{0.75})}{Re_b^2} \end{cases}$</td>
<td>Ishii and Zuber [319]</td>
</tr>
<tr>
<td><strong>Gas-Solid Drag</strong></td>
<td>$C_{D,G-S} = \begin{cases} \left(\frac{24}{Re_p}\right)(1 + 0.15Re_p^{0.687}) &amp; Re_p &lt; 1000 \ 0.44 &amp; Re_p \geq 1000 \end{cases}$</td>
<td>Schiller and Naumann [6]</td>
</tr>
<tr>
<td><strong>Liquid-Solid Drag</strong></td>
<td>$C_{D,L-S} = \alpha_s^{-1.65} \max\left(\frac{24}{\alpha_s Re_{S-L}}(1 + 0.15(\alpha_s Re_{S-L})^{0.687}), 0.44\right)$</td>
<td>Wen and Yu [5]</td>
</tr>
<tr>
<td><strong>Liquid-Gas Lift</strong></td>
<td>$C_{L,L-G} = \begin{cases} \min[0.288 \tanh(0.12Re), f(E\ddot{o}_d)] &amp; E\ddot{o}_d &lt; 4 \ f(E\ddot{o}_d) = 0.00105E\ddot{o}^3 - 0.0159E\ddot{o}_d^2 - 0.0204E\ddot{o}_d + 0.474 &amp; 4 \leq E\ddot{o}_d \leq 10 \ -0.29 &amp; E\ddot{o}_d &gt; 10 \end{cases}$</td>
<td>Tomiyama [7]</td>
</tr>
<tr>
<td></td>
<td>$E\ddot{o} = \frac{g\Delta \rho d_B^2}{\sigma}$, \quad E\ddot{o}_d = E\ddot{o}(1 + 0.163E\ddot{o}^{0.757})^{2/3}$</td>
<td></td>
</tr>
</tbody>
</table>

### 4.4 BUBBLES REPRESENTATION

In a three-phase fluidized system, bubble size variation is intimately related to bubble-particle collisions. The collisions can yield two different consequences: the particle is ejected from the bubble surface, or the particle penetrates the bubble leading to either bubble breakage or non-breakage. Bubble-particle collisions generate perturbations on the bubble surface. After the bubble-particle collision, three factors become crucial in determining the coalescence and breakage characteristics of the bubble [171]: (1) shear stress, which depends on the liquid velocity gradient and the relative bubble-particle impact speed, and tends to break the bubble; (2) surface
tension force, which tends to stabilize the bubble and drive it to recover its original shape; and (3) viscous force, which slows the growth rate of the surface perturbation, and tends to stabilize the bubble. Accordingly, bubble coalescence and breakage models are classified into four main categories [341]: (1) turbulent fluctuation and collision; (2) viscous shear stress; (3) shearing-off process; and (4) interfacial stability. The bubbles induced turbulence and bubble population balance are discussed below.

4.4.1 Bubble Induced Turbulence

The bubble induced turbulence is represented by introducing two source terms, $S_k$ and $S_\varepsilon$, into the $k-\varepsilon$ equation as [310, 342]:

$$
S_k = \left( \frac{\rho_G}{\rho_G + C_{VM} \rho_G} \right) \alpha_G \left( \frac{3 C_D}{4 d_B} \right) |\vec{u}_G - \vec{u}_L| (q_{LG} - 2k_L + \vec{u}_d \cdot \vec{u}_r); \quad S_\varepsilon = C_{\varepsilon 3} \varepsilon S_k
$$

(4-20)

Where $q_{LG}$ is the covariance of the liquid-phase and the dispersed gas-phase velocities; $u_r$ and $u_d$ are the relative and drift velocities, respectively; and $C_{\varepsilon 3} = 1.2$.

This model is rigorously derived by writing the equation of motion for a single bubble and rearranging it in terms of the fluid velocity, where the drag and mass coefficients ($C_D$ and $C_{VM}$) appear in the formulation. The equations for the relative and drift velocities are:

$$
\vec{u}_r = [\vec{u}_G - \vec{u}_L] - \vec{u}_d, \quad \vec{u}_d = -\vec{D}_{12}^{\tau} \left[ \frac{\Delta a_2}{a_2} - \frac{\Delta a_1}{a_1} \right]
$$

(4-21)

The drift velocity ($\vec{u}_d$) is a statistical quantity due to the conditional averaging; and may not be negligible as it accounts for the dispersion effects due to the bubbles transport by the turbulent fluid motion. $\vec{D}_{12}$ is the fluid-bubble dispersion tensor, which is expressed in terms of the fluid bubble velocity covariance $[q_{LG}]$ and the fluid-bubble turbulent interaction time scale $[\tau_{12}^t]$. For
the purpose of practical computations [212], the dispersion tensor is simplified to its diagonal form [273, 310, 343, 344] as:

\[ \bar{D}_{12}^t = \frac{1}{3} \bar{\tau}_{12}^t q_{LG} \cdot I, \quad \text{Where } I \text{ is a } 3 \times 3 \text{ identity matrix} \quad (4-22) \]

4.4.2 Bubble Population Balance

It is necessary to take into account bubble breakup and coalescence phenomena in the CFD model when a bubble column or a slurry bubble column operates in the heterogeneous flow regime. The usual approach is to use population balance models, which describe the variation in a given population property over the space and time within a velocity field. Therefore, a population balance model is used to represent the bubble size distribution. Assuming that each bubble class travels at the same mean algebraic velocity, the individual number density of a bubble class \( i \) can be expressed as [345]:

\[
\frac{\partial n_i}{\partial t} + \nabla (u_G n_i) = \left( \sum_j R_j \right)_i = B_C + B_B - D_C - D_B \quad (4-23)
\]

Where \( \left( \sum_j R_j \right)_i \) represents the net change in the number density distribution due to the coalescence and breakup of bubbles; and \( B_C, B_B \), and \( D_C, D_B \), represent the birth and death rates, respectively due to coalescence and breakup.

The model proposed by Lou and Svendsen [346] for the breakup rate of bubbles is used in this work. Their model was developed based on the assumption of bubble binary breakup (each bubble breaks up into two distinctly smaller bubbles) under isotropic turbulence. The ‘daughter’ bubble sizes were accounted for using a dimensionless variable \( f_{BV} \):
\[ f_{BV} = \frac{v_I}{v} = \frac{d_I^3}{d} = \frac{d_I^3}{d_I^3 + d_{II}^3} \]  

(4-24)

Where \( v_I, d_I \) and \( d_{II} \), represent the volumes and diameters of the daughter bubbles in the binary breakage of a parent bubble of diameter \( d \) and volume \( v \). The breakup rate of the bubbles can be represented as:

\[
\Omega_B(v; v f_{BV}) = 0.923(1 - \alpha_G) n \left( \frac{\varepsilon}{d^2} \right)^{1/3} \int_{\xi_{\text{min}}}^{1} \frac{(1 + \xi)^2}{\xi^{11/3}} \exp \left( -\frac{12c_f \sigma}{\beta \rho_L \epsilon^{2/3} d^{5/3} \xi^{11/3}} \right) d\xi 
\]  

(4-25)

Where \( \xi_{\text{min}} = \lambda_{\text{min}}/d \) and \( \xi = \lambda/d \), representing the size ratio between an eddy and a bubble in the inertial subrange, and \( \beta \) is a constant derived from fundamental consideration and it equals 2.

Subsequently, the birth and death rates due to breakup are represented as:

\[
B_B = \sum \Omega_B(v_j; v_i) n_i, \\
D_B = \Omega_i n_i \text{ where } \Omega_i = \sum_{m=1}^{N} \Omega_{m_i} 
\]

(4-26)  

(4-27)

On the other hand, bubble coalescence occurring due to bubble collision is caused by three major phenomena (1) wake entrainment, (2) buoyancy and (3) random turbulence. Wake entrainment has been widely accepted to be negligible [347] and the effect of buoyancy is eliminated as all bubbles of the same class have been assumed to travel at the same mean velocity. Therefore, the only remaining driving force is that of the random turbulence. The coalescence rate due to random turbulent collision is adopted from Prince and Blanch as given below [348]:

\[
\chi_{ij} = \frac{\pi}{4} \left[ d_i + d_j \right]^2 \left( u_{Ti}^2 + u_{Tj}^2 \right)^{0.5} \exp \left( -\frac{t_{ij}}{\tau_{ij}} \right) 
\]

(4-28)

\( u_T \) is the turbulent velocity in the inertial subrange of isotropic turbulence and can be estimated as: [349]
\[ u_T = \frac{r_{ij}^{2/3}}{\varepsilon^{1/3}} \]  

(4-29)

t_{ij}, is the contact time between two colliding bubbles:

\[ \tau_{ij} = \frac{r_{ij}^{2/3}}{\varepsilon^{1/3}} \]  

(4-30)

t_{ij}, is the time for two bubbles with radii \( r_i \) and \( r_j \) to coalesce:

\[ t_{ij} = \left( \frac{r_{ij}^3 \rho_i}{16 \sigma} \right)^{0.5} \ln \left( \frac{h_0}{h_f} \right) \]  

(4-31)

Where \( h_0 \) and \( h_f \) represent the initial bubble film thickness and the critical film thickness were reported to be \( 10^{-4} \) and \( 10^{-8} \) m, respectively.

\( r_{ij}, \) is the equivalent radius:

\[ r_{ij} = \frac{2r_i r_j}{(r_i + r_j)} \]  

(4-32)

Subsequently, the number density for individual bubble groups governed by birth and death due coalescence can be expressed as:

\[ B_C = \frac{1}{2} \sum_{k=1}^{i} \sum_{j=1}^{i} \eta_{jkl} \chi_{ij} n_i n_j \]  

(4-33)

Where \( \eta_{jkl} = \begin{cases} (v_j + v_k - v_{i-1})/(v_i - v_{i-1}) & \text{if } v_{i-1} < v_j + v_k < v_i \\ (v_{i+1} - (v_j + v_k)/(v_{i+1} - v_i) & \text{if } v_i < v_j + v_k < v_{i+1} \\ 0 & \text{if neither} \end{cases} \)  

(4-33)

\[ D_C = \sum_{m=1}^{N} \chi_{ij} n_i n_j \]  

(4-34)

It is important to note that this model will be developed for a SBCR operating under typical pressures and temperatures of F-T synthesis; and it is possible that other correlations/parameters would provide a better fit for different circumstances and scenarios.
4.5 KINETICS AND MASS TRANSFER

The interphase mass-transfer rate depends on the mass-transfer coefficient, the interfacial area concentration, and the rate of chemical reaction. The mass-transfer coefficient is a function of the local hydrodynamics, which are influenced on one hand by the bubble shrinkage due to physical or chemical absorption and on the other hand by the change of the physical properties due to the heterogeneous distributions of the chemical species.

In calculating the gas-liquid mass transfer in the transient CFD simulation, it is not possible to obtain the mass transfer coefficients from the hydrodynamic data generated using our multi-Eulerian simulation. This is primarily due to the limitations at the interface in the jump boundary conditions from the gas to liquid, which ideally require empirical mass transfer data or correlations to be incorporated in the CFD model.

Using CFD to model mass transfer and interfacial phenomena from the first principles is feasible at a very small scale, such a single droplet, using a Lagrangian or a Volume of Fluid (VOF) scheme. However, it should be noted that Gidaspow et al. [242, 331] used the granular temperature approach to derive the mass transfer coefficients in multiphase systems. Nonetheless, this would not be possible for our large-scale SBCR. Actually, attempting multi-fluid Eulerian to perform multiphase-multicomponent mass transfer would result in numerically unstable sources and sinks.

Therefore, the species mass transfer rate from the dispersed-phase to the continuous-phase per unit volume, which appeared in Equations (4-1) and (4-2) above, is defined as:

$$\dot{m}_{kn} = k_L a \cdot (C^* - C_L) \quad (4-35)$$

Where \(k_L a\) is the volumetric liquid-side mass transfer coefficient, which was represented using an empirical correlation developed using numerous experimental data for different three-phase F-T systems obtained under elevated pressures and temperatures in our pilot-scale SBCR [350]:

$$\dot{m}_{kn} = k_L a \cdot (C^* - C_L)$$
\[ k_{L,a} = \frac{7.99 \times 10^{-9} \rho_L^{0.82} \rho_G^{0.27} u_G^{0.387} \Gamma^{0.173}}{\mu_L^{0.25} \sigma_L^{0.976} M_{W_g}^{0.02}} \left( \frac{p}{p - p_v} \right)^{0.242} \left( \frac{d_G}{d_G + 0.3} \right)^{0.1} \times \exp[-1.3C_p + 0.8C_p^2 - C_p^3 - 1675.7d_p + 0.176X_{W}] \] (4-36)

The multi-formulation described above was implemented into the commercial CFD code, ANSYS Fluent v14.5, where the governing equations were solved using a multiphase-Eulerian segregated solver algorithm.

When accounting for chemical reactions, an additional species conservation equation has to be considered as follows:

\[ \frac{\partial (\rho_k \alpha_k y_k^i)}{\partial t} + \nabla (\rho_k \alpha_k u_k y_k^i) = \nabla (\alpha_k \rho_k D_k^i \nabla y_k^i) + r_k^i - r_{kn}^i \] (4-37)

Where \( y_k^i \) represents the mass fraction of species \( i \) in phase \( k \), whereas \( r_k^i \) and \( r_{kn}^i \) represent the F-T reaction kinetics rate and the rate of chemical absorption.

### 4.6 SOLUTION METHOD AND BOUNDARY CONDITIONS

The multi-formulation described above was implemented into ANSYS Fluent v 14.5, where the governing equations are solved using an Eulerian multiphase segregated solver algorithm. The 3-D time-dependent simulations are conducted, both due to the nature of the geometry investigated and the bubble plume oscillations, which are characteristic of the churn-turbulent flow regime [351]. The RNG \( k-\varepsilon \) turbulence model is used, as it provides the best validation results as previously demonstrated elsewhere [332]. At the bottom of the column, Dirichlet velocity and volume fraction conditions for all phases are set, and a second order spatially accurate QUICK scheme [352-354] is employed to discretize all equations.
Moreover, a multiphase variant of the SIMPLE scheme is used for pressure-velocity coupling [355]. The first order implicit time stepping is then used to advance the solution in time. Before each simulation, mesh and time independence studies are carried out in order to optimize the solution and computational time. In all simulations quasi-steady state numerical solutions are obtained. This means that at the end of the calculations, all variables exhibit small oscillations around steady-state values, indicating that the statistical averages were reached for all variables.

Additionally, outlet boundary conditions are implemented taking into account the following [301, 316]: (1) F-T SBCR reactors are typically operated in semi-batch mode where the liquid level may reach the top of the reactor [209]; and (2) Due to the F-T reaction, the liquid (mainly hydrocarbon products) formed inside the reactor is continuously removed using appropriate filtration devices within the reactor. Therefore, the following outlet boundary conditions are executed to account for the two aforementioned considerations:

1. The real computation domain is selected to be taller than the initial height of the reactor, similar to the work by Troshko and Zdravistch [316].

2. The initial liquid height is set by initializing the liquid volume fraction to 1 in the zone up to a known initial liquid height, while the gas volume fraction will be set to 1 in the region above that.

3. The ambient media in the computational zone above the reactor is set to be stagnant CO, such that the values for the pressure, backflow gas volume fraction, backflow CO gas species concentration and backflow turbulent parameters, are 1 atmosphere, 1, 1, and 0, respectively [316].
The implementation of these outlet boundary conditions allows for modeling of the slurry-phase height expansion due to the gas holdup and heterogeneous reactions without being affected by the gas-phase backflow. Moreover, due to the strong non-linear characteristics of the model, relaxation coefficients (Patankar [356]) are introduced in the momentum conservation equations. The convergence criterion adopted from Patankar [356], based on the pressure, is given by:

\[
\left| \sum_{j=2}^{N} \sum_{i=2}^{N} P_{ij}^{(n+1)} - \sum_{j=2}^{N} \sum_{i=2}^{N} P_{ij}^{(n)} \right| < 10^{-9} \quad \text{Where } N \text{ is the mesh size} \quad (4-39)
\]
5.0 CFD MODEL VALIDATION

The CFD model proposed above was implemented into ANSYS Workbench v. 13.0 and 14.5 and was systematically validated as follows:

5.1 TESTING OF CFD MODEL USING AQUEOUS AIR-WATER/GLASS BEADS DATA BY YU AND KIM [3]

The CFD model was initially tested against the radial gas holdup data by Yu and Kim [3] obtained for an air-water-glass beads system in a 0.254 m ID and 2.5 m height column using various superficial gas velocities under ambient conditions. More details of their study are given in Table 5-1.

Table 5-1: Experimental conditions by Yu and Kim [3] used for selecting of our CFD model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Diameter</td>
<td>0.254 m</td>
</tr>
<tr>
<td>Reactor Length</td>
<td>2.5 m</td>
</tr>
<tr>
<td>Liquid Velocity</td>
<td>0.06 m/s</td>
</tr>
<tr>
<td>System</td>
<td>Air-Water-Glass Beads</td>
</tr>
<tr>
<td>Particle Diameter</td>
<td>2.3 mm</td>
</tr>
<tr>
<td>Solid Concentration</td>
<td>9.47%</td>
</tr>
<tr>
<td>Solid Density</td>
<td>2500 kg/m³</td>
</tr>
<tr>
<td>Gas Velocity</td>
<td>0.01; 0.06; 0.14 m/s</td>
</tr>
</tbody>
</table>
The aim of this study was to select the gas-liquid and liquid-solid drag models and the most accurate and effective turbulence model to be used in the CFD model in order to predict the experimental data with high accuracy. Three gas-liquid drag models by (1) Wen and Yu [3], (2) Haider and Levenspiel [357] and (3) Gidaspow [242], listed in Table A-16 (Appendix A), along with two liquid-solid drag models by (1) Schallenberg et al. [299] and (2) Schiller-Naumann [6], also listed in Table A-17 (Appendix A) were investigated. Three turbulence models, (1) Standard k-ε, (2) Realizable k-ε and (3) RNG k-ε summarized in Table 5-2 were also investigated. For each turbulence model, six combinations of the gas-liquid and liquid-solid drag models were used and the CFD model predictions were performed at three different superficial gas velocities of 0.01, 0.06 and 0.14 m/s. The comparisons between experimental and predicted data using the CFD model are illustrated in Figure 5-1 and the absolute average relative errors (AARE) are presented in Table 5-3 for the three superficial gas velocities. From these figures and tables, the following observations can be made:

1. For all gas-liquid and liquid-solid drag model combinations, the Realizable k-ε turbulence model gives the worst predictions (highest AARE), which is in agreement with previous studies [292, 302];

2. The RNG k-ε turbulence model, coupled with the gas-liquid drag model by Wen-Yu [5] and the liquid-solid drag model by Schiller Naumann [6], gives the most accurate predictions of the experimental data (the lowest AARE); and

3. The accuracy of our CFD model predictions using the RNG k-ε turbulence model, at 0.01 and 0.06 m/s superficial gas velocities was not satisfactory, since their corresponding AARE values varied from 17.5% to 35.1% and from 9.6% to 28.7%, respectively. This behavior was expected since under such low velocities in an aqueous system, the bubbly flow regime prevails.
in the SBCR. At the superficial gas velocity of 0.14 m/s, however, the churn turbulent flow regime prevails and our CFD model predictions were in good agreement with the experimental data where the AARE using the RNG k-ε turbulence varied between 4.9 and 8.2%.

Table 5-2: Model equations for the three k-ε turbulence models used

<table>
<thead>
<tr>
<th>Model</th>
<th>Standard k-ε</th>
<th>Realizable k-ε</th>
<th>RNG k-ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>k-momentum</td>
<td>[ \frac{\partial (\rho k)}{\partial t} + \frac{\partial (\rho k U_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \mu + \frac{\mu_t}{\sigma_k} \frac{\partial k}{\partial x_j} \right) + G_k + G_b - \rho \varepsilon - Y_M + S_k ]</td>
<td>[ \frac{\partial (\rho k)}{\partial t} + \frac{\partial (\rho k U_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \mu + \frac{\mu_t}{\sigma_k} \frac{\partial \varepsilon}{\partial x_j} \right) + G_k + G_b - \rho \varepsilon - Y_M + S_k ]</td>
<td>[ \frac{\partial (\rho k)}{\partial t} + \frac{\partial (\rho k U_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \mu + \frac{\mu_t}{\sigma_k} \frac{\partial \varepsilon}{\partial x_j} \right) + \frac{\mu_t}{\sigma_{\epsilon}} \frac{\partial \rho}{\partial x_j} ]</td>
</tr>
<tr>
<td>\varepsilon</td>
<td>[ \frac{\partial (\rho \varepsilon)}{\partial t} + \frac{\partial (\rho \varepsilon U_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \mu + \frac{\mu_t}{\sigma_k} \frac{\partial \varepsilon}{\partial x_j} \right) + \rho C_1 \frac{\varepsilon}{k} ]</td>
<td>[ \frac{\partial (\rho \varepsilon)}{\partial t} + \frac{\partial (\rho \varepsilon U_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \mu + \frac{\mu_t}{\sigma_k} \frac{\partial \varepsilon}{\partial x_j} \right) + \rho C_1 \frac{\varepsilon}{k} ]</td>
<td>[ \frac{\partial (\rho \varepsilon)}{\partial t} + \frac{\partial (\rho \varepsilon U_i)}{\partial x_j} = \frac{\partial}{\partial x_j} \left( \mu + \frac{\mu_t}{\sigma_k} \frac{\partial \varepsilon}{\partial x_j} \right) + \frac{\mu_t}{\sigma_{\epsilon}} \frac{\partial \rho}{\partial x_j} ]</td>
</tr>
<tr>
<td></td>
<td>[ C_1 = \max \left[ 0.43, \frac{\eta}{\eta + 5} \right], \eta = S \frac{k}{\varepsilon}, S = \sqrt{2S_{ij}S_{ij}} ]</td>
<td>[ C_1 = \max \left[ 0.43, \frac{\eta}{\eta + 5} \right], \eta = S \frac{k}{\varepsilon}, S = \sqrt{2S_{ij}S_{ij}} ]</td>
<td>[ C_1 = \max \left[ 0.43, \frac{\eta}{\eta + 5} \right], \eta = S \frac{k}{\varepsilon}, S = \sqrt{2S_{ij}S_{ij}} ]</td>
</tr>
</tbody>
</table>

\[ \alpha = 1, \text{ except in the high Reynolds number limit } i.e \ \frac{\mu_{mol}}{\mu_{eff}} \ll 1, \alpha_k = \alpha_k \approx 1.393 \]

\[ d \left( \frac{\rho^2 k}{\sqrt{\mu}} \right) = 1.72 \left( \frac{\mu_{eff}}{\mu} \right)^{0.6321} \left( \frac{\alpha + 2.3929}{\alpha_0 + 2.3929} \right)^{0.3679} \]

\[ \mu_t = C_{\mu} \frac{\rho \varepsilon}{k}; \ C_{\mu} = 0.0845 \]
Table 5-3: Absolute average relative errors (AARE) for different turbulence and drag
G-L and L-S models against experimental data by Yu and Kim [3]

<table>
<thead>
<tr>
<th>$u_g$ (m/s)</th>
<th>Gas-Liquid/Liquid-Solid Drag models</th>
<th>AARE (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>RNG $k-\varepsilon$</td>
<td>Realizable $k-\varepsilon$</td>
<td>Standard $k-\varepsilon$</td>
</tr>
<tr>
<td>0.01</td>
<td>Wen-Yu [5] / Schallenberg et al. [299]</td>
<td>30.83</td>
<td>56.94</td>
<td>25.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Haider-Levenspiel [357] / Schallenberg et al. [299]</td>
<td>27.28</td>
<td>57.98</td>
<td>17.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gidaspow [242] / Schallenberg et al. [299]</td>
<td>35.08</td>
<td>61.11</td>
<td>36.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gidaspow [242] / Schiller Naumann [6]</td>
<td>24.01</td>
<td>60.07</td>
<td>17.03</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>Wen-Yu [5] / Schallenberg et al. [299]</td>
<td>11.63</td>
<td>63.20</td>
<td>13.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Haider-Levenspiel [357] / Schallenberg et al. [299]</td>
<td>28.73</td>
<td>64.24</td>
<td>15.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gidaspow [242] / Schallenberg et al. [299]</td>
<td>10.54</td>
<td>53.81</td>
<td>9.56</td>
<td></td>
</tr>
<tr>
<td>0.14</td>
<td>Wen-Yu [5] / Schallenberg et al. [299]</td>
<td>6.7</td>
<td>27.7</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Haider-Levenspiel [357] / Schallenberg et al. [299]</td>
<td>8.2</td>
<td>29.4</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gidaspow [242] / Schallenberg et al. [299]</td>
<td>7.1</td>
<td>28.7</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gidaspow [242] / Schiller Naumann [6]</td>
<td>5.6</td>
<td>33.5</td>
<td>8.8</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5-1: Evaluation of various G-L and L-S drag model combinations using the standard $k$-$\varepsilon$ ((a) to (c)) and the RNG $k$-$\varepsilon$ ((d) to (f)) turbulence models against experimental data by Yu and Kim [3].
5.2 VALIDATION OF OUR CFD MODEL USING ORGANIC N\textsubscript{2}-DRAKEOL-GLASS BEADS DATA BY CHEN ET AL. [4]

Our CFD model was subsequently validated against the experimental data by Chen et al. [4] for an organic system, N\textsubscript{2}-Drakeol-Glass beads as detailed in Table 5-4. The experimental data were conducted inside a bubble column reactor of 0.44 m ID and 2.44 m height. Inside this bubble column, 1-inch pipe internals are arranged in two concentric rings as shown in Figure 5-2 (a). This geometry is reconstructed in ANSYS Fluent as displayed in Figure 5-2 (b). It should be noted that the mesh size shown is very refined as the simulation was conducted at small mesh size to investigate the mesh dependency. This work was one of the first CFD simulation with internals.

The aim of the validation was to test the viability of our CFD model when using organic liquids and to check its ability in handling reactor internals. Three simulations were performed using our CFD model with the RNG \textit{k-\varepsilon} turbulence model, coupled with the gas-liquid drag model by Wen-Yu [5] and the liquid-solid drag model by Schiller Naumann [6], at inlet superficial gas velocities of 0.02, 0.05 and 0.1 m/s. Since the sparger has not yet been configured in our CFD model, the inlet boundary conditions were set at 70% of the total cross-sectional area at the bottom of the column similar to that used by Silva et al. [302]. The CFD modeling was conducted for 60 seconds with time steps of 0.01 s in order to investigate the effect of internals as shown in Table 5-5 and Figure 5-3; and as can be seen our CFD model is able to predict the radial gas holdup with an absolute average relative error between 4.45% and 15%. Although the real computation time for this simulation was relatively long, requiring around 220 hours for completion, no computational difficulties or divergences were exhibited, which provided confidence in using our CFD model for investigating different internal configurations.
Table 5-4: Experimental details by Chen et al. [4]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor diameter</td>
<td>0.44 m</td>
</tr>
<tr>
<td>Reactor length</td>
<td>2.44 m</td>
</tr>
<tr>
<td>Liquid velocity</td>
<td>0 m/s</td>
</tr>
<tr>
<td>System</td>
<td>Air-Drakeol-glass beads</td>
</tr>
<tr>
<td>Internals fraction of the reactor cross-sectional area</td>
<td>5.33%</td>
</tr>
<tr>
<td>Pipe diameter</td>
<td>0.0254 m</td>
</tr>
<tr>
<td>Number of internal pipes</td>
<td>16</td>
</tr>
<tr>
<td>Gas velocity</td>
<td>0.02; 0.05; 0.1 m/s</td>
</tr>
</tbody>
</table>

Figure 5-2: Geometry sketch and mesh of the column used by Chen et al. [4]

Table 5-5: Comparison between average relative errors (ARE) and absolute average relative errors (AARE) between experimental results and CFD predictions

<table>
<thead>
<tr>
<th>Gas Velocity</th>
<th>AARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 m/s</td>
<td>11.78%</td>
</tr>
<tr>
<td>0.05 m/s</td>
<td>4.45%</td>
</tr>
<tr>
<td>0.10 m/s</td>
<td>15%</td>
</tr>
</tbody>
</table>
5.3 VALIDATION AGAINST OUR EXPERIMENTAL DATA OBTAINED FOR N₂-F-T REACTOR WAX-IRON-BASED CATALYST SYSTEM

5.3.1 Experimental Setup

The characteristics of the SBCR used in this study are shown in Figure 5-4 and given in Table 5-6, and a schematic diagram of the experimental setup and photographs of the SBCR and gas sparger are shown in Figures 5-5 and 5-6, respectively. The SBCR consists mainly of: reactor (column), gas sparger, damper, filter, demister, compressor, Coriolis mass flow-meter, gas supply vessel, and...
gas cylinder. The reactor is provided with two Jerguson sight-windows in order to enable recording the bubbles size/behavior under a given operating condition. The reactor’s hydro-pressure is 85.5 bar at 295 K and its maximum allowable working pressure is 57 bar at a maximum temperature of 590 K. The reactor is equipped with 8 heating elements and an internal cooling coil of 0.306 m² total contact area. The heating elements, covered with a heavy-duty insulation jacket, operate with 460 V and are controlled by Solid State Contactors rated up to 50 A. The gas is introduced from a supply vessel through the bottom of the column using a six-arm spider-type gas distributor. The gas is recycled through the reactor using a single-stage compressor built by Fluitron Inc., Ivy land, USA. The compressor has a nominal displacement of 4.8x10⁻³ m³/rev. using 30 Horsepower, 1160 rpm electric motor. The gas flow rate is measured using a Coriolis mass and density meter model CMF100M330NU that gives a current output signal through a transmitter model RFT9739E4SUJ, manufactured by MicroMotion, USA. The gas velocity can be adjusted with a needle valve through a bypass line around the compressor inlet and outlet. The damper vessel is placed at the compressor’s outlet in order to dampen the vibrations and fluctuations created by the movements of the piston.

Table 5-6: Characteristics of the SBCR

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Diameter</td>
<td>12 in (0.3048 m)</td>
</tr>
<tr>
<td>Schedule</td>
<td>80</td>
</tr>
<tr>
<td>Material</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>Outside diameter, m</td>
<td>0.324</td>
</tr>
<tr>
<td>Inside diameter, m</td>
<td>0.3</td>
</tr>
<tr>
<td>Wall thickness, m</td>
<td>0.017</td>
</tr>
<tr>
<td>Inside cross sectional area, m²</td>
<td>0.066</td>
</tr>
<tr>
<td>Outside surface area, m²/m</td>
<td>1.017</td>
</tr>
<tr>
<td>Inside surface area, m²/m</td>
<td>0.908</td>
</tr>
<tr>
<td>Weight, kg/m</td>
<td>131.895</td>
</tr>
<tr>
<td>Height, m</td>
<td>3.00</td>
</tr>
<tr>
<td>Height/Diameter ratio</td>
<td>10.38</td>
</tr>
</tbody>
</table>
The demister is placed at the outlet of the column in order to prevent the liquid and solid particles from entering the compressor. In addition, a filter manufactured by Parker Hannifin Corp., USA is inserted between the demister and the compressor as a second stage device to prevent any solid particles or liquid mist from entering the compressor. There are two differential pressure cells (dP), model IDP10-V20A11F manufactured by Foxboro, USA rated at 7.5 kPa connected at different positions on the reactor, which allow the measurement of the hydrostatic pressure head between any two levels in the reactor. The pressure and the temperature in the system are recorded with 5 pressure transducers manufactured by Wika, Germany, and 7 thermocouples type J manufactured by Omega Engineering Inc., USA. The design of the entire unit allows the gas to flow through or bypass the liquid using the two pneumatically actuated valves (AV-1 and AV-2); and permits up to 60% of the gas in the reactor to be sent back to the supply vessel without venting to the hood.

An online data acquisition from the thermocouples, pressure transducers, dP cells and the Coriolis mass flow meter is performed using the National Instrument FieldPoint modules FP-TC-120 and FP-AI-110, which are connected to a serial bus module (FP-1000) with RS-232 interface to a host PC. The output signals from the host PC are received by the FieldPoint module FP-AOV10 for controlling the pneumatically activated valves and the heating elements of the reactor. The LabView software is used to monitor the entire process and perform the appropriate programs for I/O applications.

The gas sparger used in the SBCR is a spider-type with six identical legs. Each leg has 6 orifices of 0.005 m inside diameter (ID) on each side and on the bottom, totaling 18 holes in each leg and a total of 108 on the sparger. There are no orifices oriented towards the top of the legs so that solid particles could not block the orifices and the gas should be able to lift any solid particles.
which might settle at the bottom flange. The gas sparger is screwed to a 0.0254 m ID pipe and its height from the bottom of the column is about 0.102 m (4 in).

This gas sparger is designed so that the reactor could operate in the fully developed hydrodynamic regime. This condition is attained if Weber number defined in Equation (5-1) is maintained at a value > 2 within the range of sparger geometry in combinations with the operating conditions [359].

\[
We = \frac{\rho_G U_G^2 d_o}{\sigma} = \frac{\rho_G U_G^2 d_R^4}{N_o d_o^3 \sigma} > 2
\]  

(5-1)

Where \( N_o \) is the number of openings on the sparger and \( d_o \) is the inside diameter of the orifice.
Figure 5-4: Mechanical Specifications of the SBCR
Figure 5-5: Schematic of the Experimental Setup
Figure 5-6: Photographs of the SBCR and Gas Sparger
5.3.2 Gas-Liquid-Solid System and Operating Conditions Used

5.3.2.1 Gas Phase  The gases used were He and N₂ as surrogates of H₂ and CO, respectively. N₂ and He were purchased from Valley National Gases (USA). Some thermodynamic parameters [360] of these gases are given in Table 5-7.

<table>
<thead>
<tr>
<th>Gases</th>
<th>MW (kg/kmol)</th>
<th>( T_b ) (K)</th>
<th>( T_C ) (K)</th>
<th>( P_C ) (bar)</th>
<th>( V_C ) (m³/kmol)</th>
<th>( Z_C )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>28.013</td>
<td>77.35</td>
<td>126.10</td>
<td>33.94</td>
<td>0.0901</td>
<td>0.292</td>
<td>0.040</td>
</tr>
<tr>
<td>He</td>
<td>4.003</td>
<td>4.22</td>
<td>5.20</td>
<td>2.28</td>
<td>0.0573</td>
<td>0.302</td>
<td>-0.390</td>
</tr>
<tr>
<td>H₂</td>
<td>2.016</td>
<td>20.39</td>
<td>33.18</td>
<td>13.13</td>
<td>0.0642</td>
<td>0.305</td>
<td>-0.220</td>
</tr>
<tr>
<td>CO</td>
<td>28.010</td>
<td>81.70</td>
<td>132.92</td>
<td>34.99</td>
<td>0.0931</td>
<td>0.295</td>
<td>0.066</td>
</tr>
</tbody>
</table>

5.3.2.2 Liquid Phase  The liquid phase used is a molten reactor wax provided by NICE, China using the F-T process. The molten reactor wax is solid at room temperature with a melting point above 90 ºC. It consists of saturated and straight chains hydrocarbons with almost no branches. The wax composition in weight fraction is shown in Figure 5-7. The components containing less than 14 carbon atoms as well as those containing more than 82 carbon atoms were grouped into 2 pseudo components consisting of C₇ and C₁₀₁ respectively, as shown in Equation (5-2). Assuming the composition before C₁₄ and beyond C₈₂ follows the well-known geometric progression that is the Anderson-Schulz-Flory distribution the properties of algebraic series were used to estimate the numbers of carbon atoms in those 2 pseudo components [361]:

\[
n = \begin{cases} 
1 + \frac{\alpha}{1 - \alpha} - \frac{14\alpha^{14}}{1 - \alpha^{14}}; & CN < 14 \\
82 + \frac{\alpha}{1 - \alpha}; & CN > 82 
\end{cases}
\]  

(5-2)

Jager and Espinoza [362] reported that for an existing pilot reactor, new iron and cobalt catalysts have shown \( \alpha \) values between 0.8 and 0.95. Since 1955 Sasol, using iron based catalyst in their
tubular fixed bed Arge reactors, have been producing a product slate with an alpha value of about 0.95. An average chain growth probability factor for the NICE wax of 0.95 was used for the calculation of the pseudo components carbon numbers. It should be noted that in the next sections when density, viscosity and surface tension of the molten wax are calculated, the first pseudo component for CN < 14 which was vaporizing at the higher temperature was omitted.

The molecular weight of the reactor wax is 507.64 kg/kmol, as calculated from its compositions according to the following equation:

\[
MW_{\text{wax}} = \sum_{i=1}^{n} x_{i} MW_{i}
\]  

(5-3)

Where \( x_{i} \) represents the mole fraction of species \( i \).

![Figure 5-7: Wax composition in weight fraction](image)
The density, viscosity and surface tension of the molten wax were measured in our laboratory at different temperatures ranging from 380 to 460 K using graduated flasks, Cannon-Fenske routine viscometers and a Fisher Surface Tensiomat, respectively. These experimental data were modeled as a function of temperature and predictive correlations were developed. The vapor pressure was predicted with the Asymptotic Behavior Correlations (ABC) developed by Marano and Holder [363, 364], assuming the wax composition consists mainly of linear paraffins. From the values obtained a simple equation was developed for calculating the vapor pressure as a function of temperature. The different correlations for predicting the physical properties of the molten reactor wax as a function of temperature are grouped in Table 5-8 and comparisons between the predicted and experimental values are shown in Figure 5-8.

Table 5-8: Correlations for predicting the physicochemical properties of the reactor wax

<table>
<thead>
<tr>
<th>Property</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>$\rho_L = 978.05 - 0.5403 \cdot T$ (5-4)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>$\mu_L = \exp\left(\frac{2504.2}{T} - 4.3371\right)$ (5-5)</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>$\sigma_L = \frac{1.367 \times 10^{-4} T^2 - 0.1915 T + 80.486}{1000}$ (5-6)</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>$\log_{10}(P_V) = -\frac{50951}{T^2} - \frac{1694.1}{T} + 3.146$ (5-7)</td>
</tr>
</tbody>
</table>
Figure 5-8: Effect of temperature on the density (a), viscosity (b), surface tension (c) and vapor pressure (d) of the molten reactor wax
5.3.2.3 Solid Phase  The solid-phase used in the experiments is an iron-based catalyst with a skeletal density of 3,380 kg/m³. The particle size distribution of the catalyst is listed in Table 5-9 and accordingly the average particle diameter = 81 μm.

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Volume % finer than</th>
</tr>
</thead>
<tbody>
<tr>
<td>39 μm</td>
<td>10%</td>
</tr>
<tr>
<td>56 μm</td>
<td>30%</td>
</tr>
<tr>
<td>80 μm</td>
<td>60%</td>
</tr>
<tr>
<td>169 μm</td>
<td>95%</td>
</tr>
</tbody>
</table>

5.3.2.4 Operating Conditions Used  The gas holdup, bubble size and mass transfer coefficients were measured under the operating conditions listed in Table 5-10, which are typical to those of F-T synthesis. A test matrix covering these conditions was devised following the Central Composite Statistical Design (CCSD) developed at the University of Pittsburgh. Repeat runs were also carried out in order to ensure the reproducibility of the experimental data. The distribution of experiments according to this Central Composite Statistical Design is given in Figure 5-9. The experimental procedures and calculation methods used in the experimental portion of this work are provided in Appendix B.
Table 5-10: Experimental conditions

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>1, 1.5, 2, 2.5, 3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>140, 155, 170, 185, 200</td>
</tr>
<tr>
<td>He/N₂ Ratio</td>
<td>0, 1, 2, 3</td>
</tr>
<tr>
<td>Superficial Gas Velocity (m/s)</td>
<td>0.1, 0.15, 0.2, 0.25, 0.3</td>
</tr>
<tr>
<td>Solid Concentration (vol. %)</td>
<td>5, 10, 15</td>
</tr>
</tbody>
</table>

P: Pressure; S: Solid Concentration; T: Temperature; U: Superficial Gas Velocity

Figure 5-9: CCSD experimental design matrix [8, 151, 365]
5.3.3 Hydrodynamic and Mass Transfer Parameters in the Pilot Scale SBCR under F-T Conditions

In this section, the effects of pressure, temperature, gas and liquid velocities, gas nature and composition, solid concentration, liquid and solid phases natures on the hydrodynamics ($\varepsilon_G$ and $d_{32}$) and mass transfer ($k_{Ld}$) parameters for N$_2$ and He as single components as well as for different mixtures of these two gases obtained in the NICE molted reactor wax in the presence and absence of iron-based catalyst using the pilot-scale SBCR are discussed.

5.3.3.1 Gas Holdup The gas holdup values for N$_2$ and He/N$_2$ gas mixtures in molten reactor wax generally decrease with increasing the solid concentration under the various operating conditions as shown in Figure 5-10. This is due to the increase of the slurry viscosity and density, resulting in low gas momentum/mass of slurry and large gas bubbles. This behavior is in agreement with previous findings by Vandu et al. [366] using alumina particles in a C$_9$-C$_{11}$ paraffins mixture; Deckwer et al. [75, 367] using alumina particles in paraffin wax; Krishna et al. [368] using silica particles in paraffins oil, Behkish et al. [8] using alumina particles in iso-paraffins mixture (Isopar-M), and Sehabiague and Morsi [81] using alumina and iron oxide particles in C$_{12}$-C$_{13}$ paraffins mixture and F-T cuts. Moreover, in the absence and presence of solid particles up to 15 vol. %, the gas holdup for N$_2$ in molten reactor wax appear to increase with temperature as depicted in Figures 5-11 to 5-13, which is in accord with other literature data [8, 81]. This behavior can be attributed to the
decrease of the liquid-phase viscosity and surface tension with increasing temperature which led to high gas holdup values.

Moreover, as shown in Figure 5-14, gas holdup values are found to increase with reactor pressure, which is in agreement with other reported findings [8, 81, 369]. This behavior can be attributed to the increase of the gas density and the gas-phase momentum, which led to the increase of the gas holdup. Similarly, the gas holdup of N\(_2\) in the molten reactor wax appear to increase with the superficial gas velocity, as shown in Figure 5-15.

The gas holdup values are also found to increase with increasing the mole fraction of N\(_2\) or decreasing the mole faction of He in the gas mixture, as shown in Figure 5-16, which is in agreement with earlier findings for He, N\(_2\) and He/N\(_2\) mixtures in an iso-paraffinic mixture (Isopar-M), and in 3 different F-T liquids [8, 81]. The presence of the heavier gas (N\(_2\)) increases the density and thus the momentum of the gaseous mixture which led to the increase of the gas holdup and to the formation of smaller gas bubbles, which resulted in a greater gas-liquid interfacial area and consequently \(k_{L\alpha}\). Indeed, \(k_{L\alpha}\) values increased with increasing the mole fraction of N\(_2\) in the gas mixture, with the highest \(k_{L\alpha}\) values observed for N\(_2\) as a single component.
Figure 5-10: Effect of solids concentration on $\varepsilon_G$ in F-T reactor wax

- $T=415$ K; $P=20.6$ bar; $U_g=0.20$ m/s
- $T=440$ K; $P=20.4$ bar; $U_g=0.19$ m/s
- $T=441$ K; $P=21.6$ bar; $U_g=0.20$ m/s; $x_{He}=0.50$
- $T=443$ K; $P=10.6$ bar; $U_g=0.20$ m/s
- $T=444$ K; $P=20.6$ bar; $U_g=0.12$ m/s
- $T=447$ K; $P=14.4$ bar; $U_g=0.20$ m/s

Figure 5-11: Effect of temperature on $\varepsilon_G$ in F-T reactor wax at 0-5 vol. % solid concentrations

- $C_s=0$ vol.%; $P=20.3$ bar; $U_g=0.20$ m/s
- $C_s=5$ vol.%; $P=21.7$ bar; $U_g=0.20$ m/s
- $C_s=5$ vol.%; $P=21.1$ bar; $U_g=0.20$ m/s; $x_{He}=0.25$
- $C_s=5$ vol.%; $P=25.9$ bar; $U_g=0.15$ m/s
- $C_s=5$ vol.%; $P=25.9$ bar; $U_g=0.25$ m/s
Figure 5-12: Effect of temperature on $\varepsilon_G$ in F-T reactor wax at 10 vol. % solid concentrations

Figure 5-13: Effect of temperature on $\varepsilon_G$ in F-T reactor wax at 15 vol. % solid concentrations
Figure 5-14: Effect of pressure on $\varepsilon_G$ in F-T reactor wax

- $C_s=0$ vol.%; $T=443$ K; $U_g=0.20$ m/s
- $C_s=0$ vol.%; $T=447$ K; $U_g=0.20$ m/s
- $C_s=5$ vol.%; $T=448$ K; $U_g=0.20$ m/s
- $C_s=5$ vol.%; $T=462$ K; $U_g=0.15$ m/s
- $C_s=10$ vol.%; $T=417$ K; $U_g=0.20$ m/s
- $C_s=10$ vol.%; $T=443$ K; $U_g=0.20$ m/s

Figure 5-15: Effect of superficial gas velocity on $\varepsilon_G$ in F-T reactor wax

- $C_s=0$ vol.%; $T=443$ K; $P=20.5$ bar
- $C_s=0$ vol.%; $T=447$ K; $P=7.3$ bar
- $C_s=5$ vol.%; $T=446$ K; $P=26.0$ bar
- $C_s=5$ vol.%; $T=461$ K; $P=15.6$ bar
- $C_s=5$ vol.%; $T=462$ K; $P=25.9$ bar
- $C_s=11$ vol.%; $T=443$ K; $P=20.5$ bar
Figure 5-16: Effect of gas density on $\varepsilon_G$ in F-T reactor wax
5.3.3.2 Sauter Mean Bubble Diameter  The Sauter-mean diameter ($d_{32}$) of gas bubbles appear to increase with increasing the concentration of solid particles under the operating conditions used as shown in Figure 5-17, which is in agreement with other findings [8, 81]. This behavior is due to the increased slurry viscosity at higher solid concentrations, which increases the rate of gas bubbles coalescence, leading to the formation of large gas bubbles and consequently large Sauter mean bubble diameters. It seems that the addition of solid particles prevented the breakup of gas bubbles.

Figures 5-18 and 5-19 also show that in the absence and presence of solid particles up to 10 vol%, the values of the Sauter mean bubble diameters decrease with increasing temperature, which can be attributed to the decrease of the liquid viscosity and surface tension with increasing temperature, leading to the formation of small gas bubbles. [8] Figure 5-18 also shows that a minimum Sauter mean bubble diameter of about 0.2 mm is reached for solid concentrations up to 5 vol%. Also, at the highest solid concentration of 15 vol%, as shown in Figure 5-20, the temperature has no effect on the gas bubble size.

Moreover, as shown in Figures 5-21 and 5-22, both the superficial gas velocity and the pressure appear to have an insignificant effect on the Sauter-mean gas bubble diameter for N2 in wax in the presence of solid particles up to 15 vol%.
Figure 5-17: Effect of solids concentration on $d_{32}$ in F-T reactor wax

Figure 5-18: Effect of temperature on $d_{32}$ in F-T reactor wax at 0 – 5 vol. % solid concentrations
Figure 5-19: Effect of temperature on $d_{32}$ in F-T reactor wax at 10 vol. % solid concentrations

Figure 5-20: Effect of temperature on $d_{32}$ in F-T reactor wax at 15 vol. % solid concentrations
Figure 5-21: Effect of Pressure on $d_{32}$ in F-T reactor wax

Figure 5-22: Effect of superficial gas velocity on $d_{32}$ in F-T reactor wax
5.3.3.3 Volumetric Mass Transfer Coefficients  Figures 5-23 and 5-24 show that in the absence and presence of solid particles up to 10 vol.%, the volumetric mass transfer coefficients ($k_{L,a}$) values for N\textsubscript{2} and He/N\textsubscript{2} mixtures in NICE molten wax increase with increasing temperature. However, at high solid concentrations of 15 vol.%, the effect of temperature on $k_{L,a}$ seems to be governed by the pressure, where at low pressures $k_{L,a}$ values increase with increasing temperatures, whereas at higher $k_{L,a}$ values the effect of temperature is insignificant.

Also, at similar temperatures, $k_{L,a}$ values for the same gas-liquid system decrease with increasing solid concentration, as shown in Figure 5-25, which is in agreement with other findings [80, 81]. This behavior can be related to the decrease of the gas holdup and the increase of the Sauter mean bubble diameter with increasing solid concentration as shown in Figures 1 and 8.

The $k_{L,a}$ for N\textsubscript{2} in NICE molten wax, with and without solid particles, also appear to increase with increasing pressure, as shown in Figure 5-26, which is due to the increase of the gas holdup and the decrease of the Sauter mean gas bubble diameter, which led to the increase of the gas-liquid interfacial area ($a$). Moreover, as expected, $k_{L,a}$ for N\textsubscript{2} in NICE molten reactor wax always increased with increasing the superficial gas velocity (Figure 5-27), which was attributed to an increase of the gas holdup and turbulences, which increased the gas-liquid interfacial area ($a$) and the mass transfer coefficient ($k_L$), respectively.
Figure 5-23: Effect of temperature on $k_L a$ in F-T reactor wax at 0 – 5 vol. % solid concentrations

Figure 5-24: Effect of temperature on $k_L a$ in F-T reactor wax at 10 vol. % solid concentrations
Figure 5-25: Effect of solids concentration on $k_{La}$ in F-T reactor wax

Figure 5-26: Effect of pressure on $k_{La}$ in F-T reactor wax
Figure 5-27: Effect of superficial gas velocity on $k_{La}$ in F-T reactor wax
5.3.4 Geometry and Numerical Meshing of the Pilot-Scale SBCR

A picture of the gas sparger described above is given in Figure 5-28 (a). The gas sparger is screwed onto a 0.0254 m ID pipe to a height of 0.102 m from the bottom flange of the reactor. Also, its maximum height from the bottom of the reactor is about 0.152 m. The constructed geometry of this gas sparger is shown in Figure 5-28 (b).

![Figure 5-28: (a) Picture and (b) Constructed geometry of the sparger used in this study](image)

The numerical meshing structure used is shown in Figure 6. A quadrilateral/hexahedral meshing combination is generated in order to discretize the domain limited by the geometry. After preliminary numerical tests, it was proved that around 1,150,000 control volumes are enough to obtain mesh numerical independence, as shown in Figure 5-29. Also, due to the strong non-linear characteristics of our model, relaxation coefficients (Patankar [356]) are introduced in the momentum conservation equations as previously discussed by Silva Jr. et al. [302]. The convergence criterion adopted from Patankar [356], based on the pressure, is shown in Equation (4-39).
The simulations were carried out with a 0.01 s time step for a duration of 60 s, or until steady state is reached. An upwind QUICK (Quadratic Upstream Interpolation for Convective Kinematics) scheme was used to solve the model equations. This is because the upwind QUICK is superior than the second order upwind since QUICK has less dispersion and dampens the high frequency components much less. Typically, the simulations took around 220 hours to complete.

![Figure 5-29: Mesh Independence analysis](image-url)

**Figure 5-29: Mesh Independence analysis**
Figure 5-30: Geometry and mesh details of the numerical structure employed in our simulations: (a) Cross section view, (b) Side view in sparger vicinity, (c) Side view of whole column
5.3.5 Comparison between the CFD model predictions and our experimental data

The aim of this validation was to test our CFD model, with its optimized interphase drag coefficients, turbulence models, mesh size and structure, step size and solution method, using actual gas holdup data obtained under typical F-T conditions. All simulations were performed for a time period of 60 s with a time step of 0.01 s, which was enough to obtain quasi-steady state values of the hydrodynamic parameters. The model predictions were compared with the experimental data as shown in Figure 5-31. As can be observed in Figure 5-31 (a), our CFD model is capable of predicting the gas holdup as a function of temperature under different superficial gas velocities, solid concentrations, and pressures with an absolute averaged relative error (AARE) of 4.8%. Similarly, Figure 5-31 (b) shows that the model was able to predict the gas holdup data as a function of superficial gas velocities under different solid concentrations, temperatures and pressures with an AARE of 6.8%.
Figure 5-31: Time averaged CFD model validation vs. gas holdup data as a function of (a) temperature and (b) superficial gas velocity.
Moreover, the performance of the CFD model with and without incorporating mass transfer coefficients was validated against the experimental data measured in our pilot-scale reactor at a pressure of 20.5 bars, temperature of 443 K and solid concentration of 11 vol% at different superficial gas velocities as illustrated in Figure 5-32. As can be seen in this figure, when ignoring mass transfer coefficients, the model predictions of the experimental data were with AARE of 11.1%, whereas when considering the mass transfer coefficients, the predictions were more accurate with only AARE of 1.3 %. This underscores the importance of incorporating the mass transfer coefficients in our CFD model in order to obtain precise and accurate predictions.

Figure 5-32: Effect of mass transfer coefficients on our CFD model predictions of the gas holdup data under different operating conditions
6.0 CFD MODEL PREDICTIONS OF THE HYDRODYNAMICS INSIDE A SBCR

Following the model testing and validation, the CFD model was used to predict the local phase holdups, liquid velocity vectors, solids distribution, axial distribution of the Sauter mean bubble diameter, and the local turbulence intensity and contours within the reactor as detailed below.

6.1 EFFECT OF THE GAS SPARGER TYPE ON THE LOCAL HYDRODYNAMICS IN THE PILOT-SCALE SBCR

Gas sparger type is an integral component in SBCRs as it can alter the bubble characteristics and consequently the gas holdup, gas-liquid interfacial area and many other parameters affecting the performance of the reactor. Some common gas spargers used in literature include perforated plates, porous plates, porous membranes, rings type distributors and multiple-arms spargers [370]. Although significant work has been done investigating bubbles formation at the orifice [371-391], the effect of sparger design on the performance of bubble columns and SBCRs has received little attention. An efficient sparger design should aim at minimizing the pressure drop across the sparger while maintaining a uniform distribution of gas bubbles at the orifices, which would translate into significant savings in operating costs and overall process energy requirements. Generally, when the diameter of the SBCR is large (> 1 m) multi-arms spiders or concentric-rings spargers are preferred over perforated plates [392]. Moreover, some studies reported that the
effects of sparger type on the gas holdup and bubble diameter were more significant at low superficial gas velocities (10 cm/sec), however, such effects become insignificant at higher superficial gas velocities or in the churn-turbulent flow regime [393, 394].

In this section, the effect of three different distributors, namely 6-arms spider, concentric-rings and perforated plate, on the gas holdup, bubble size and liquid-phase recirculation within the pilot-scale SBCR are investigated using the built CFD model. The spider-type sparger used consists of six arms, each arm has 6 orifices of 5 mm ID on each side and on the bottom, totaling 18 orifices. Thus, there are a total of 108 orifices on the 6-arms spider gas sparger. It should be emphasized that there are no orifices at the top of the arms so that the solid particles could not plug them and the gas downward jets should be able to lift any solid particles, which might settle at the bottom flange of the reactor. The gas sparger is screwed onto a 0.0254 m ID pipe to a height of 0.102 m from the top of the bottom flange. Also, its maximum height from the bottom of the reactor is about 0.152 m. A picture of the spider-type sparger is shown in Figure 6-1 and the geometry and numerical mesh details are shown in Figure 6-2.

The concentric ring sparger consists of three concentric rings with 30, 15 and 10 orifices per ring, respectively, totaling 55 identical orifices. Each orifice has an ID of 7 mm. The geometry and numerical mesh details of the concentric ring sparger are shown in Figure 6-3.

The perforated plate consists of 1580 identical orifices of 1.3 mm ID, as shown in Figure 6-4. It should be noted that the dimensions of the concentric ring and perforated plate spargers were selected such that the total orifice area for gas sparging is the same (2.12 m²). Moreover, the effect of nozzles orientation on the flow dynamics within the SBCR for both the multi-arms spider and concentric-rings sparger are investigated.
Table 6-1: Description of the spargers investigated in this work

<table>
<thead>
<tr>
<th>Sparger type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spider-type sparger</td>
<td>Six arms, each arms has 6 orifices of 5 mm ID on each side and on the bottom, totaling 18 orifices. Thus, there are a total of 108 orifices on the gas sparger.</td>
</tr>
<tr>
<td>Concentric-rings</td>
<td>Three concentric-rings, with 30, 15 and 10 orifices per ring, respectively, totaling 55 identical orifices. Each orifice has an ID of 7 mm.</td>
</tr>
<tr>
<td>Perforated plate</td>
<td>1580 identical orifices of 1.3 mm ID</td>
</tr>
</tbody>
</table>

Figure 6-1: (a) Picture and (b) Constructed geometry of the spider sparger used in this study

Figure 6-2: Geometry and mesh details of the spider sparger: (a) Cross-section view, (b) Side-view
Figure 6-3: Geometry and mesh details of the concentric-rings sparger: (a) Built geometry, (b) Cross-section view of the mesh, (c) Side-view of the mesh

Figure 6-4: Geometry and mesh details of perforated plate: (a) Cross-section view, (b) Mesh structure
6.1.1 Effect of Sparger Design on the Gas Holdup Inside the Pilot-Scale SBCR

The spatial variations of the local gas holdup in the SBCR give rise to the local pressure variations, which induce liquid recirculations inside the reactor. These liquid recirculations are crucial as they govern the rate of mixing, affecting the heat and mass transfer characteristics. Our CFD model predictions illustrated in Figures 6-5, 6-6 and 6-7 for the spider, concentric-rings and perforated plate spargers, respectively, show several snapshots of the gas holdup inside the reactor at different times of 1, 20, 40 and 60 s. Also, Figures 6-8 to 6-14 compare the radial gas holdup profiles while using the three spargers at H/D values of 0.5, 1, 2, 3, 5 and 7, respectively. These data were obtained using an inlet superficial gas velocity of 0.20 m/s at temperature of 443 K, pressure of 20.5 bar and catalyst concentration of 11 vol%. Under these operating conditions, the overall gas holdup in the SBCR were 0.42, 0.36 and 0.45 for the spider, concentric-rings and perforated plate, respectively.

As can be seen in these figures, the gas holdups obtained using the three spargers vary with the axial and radial positions in the SBCR and the radial gas holdup exhibits a non-linear behavior at any axial position as illustrated by the gradual variation in the color shades of the gas holdup from the center to the wall of the reactor. It should be pointed out that the maximum gas holdup value can be mainly seen near the center of the reactor before it gradually decreases along the radii with various profiles in the axial direction. Also, the 6-arms spider and concentric-rings spargers showed distinctly steeper radial gas holdup profiles, whereas, the perforated plate showed a more uniform gas holdup distribution, which reached the steady-state much sooner than the other two spargers.
Figure 6-5: Snapshots of gas holdup contours at different times for the spider sparger
Figure 6-6: Snapshots of gas holdup contours at different times for the concentric-ring sparger
Figure 6-7: Snapshots of gas holdup contours at different times for the perforated plate.
Figure 6-8: Comparison of time averaged radial profiles of gas holdup at H/D = 0.5 for the three gas spargers used.

Figure 6-9: Comparison of time averaged radial profiles of gas holdup at H/D = 1 for the three gas spargers used.
Figure 6-10: Comparison of time averaged radial profiles of gas holdup at H/D = 2 for the three gas spargers used

Figure 6-11: Comparison of time averaged radial profiles of gas holdup at H/D = 3 for the three gas spargers used
Figure 6-12: Comparison of time averaged radial profiles of gas holdup at \( H/D = 5 \) for the three gas spargers used

Figure 6-13: Comparison of time averaged radial profiles of gas holdup at \( H/D = 7 \) for the three gas spargers used
6.1.2 Effect of Sparger Design on the Liquid Recirculations inside the SBCR

The CFD model was also used to predict the liquid circulations as shown in Figures 6-14, 6-15 and 6-16 for the 6-arms spider, concentric-rings and perforated plate, respectively, which shows snapshots of liquid velocity vectors in the SBCR at 1, 20, 40 and 60 s. In general, these figures show strong liquid recirculations and backmixing are present near the reactor walls because the liquid-phase rises upward with the gas bubbles at the center of the reactor and then flows downward near the reactor wall.

Figure 6-14 shows that for the 6-arms spider sparger, smaller and faster liquid recirculation cells are present in the vicinity of the sparger from the startup until the steady-state. Also, larger and slower liquid recirculation cells appeared after about 0.36 m measured from the bottom flange. These smaller and faster liquid recirculations in the vicinity of the sparger are primarily due to the geometry of this sparger type because all gas sparging orifices are located on the sides and bottom and none on the top of each sparger arms.

Figures 6-15 and 6-16 show that for the concentric-rings and perforated plate spargers, only large and slow recirculation cells are present throughout the column above the distributor zone, which is in contrast with liquid velocity vectors observed when using the 6-arms spider, Figure 6-14.

It is important to mention also that the CFD model predictions indicated that the solid-phase velocity vectors followed very closely those of the liquid-phase, which is due primarily to the small particle-liquid slip velocity.
Figure 6-14: Snapshots of liquid velocity vectors at different times for the spider sparger.
Figure 6-15: Snapshots of liquid velocity vectors at different times for the concentric-rings sparger.
Figure 6-16: Snapshots of liquid velocity vectors at different times for the perforated plate
6.1.3 Effect of Sparger Design on the Liquid Turbulence Intensity inside the SBCR

The CFD model was also used to predict the turbulence intensity profiles inside the pilot-scale SBCR using the three different spargers. The turbulence intensity is defined as the root-mean-square of the velocity fluctuations to the mean flow velocity. It is expressed as:

$$ I = \frac{u'}{U} = \sqrt{\frac{1}{3} \left( u_x'^2 + u_y'^2 + u_z'^2 \right)} $$

(6-1)

In general, a turbulence intensity of $\leq 1\%$ is considered low and that of $\geq 10\%$ is considered high [395]. The CFD model turbulence intensity predictions for the 6-arms spider, concentric-rings and perforated plate are shown in Figures 6-17, 6-18 and 6-19, respectively. As can be seen in these figures, the turbulence intensities for the three spargers throughout the reactor appear to increase with time.

Figure 6-17 shows that for the 6-arms spider, relatively high liquid turbulence intensities can be observed in the vicinity of the sparger during the startup time, however, after reaching steady-state, the turbulence intensities become more evenly distributed throughout the reactor. Figure 6-18 shows that for the concentric-rings sparger, the turbulence intensities are more uniform throughout the reactor during the first 40 s, however, their values increase drastically near the walls at 60 s, due to the development of large recirculation cells as shown in Figure 6-15. On the other hand, Figure 6-19 shows that the perforated plate exhibits higher turbulence intensities throughout the reactor with higher values near the top after 40 s, which is different from those shown using the other two spargers.

Thus, the CFD model confirmed that the sparger design and configuration have significant impact on the local hydrodynamics. This is a critical criterion for optimizing mixing characteristics inside the SBCR, which directly impact its overall performance.
Figure 6-17: Snapshots of local turbulence intensity contours at different times for the spider sparger
Figure 6-18: Snapshots of local turbulence intensity contours at different times for the concentric-ring sparger
Figure 6-19: Snapshots of local turbulence intensity contours at different times for the perforated plate.
6.1.4 Effect of Sparger Orifices Orientation on the Local Hydrodynamics in the SBCR

The effect of the sparger nozzles orientation on the overall gas holdup and the axial solids dispersion was investigated using our CFD model. The 6-arms spider sparger similar to that shown in Figure 6-1, provided with upward pointing orifices and the concentric-rings sparger shown in Figure 6-3 with downward pointing orifices were used in this investigation. The effect of the sparger design and orientation on the overall gas holdup, axial solid loadings and axial bubble size variation were investigated using three different superficial gas velocities of 0.1, 0.2 and 0.3 m/s at temperature of 443 K, pressure of 20.5 bar and catalyst concentration of 11 vol%.

A sparger with downward pointing orifices or nozzles is expected to be more effective in solids dispersion in a SBCR when compared with a similar sparger provided with upward pointing orifices or nozzles. It is argued that the gas jets from downward facing orifices or nozzles provide the agitation to facilitate solids dispersion. Also, the sparger used definitely determines the bubble sizes observed in the reactor, hence small orifices or nozzles enable the formation of small gas bubbles.

A general rule-of-thumb used for the determination of the effect of sparger design on the bubble size in a SBCR is given in Equation (6-2) [393, 394]. For the experimental conditions used in this study, this rule seems to hold only at high solid concentrations and superficial gas velocities > 0.2 m/s as shown in Figure 6-20. Nonetheless, at low solid concentrations or low superficial gas velocities, the effect of sparger type will remain significant.

\[ E \bar{\omega}Fr^{0.5} > 16 \]  

(6-2)

Where
\[ E\ddot{\omega} = \frac{\Delta \rho g d_o^2}{\sigma} \]  
\[ Fr = \frac{U_G^2}{\sqrt{gd_o}} \]  

Figure 6-20: Effect of temperature on \(E\ddot{\omega}Fr^{0.5}\) under the experimental conditions used in this study 
(NICE reactor wax, \(P = 4-31\) bar, \(T = 380-500\) K, \(u_G = 0.1-0.3\) m/s, and \(C_s = 5-15\) vol.%)

Figure 6-21 shows the effect of the 6-arms sparger orifice orientations on the overall gas holdup at different superficial gas velocities. As can be observed in this figure, both the upward and downward 6-arms spider orifice orientations give higher gas holdup values when compared with those of the concentric-rings spargers. The 6-arms spider with upward facing orifices resulted in the highest gas holdups. However, at low superficial gas velocities \((u_G < 0.15\) m/s), the concentric-
rings sparger with downward facing orifices gives higher gas holdup values than those using the sparger provided with upward facing orifices.

Figure 6-22 shows the effect of the sparger orifice orientations on the Sauter mean bubble diameter \( d_{32} \) at different superficial gas velocities. As can be observed in this figure, the concentric-rings spargers resulted in greater \( d_{32} \) when compared with those of the 6-arms spider, which can be attributed to the larger orifice size (7 mm ID) for the concentric-rings sparger versus 5 mm ID for the 6-arms spider. The effect of the superficial gas velocity on the \( d_{32} \) obtained with the 6-arms spider was insignificant, which is in agreement with the experimental data presented in Section 5.3.3.4. The effect of superficial gas velocity on the \( d_{32} \), however, was more significant for the concentric-rings upward facing orifices sparger as a result of the turbulent eddies created, which enhanced the bubbles coalescence. This is because bubbles coalescence and breakup mechanisms is primarily governed by the turbulent eddies, which in turn, are controlled by the liquid and gas velocities [288]. The bubble breakup, however, is governed by the turbulent stresses, which are controlled by the pressure variations within the fluid and subsequently are related to the physical property gradients within the continuous-phase [348]. This behavior also explains why the temperature changes, affecting the physical properties, have a stronger influence on bubbles breakup than on the bubbles coalescence.

Figures 6-23 to 6-25 show the effects of the sparger orifices orientations on the axial solid concentration profiles at superficial gas velocities of 0.1, 0.2 and 0.3 m/s, respectively. As can be seen in these figures, the downward facing orifices spargers give a more uniform axial solids distribution, whereas, the upward facing orifices spargers result in a solid accumulation near the bottom of the reactor. Actually, high solid concentrations (up to 17.2 vol %) can be seen at the
bottom of the reactor at superficial gas velocity 0.2 m/s, leading to lower solid concentrations above and far from the sparger.

It is important to note that the concentric-rings sparger with upward facing orifices resulted in higher solid concentrations at the bottom of the reactor when compared with those of the 6-arms spider with upward facing orifices. This behavior could be due to the fact that the 6-arms spider has also nozzles on the sides of each arms, which helped in enhancing mixing around this sparger. The effect of sparger orifices orientation on the axial solids distribution profile at an axial position \((z)\) to the total height \((H)\) ratio \((z/H)\) greater than 0.2 appear to decrease with increasing the superficial gas velocity. Generally, the spargers with downward facing orifices were more effective in solids distribution when compared with those with upward facing orifices. This is due to the increased mixing provided by the gas jets from the downward facing orifices, which increased the solid particles distribution.
Figure 6-21: Effect of sparger type and nozzles orientation on the gas holdup at different superficial gas velocities

Figure 6-22: Effect of sparger type and nozzles orientation on the Sauter bubble diameter at different superficial gas velocities
Figure 6-23: Comparison of axial solid loadings for different sparger nozzles orientations at $U_G = 0.1 \text{ m/s}$

Figure 6-24: Comparison of axial solid loadings for different sparger nozzles orientations at $U_G = 0.2 \text{ m/s}$
Basha et al. [2] classified the different liquid recirculation profiles typically observed in bubble columns and SBCRs into three patterns as discussed in Section 2.5.2. Pattern (a) is characterized by large segmented liquid recirculations along the height of the reactor, pattern (b) is characterized by a single large liquid recirculation flow structure across the entire reactor, and pattern (c) is characterized by smaller and faster liquid recirculations throughout the reactor.

The CFD model predictions of the mean axial velocity profiles in the SBCR are presented in Figures 6-26 through 6-28 for the different gas spargers used at a superficial gas velocity of 0.2 m/s for height to diameter ratios (H/D) of 1, 3 and 6, respectively. As can be observed in these figures, the sparger design and orifices orientation appear to significantly affect the mean axial velocity profiles throughout the entire length of the reactor. Thus, the previous claims that the sparger design has no effect on the flow structure at high superficial gas velocities in bubble
columns and SBCRs, which were based on experiments conducted at ambient temperature [393, 394], are not applicable to the SBCRs operating under typical Fischer-Tropsch conditions.

Furthermore, these figures show that the concentric-rings and the 6-arms spider with downward facing orifices exhibit flow profiles which are similar to the circulation pattern (c). Also, the concentric-rings and 6-arms spider spargers with upward facing orifices follow the circulation pattern (a). It should be mentioned, however, that the perforated plate exhibited a unique flow profile, which follows the circulation pattern (b).

Figure 6-26: Mean axial liquid velocity profiles at H/D = 1 for different gas spargers at $u_g = 0.2$ m/s
Figure 6-27: Mean axial liquid velocity profiles at H/D = 3 for different gas spargers at $u_g = 0.2 \text{ m/s}$

Figure 6-28: Mean axial liquid velocity profiles at H/D = 6 for different gas spargers at $u_g = 0.2 \text{ m/s}$
6.1.5 Sensitivity Analysis of the Model Parameters

In order to use our model as an efficient design tool, it is critical to identify the relative importance of each of the incorporated sub-models and parameters, and to eventually eliminate any unnecessary terms that needlessly increase the computational time without an acceptable increase in the prediction accuracy. In this work, the effect of incorporating a bubble population balance (Equation (4-23)) and the effect of incorporating momentum exchange terms (Equation (4-19)), on the model predictions were investigated. More precisely, the predictions were carried out under six different cases were compared with those of the original model described in Section 4 (Base Case). These cases are: 1. eliminating the bubble population balance; 2. accounting for the bubble population balance with only the coalescence kernel activated; 3. accounting for the bubble population balance with only the breakup kernel activated; 4. accounting only for the drag in the momentum exchange terms; 5. accounting only for Drag and Lift; and 6. accounting only for Drag, Lift and Virtual Mass.

The cases were validated against two sets of experimental data to test both the spatial and overall model predictions. The data of Chen et al. [4] for N₂-Drakeol-Glass beads system at superficial gas velocities of 0.05 as described in Section 6.6.3, were used to investigate the model’s prediction of the radial gas holdup profiles. Also, our experimental data, as described in Section 6.6.4, were used to investigate the overall model performance at an inlet superficial gas velocity = 0.20 m/s, temperature = 443 K and catalyst concentration = 11 vol%. Three main criteria were used to evaluate the relative importance of each of those parameters: (i) the overall computational time, (ii) the Absolute Average Relative Error (AARE), and (iii) the Percent Bias (PBIAS), which is used to identify the model’s bias to underestimate or overestimate the data [396] as shown in Equation (6-5):
\[ PBIAS = \frac{\sum_1^n (\text{Pred.} - \text{Exp.})}{\sum_1^n \text{Pred.}} \times 100\% \] (6-5)

Positive values indicate the model’s underestimation bias, whereas positive values indicate the model’s overestimation bias.

Tables 6-2 and 6-3 show the model performance using the two sets of experimental data. As can be seen in these tables, the greatest reduction in computation time for two sets was achieved by accounting only for the drag momentum exchange term, while eliminating the other terms (Case # 4), which resulted in a decrease of computational time by 25.5% and 27.1% for set 1 and set 2, respectively, with an almost insignificant change in the AARE. Moreover, eliminating the bubble population balance significantly reduced the computation time by 19% and 23.3% for set 1 and set 2, respectively, however, a significant increase in AARE of 9.47% and 6.57% was observed. Thus, the degree of complexity employed in our model is dependent on the required prediction accuracy. Obviously, increased accuracy will significantly increase the required computational time.

<table>
<thead>
<tr>
<th>Case #</th>
<th>Eliminated sub-model</th>
<th>AARE</th>
<th>PBIAS</th>
<th>Computation Time (hrs)</th>
<th>Time Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>-</td>
<td>4.45%</td>
<td>1.07%</td>
<td>220</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>Bubble population balance</td>
<td>13.92%</td>
<td>-1.3%</td>
<td>178</td>
<td>19.1%</td>
</tr>
<tr>
<td>2</td>
<td>Breakup kernel</td>
<td>7.98%</td>
<td>0.07%</td>
<td>184</td>
<td>16.4%</td>
</tr>
<tr>
<td>3</td>
<td>Coalescence kernel</td>
<td>11.21%</td>
<td>1.21%</td>
<td>192</td>
<td>12.7%</td>
</tr>
<tr>
<td>4</td>
<td>Lift, Virtual Mass, Wall, Turbulence dispersion</td>
<td>4.75%</td>
<td>1.12%</td>
<td>164</td>
<td>25.5%</td>
</tr>
<tr>
<td>5</td>
<td>Virtual Mass, Wall, Turbulence dispersion</td>
<td>4.69%</td>
<td>1.09%</td>
<td>207</td>
<td>5.9%</td>
</tr>
<tr>
<td>6</td>
<td>Wall, Turbulence dispersion</td>
<td>4.56%</td>
<td>1.06%</td>
<td>214</td>
<td>2.7%</td>
</tr>
</tbody>
</table>
Table 6-3: Model performance against overall gas holdup data measured in our lab

<table>
<thead>
<tr>
<th>Case #</th>
<th>Eliminated sub-model</th>
<th>AARE</th>
<th>PBIAS</th>
<th>Computation time (hrs)</th>
<th>Time Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>-</td>
<td>2.75%</td>
<td>0.32%</td>
<td>218</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>Bubble population balance</td>
<td>9.32%</td>
<td>8.1%</td>
<td>167</td>
<td>23.4%</td>
</tr>
<tr>
<td>2</td>
<td>Breakup kernel</td>
<td>5.64%</td>
<td>6.5%</td>
<td>181</td>
<td>17.0%</td>
</tr>
<tr>
<td>3</td>
<td>Coalescence kernel</td>
<td>7.21%</td>
<td>8.1%</td>
<td>173</td>
<td>20.6%</td>
</tr>
<tr>
<td>4</td>
<td>Lift, Virtual Mass, Wall, Turbulence dispersion</td>
<td>2.86%</td>
<td>0.44%</td>
<td>159</td>
<td>27.1%</td>
</tr>
<tr>
<td>5</td>
<td>Virtual Mass, Wall, Turbulence dispersion</td>
<td>3.07%</td>
<td>3.70%</td>
<td>203</td>
<td>6.9%</td>
</tr>
<tr>
<td>6</td>
<td>Wall, Turbulence dispersion</td>
<td>3.22%</td>
<td>3.63%</td>
<td>217</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
6.2 EFFECTS OF INTERNALS ON THE LOCAL HYDRODYNAMICS IN SBCRS

Reactor internals with different shapes and configurations are an integral part of the design and optimization of numerous industrial applications. For instance, different types of internals, such as rings, inverse-cone tubes, horizontal ring-type baffles, and perforated plates were used in the circulating fluidized bed (CFB) to improve the solids radial distribution [397]. Fixed and floating internals were used in the fast fluidized-beds to reduce the agglomerate size in cohesive powders for fluidization improvement [398]. Porous draft tubes, open-sided draft tubes and non-porous draft tubes were used in conical spouted beds to increase the gas flow rate from the spout into the annulus and enhance heat transfer [399, 400]. Different internals were also used in SBCRs to maintain a near isothermal operation using the highly exothermic processes.

Generally, heat transfer rate in multiphase systems is controlled by many variables, such as heat transfer area, heat transfer coefficient, superficial gas velocity, liquid circulation velocity, and bubble dynamics, including the local and overall phase holdups, bubble velocities, bubble sizes, and bubble frequency.

In SBCRs, the good mixing and high heat capacity of the slurry-phase allow for excellent temperature control, making it ideal for the F-T synthesis process, which is highly exothermic. Kolbel and Ralek [221] reported a temperature difference of less than 1 °C over the total length of a pilot-scale SBCR (1.29-m ID, 8-m height) used for F-T synthesis at 268 °C. The cooling surface requirements in slurry bubble reactor reactors have been reported to be less than a quarter of those used in a multitubular fixed bed reactors, due to the improved heat transfer film coefficient in addition to a higher permissible ΔT between reactant and coolant [165, 401].
In this section, the effect of internals on the internal hydrodynamics in our pilot-scale SBCR are investigated using the CFD model in two steps. In the first step, the effect of internals on the experimental and predicted hydrodynamics previously discussed in Section 6.1 was investigated. In the second step, the effect of different internals configurations on the gas holdup structure and liquid backmixing was investigated.

6.2.1 Effect of Internals in the Pilot-Scale Reactor on the Liquid Backmixing, Gas Holdup and Local Turbulence Intensity

The internals configuration used in the pilot-scale SBCR, shown in Figure 6-29 consists of a bundled arrangement of one, 2.5-inch pipe at the center of the reactor, surrounded by 6, 1.75-inch pipes in a hexagonal pattern. The overall cross sectional areal coverage of the internals was 17.65%. The internal pipes were 2.1-m in length each, and extended from the top of the reactor up to 70% of the total length of the reactor, with a volume fraction of 12.3%.

In the CFD modeling, a tetrahedral mesh was used with 4.95 million nodes and 2.85 million cells. The mesh has an average element quality of 0.84 and the cross-sectional contour of the mesh is shown in Figure 6-29. The simulations were carried out at an inlet superficial gas velocity = 0.20 m/s, temperature = 443 K, pressure = 20.5 bar and catalyst concentration = 11 vol. %. The local values of the gas holdup, local turbulence intensity and liquid velocity were determined over 60 s, which is the time required to achieve a steady-state within the pilot-scale reactor.
Figure 6-29: Geometry and mesh structure used in this section: Cross sectional view (a) and view in the vicinity of the sparger (b)

Figure 6-30 shows snapshots of gas holdup contours at different times. As can be observed in this figure, the presence of internals generally increases the gas holdup when compared with the reactor without internals shown in Figure 6-5. This behavior could be due to a decrease of the area available for gas flow. Moreover, there is a significant effect on the radial distribution of the gas holdup, as more even radial distribution can be seen in the presence of internals.
Figure 6-30: Snapshots of gas holdup contours at different times.

Gas Holdup

(a) $t = 1$ s  $t = 20$ s  $t = 40$ s  $t = 60$ s
Figure 6-31 shows snapshots of turbulence intensity contours at different times in the pilot-scale SBCR and as can be observed the presence of internals does not have a significant effect on the turbulence intensity during the first 40 s, when compared with the case without internals shown in Figure 6-17. However, after 40 s, there is a significant increase in the turbulence intensity in the presence of internals, particularly in the upper region of the reactor where the internals are present. This is primarily due to the effect of internals on the longitudinal funneling of the flow, which tends to control the size of large scale eddies, resulting in a more turbulent flow. This effect is also supported by Figure 6-32 which shows snapshots of the liquid velocity vectors at different times in the SBCR. As shown in this figure, the presence of internals results in a significantly different flow structure throughout the reactor after the 40 s, with smaller and faster liquid recirculation cells in the vicinity of the sparger, and larger liquid recirculation in the upper part of the reactor where the internals are present.
Figure 6-31: Snapshots of turbulence intensity contours at different times

Local Turbulence Intensity

- t = 1 s
- t = 10 s
- t = 25 s
- t = 40 s
- t = 50 s
- t = 60 s

Figure 6-31: Snapshots of turbulence intensity contours at different times
Figure 6-32: Snapshots of liquid velocity vectors at different times

Liquid Velocity (m/s)

- t = 1 s
- t = 10 s
- t = 25 s
- t = 40 s
- t = 50 s
- t = 60 s
The effect of internals length on the local hydrodynamics was also investigated. The simulations were carried out in the pilot-scale SBCR under the same operating conditions, however, the internals were extended from 2.1 m to 2.6 m, covering 86% of the total reactor length and representing a volume fraction of 15.3%, as shown in Figure 6-33. As can be observed in the figure, increasing the internals length increases the overall gas holdup and results in less steep radial gas holdup profiles in the vicinity of the internals. Also, there is a general increase of the turbulence intensity, primarily in the upper regions of the reactor. Moreover, there is a significant liquid funnelling and larger recirculations at the internals zone and smaller, faster recirculations in the vicinity of the sparger.

Figure 6-33: Steady state Gas holdup (a), Local turbulence intensity (b) and liquid velocity vectors (c) of the pilot-scale reactor with vertically extended internals
6.2.2 Effect of Parallel Internal Configurations on the Liquid Backmixing and Gas Holdup

The effect of internals configurations on the liquid backmixing and gas holdup was predicted using our CFD model in three different parallel (baffled) configurations inside a conceptual large-scale reactor (1-m ID and 10-m height). The areal coverage and volume fraction of the internals in both reactors are shown in Table 6-4. In all the cases investigated, the internals extended from the top of the reactor up to 86% of the reactor height. The gas was introduced using a concentric-ring sparger, consisting of 3 concentric-rings with 333, 167 and 111 orifices, totaling 611 identical orifices, each with an ID of 7-mm.

The simulations were carried out at an inlet superficial gas velocity of 0.20 m/s, temperature of 443 K, pressure of 20.5 bar and catalyst concentration of 11 vol. %. In order to prevent numerical problems, however, the calculations were carried out with a 0.05 s increment for the first 1000 time steps, increased to 0.1 s for the next 1000 time steps, then increased to 0.25 s until the end of the simulation time. The simulated physical time was for 300 s, at which the statistical quasi-steady state was attained, i.e. once the converging time averages of the local holdups and axial velocities were stabilized. The cross-sectional contours for both the liquid axial velocity and gas holdup at different z/D points throughout the reactor are shown in Figures 6-34 to 6-37.
Table 6-4: Details of parallel internal configurations used in this study

<table>
<thead>
<tr>
<th>Parallel Arrangement</th>
<th>P-1</th>
<th>P-2</th>
<th>P-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>19% CSA Coverage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.34% Volume coverage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>293 – 1 in internal pipes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 m – ID, 10 m high SBCR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% CSA Coverage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.6% Volume Coverage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>155 – 1 in internal pipes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1m – ID, 10 m high SBCR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% CSA Coverage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.3% Volume Coverage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>77 – 1 in internal pipes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1m – ID, 10 m high SBCR</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6-34: Liquid axial velocity cross-sectional contours at different heights for the parallel internals configurations at 30 s
Figures 6-34 and 6-35 show the axial liquid velocity contours for cases P-1 through P-3. As can be seen in this Figure, strong liquid recirculations are exhibited at a much earlier time, marked by smaller scale liquid circulations throughout the reactor, which eventually grow into large scale recirculation cells with positive axial velocity near the reactor center and strong backmixing near the reactor wall at steady-state conditions. Similar flow structure and behavior is also exhibited for cases P-1 and P-2, in which the liquid recirculations develop at a much faster rate, and eventually result in large liquid recirculations throughout the reactor. This behavior is primarily due to liquid funneling because of the presence of internals in the reactor, which
significantly affect the flow structure, resulting in large, fast and more turbulent liquid recirculations.

Figure 6-36: Gas holdup cross-sectional contours at different heights for the parallel internals configurations at 30 s
Figures 6-36 and 6-37 shows the presence of internals increases the gas holdup throughout the reactor, which is in agreement with earlier findings [223, 226]. Also, in all cases at z/D value of 2.5, the radial gas holdup profiles exhibit higher values near the reactor center and lower values near the reactor wall, which eventually flatten along the reactor height, with more distinctly flatten gas holdup profiles at higher z/D values of 5 and 7.5.
6.2.3 Effect of Bundled Internal Configurations on the Gas Holdup and Liquid Backmixing in the Conceptual Reactor

Four different bundled configurations in the conceptual reactor (1-m ID and 10-m height) with 1, 3, 4 and 5 bundles, as shown in Table 6-5, were investigated. This was performed to investigate the effect of the reactor geometry on the local hydrodynamics in the presence of internals, and the impact of inserting a large number of internals inside the reactor. In all the cases investigated, the internals extended from the top of the reactor up to 86% of the reactor height, which is equivalent to 2.58 m for the 3 m height reactor and 8.6 m for the 10 m reactor. The simulations were carried out at an inlet superficial gas velocity of 0.20 m/s, temperature of 443 K, pressure of 20.5 bar and catalyst concentration of 11 vol. %. The cross-sectional contours for both the liquid axial velocity and gas holdup at different z/D points throughout the reactor are shown in Figures 6-38 and 6-8.

Table 6-5: Details of bundled internal configurations used in this study
(1-m ID, 10-m high SBCR)

<table>
<thead>
<tr>
<th>Bundled Arrangement</th>
<th>B-1</th>
<th>B-2</th>
<th>B-3</th>
<th>B-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.7% CSA Coverage</td>
<td>16.3% CSA Coverage</td>
<td>16% CSA Coverage</td>
<td>17.5% CSA Coverage</td>
<td></td>
</tr>
<tr>
<td>14.3% Volume Coverage</td>
<td>14.0% Volume Coverage</td>
<td>13.8% Volume Coverage</td>
<td>15.1% Volume Coverage</td>
<td></td>
</tr>
<tr>
<td>1 - 7 in bundle center</td>
<td>3, 3, 5 in bundle centers</td>
<td>4, 3 in bundle centers</td>
<td>5, 3 in bundle centers</td>
<td></td>
</tr>
<tr>
<td>134 - 1.25 in internal pipes</td>
<td>138, 1.25 in internal pipes</td>
<td>136, 1.25 in internal pipes</td>
<td>145, 1.25 in internal pipes</td>
<td></td>
</tr>
<tr>
<td>1 m – ID, 10 m high SBCR</td>
<td>1 m – ID, 10 m high SBCR</td>
<td>1 m – ID, 10 m high SBCR</td>
<td>1 m – ID, 10 m high SBCR</td>
<td></td>
</tr>
</tbody>
</table>
Figures 6-38 and 6-39 show the axial liquid velocity contours for cases B-1 through B-4; and as can be seen the presence of bundled internals results in significantly different backmixing profiles. Strong liquid recirculations are exhibited for cases B-1 and B-2 for the 1 and 3 bundle configurations, whereas weaker liquid recirculations are shown for cases B-3 and B-4 for the 4 and 5 bundle configurations. Generally, backmixing zones in the bundled arrangements seem to be affected by the presence of wall clearance zones, especially in the configurations which promote large wall clearances, such as the 3 bundle and 5 bundle arrangements, where the large wall clearance zones generated unique backmixing profiles.

![Liquid Axial Velocity Cross-Sectional Contours](image)

*Figure 6-38: Liquid axial velocity cross-sectional contours at different heights for the bundled internals configurations at 30 and 300 s (1-m ID, 10-m high SBCR)*
Figures 6-39 and 6-40 show the gas holdup contours for cases B-1 to B-4, at 30 and 300 s, respectively. As can be observed for all cases, the presence of internals results in smoother radial gas holdup profiles, however, the local gas holdup values were lower than those exhibited for the parallel configurations (Figure 6-36). This behavior is primarily due to the increase of the average bubble size for bundled internals when compared with those for parallel internals, as shown in in Figure 6-42.
Figure 6-40: Gas holdup cross-sectional contours at different heights for the bundled internals configurations at 30 s (1-m ID, 10-m high SBCR)
Figure 6-41: Gas holdup cross-sectional contours at different heights for the bundled internals configurations at 300 s (1-m ID, 10-m high SBCR)

Figure 6-42 shows that the bundled internals result in higher Sauter mean bubble diameter ($d_{32}$) values when compared with those for the parallel internals. This behavior could be due to the fact that the presence of parallel internals enhances bubble breakup and inhibits bubble coalescence, whereas the presence of bundled internals enhances bubble coalescence. This is clearly shown when comparing the bubble diameters of case P-1 to the values obtained with no internals (Figure 6-42). Moreover, the bubble size appears to increase with decreasing the cross-sectional area for the parallel internals and increasing the number of bundled internals. This behavior could be related to the effect of the distance between the internals in the case of parallel configurations, where lower cross-sectional area coverages result in wider distance between the
internals, leading to the formation of large gas bubbles. For bundled internals, on the other hand, this effect is due to the wall clearance, where bigger clearances resulted in increased bubble diameter.

Figure 6-42: Axial Sauter mean bubble diameter for different internals configurations

Additionally, the effect of the number of internals and the internals cross-sectional area coverage on both the gas holdup and backflow fraction, has been investigated, as shown in Figures 6-43 and 5-21. As shown in these figures, the number of internals does not have a significant effect on the gas holdup, which seems to be governed by the internal cross-sectional areal coverage of the internals. On the other hand, the number of internals appears to have significant effect on enhancing liquid backmixing when compared with that of the cross-sectional area coverage. Thus, the presence of internals and their combination can increase or decrease backmixing depending on their design and arrangement.
Figure 6-43: Effect of number of internal pipes and internals CSA coverage on the gas holdup

Figure 6-44: Effect of number of internal pipes and internals CSA coverage on the liquid backflow fraction
6.3 CFD MODEL PREDICTIONS OF PERFORMANCE OF A PILOT- AND LARGE-SCALE SBCRs FOR F-T SYNTHESIS

The use of CFD models to predict the F-T reactor performance at relatively large scales has been rarely attempted as previously discussed in Section 2.5.3, due to the computational and physical complexity of the process. Most modeling attempts have been limited to 1-D axial dispersion models. In this investigation, our CFD model was used to predict the performance of the pilot-scale SBCR reactor available in our laboratory and an industrial-scale SBCR for F-T synthesis using iron catalyst. The kinetic rate expressions used for both the F-T and WGS reactions are given in Table 6-6.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
<th>Equation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>NICE Catalyst (Fe)</td>
<td>F-T</td>
<td>( r_{FT} = \frac{kP_{CO}P_{H_2}}{P_{CO} + aP_{H_2} + bP_{CO_2}} )</td>
<td>( k = 0.118 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1} \cdot \text{MPa}^{-1} ) at 528 K, ( a = 5.9 ), ( b = 5.9 )</td>
</tr>
<tr>
<td>WGS</td>
<td>( r_{WGS} = \frac{k \left( \frac{P_{CO}P_{H_2} - P_{H_2}P_{CO_2}}{K_p} \right)}{\left( P_{CO} + aP_{H_2} + bP_{CO_2} \right)^2} )</td>
<td>( k = 0.083 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1} ), ( a = 1.9 ), ( b = 1.9 ), ( K_p = 79.7 ) at 528 K</td>
<td></td>
</tr>
</tbody>
</table>

The composition of the syngas used in the CFD simulation is given in Table 6-7.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>52.47</td>
</tr>
<tr>
<td>O(_2)/Ar</td>
<td>0.27</td>
</tr>
<tr>
<td>N(_2)</td>
<td>12.72</td>
</tr>
<tr>
<td>CO</td>
<td>34.46</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.02</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>0.03</td>
</tr>
</tbody>
</table>
The F-T products distribution was determined using the 2-\(\alpha\) model [46]. The mole fraction of the products with an \(n\) carbons is calculated using Equation (6-6):

\[
x_n = \frac{\alpha_1^{n-1} + \left(\frac{\alpha_1}{\alpha_2}\right)^{\xi - 1} \alpha_2^{n-1}}{1 - \alpha_1 + \left(\frac{\alpha_1}{\alpha_2}\right)^{\xi - 1} \frac{1}{1 - \alpha_2}}
\]

Where \(\xi\) represents the break point of the products distribution in the 2-\(\alpha\) model.

The products selectivities obtained by Withers et al. [402] were used to fit the values of the parameters \(\xi\), \(\alpha_1\) and \(\alpha_2\) and they were found to be 13, 0.79 and 0.91, respectively. Furthermore, the literature data by Chang et al. [403] available for an iron-based catalyst, similar to the one used in this study, were used to develop Equation (6-7) in order to predict the ratio of \(\alpha\)-olefins to paraffins (\(R_{op}\)).

\[
\begin{align*}
  n < 5 & \quad R_{op_n} = -1.06n^2 + 7.18n - 6.25 \\
  n \geq 5 & \quad R_{op_n} = -0.000115n^4 + 0.00804n^3 - 0.188n^2 + 1.4n + 1.47
\end{align*}
\]

The solubilities of gases, other than \(\text{H}_2\) and \(\text{CO}\), were calculated using the Marano and Holder [361, 363, 364, 404] correlations for the multi-component vapor-liquid equilibrium model. The design data and operating conditions for the pilot-scale and the industrial-scale SBCRs used in this CFD modeling are given Table 6-8.
Table 6-8: Design data for the pilot-scale and industrial-scale SBCRs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pilot-scale</th>
<th>Industrial-Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor inside diameter ( (D_R) )</td>
<td>0.3 m</td>
<td>5.8 m</td>
</tr>
<tr>
<td>Reactor effective height ( (H_R) )</td>
<td>3 m</td>
<td>42 m</td>
</tr>
<tr>
<td>Sparger Type</td>
<td>6-arms spider</td>
<td>Concentric circles</td>
</tr>
<tr>
<td>Orifices inside diameter ( (ID_{orifice}) )</td>
<td>5 mm</td>
<td>3 mm</td>
</tr>
<tr>
<td>Number of orifices ( (N_{orifice}) )</td>
<td>108</td>
<td>29,000</td>
</tr>
<tr>
<td>Cooling Pipes</td>
<td>Stainless Steel</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>Number of cooling pipes × Cooling pipe size</td>
<td>1 × 63.5 mm OD (58.42 mm ID)</td>
<td>151 × 89 mm OD (77 mm ID)</td>
</tr>
<tr>
<td></td>
<td>6 × 44.45 mm OD (39.37 mm ID)</td>
<td>453 × 57 mm OD (47 mm ID)</td>
</tr>
<tr>
<td>Pressure</td>
<td>20.5 bar</td>
<td>29 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>443 K</td>
<td>528 K</td>
</tr>
<tr>
<td>Superficial gas velocity</td>
<td>0.24 m/s</td>
<td>0.12, 0.24, 0.30 and 0.40 m/s</td>
</tr>
<tr>
<td>Slurry or Liquid flow rate</td>
<td>0.00015 m/s</td>
<td>0.00015 m/s</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Iron (Table 6-6)</td>
<td>Iron (Table 6-6)</td>
</tr>
<tr>
<td>Average particle size</td>
<td>81 micron</td>
<td>81 micron</td>
</tr>
<tr>
<td>Particle skeletal density (NICE catalyst)</td>
<td>3,380 kg/m³ (Iron)</td>
<td>3,380 kg/m³ (Iron)</td>
</tr>
<tr>
<td>Catalyst loading (solid concentration)</td>
<td>0-15 vol% (0-45 wt. %)</td>
<td>10 vol% (34 wt. %)</td>
</tr>
</tbody>
</table>

6.3.1 Prediction of the Pilot-Scale SBCR Performance

Our CFD model was first used to predict the performance of the pilot-scale SBCR for F-T synthesis. The effect of catalyst concentration on the \( \text{H}_2 \) and \( \text{CO} \) conversions and the overall \( \text{C}_5^+ \) products yield was investigated at three solid concentrations of 5, 10 and 15 vol\% for three \( \text{H}_2/\text{CO} \) ratios of 1, 1.5 and 2. The simulations were carried out at a pressure of 20.5 bar, a temperature of 443 K, and superficial gas velocity of 0.24 m/s. The geometry used is shown in Figure 6-29.

The simulations were carried out for a period of 120 minutes, using a 0.25 s time step, for a total of 28,800 time steps per simulation. Each simulation took an average of 270 hours to
complete. It should be noted that the addition of the reaction kinetics resulted in significant convergence difficulties and that the simulation had to be initialized using a first order steady state solution before advancing the transient solution. The results for the yield were ultimately expressed in tons of $C_5^+$ products per day.

Our CFD model was able to predict the performance of the pilot-scale SBCR as shown in Figures 6-45 through 6-47. The predictions indicated that increasing catalyst concentration increases the CO and H$_2$ conversions. Also, Figure 6-47 shows that this pilot-scale SBCR could produce a maximum of 1.87 tons/day of $C_5^+$ products when using a catalyst concentration of 15 vol. % under the operating conditions given in Table 6-8.

![Figure 6-45: CFD model predictions of CO conversion for different H$_2$/CO ratios at different catalyst concentrations for F-T synthesis in the pilot-scale SBCR](image-url)
Figure 6-46: CFD model predictions of H\textsubscript{2} conversion for different H\textsubscript{2}/CO ratios at different catalyst concentrations for F-T synthesis in the pilot-scale SBCR

Figure 6-47: CFD model predictions of the C\textsubscript{5+} products yield for different H\textsubscript{2}/CO ratios at different catalyst concentrations for F-T synthesis in the pilot-scale SBCR
6.3.2 Effect of Incorporating Kinetics on the Local Hydrodynamics in the Pilot-Scale SBCR

The impact of incorporating the F-T reaction kinetics on the hydrodynamics in the pilot scale SBCR was investigated. Generally, the effect of the chemical reaction on the hydrodynamics in a SBCR is expected, primarily due to gas and liquid velocity changes along the reactor axial position, and the net molar gas consumption or production as the reaction proceeds. The changes in the local gas velocities are expected to change the gas holdup and bubble size, which in turn affect the gas-phase continuity equation, and the momentum balance for the gas and liquid phases. In this analysis the CFD results, with and without F-T reaction kinetics, were compared at pressure = 20.5 bar, temperature = 443 K, inlet superficial gas velocity = 0.20 m/s, catalyst concentration = 10 vol. %, and at H$_2$/CO ratio = 2. The geometry used in this work is shown in Figure 6-29. It includes a 6-arms spider sparger, and one bundled internal, consisting of one, 2.5-inch pipe at the center of the reactor, surrounded by 6, 1.75-inch pipes in a hexagonal pattern. The internals had a cross sectional areal coverage of 17.65% and extended for 86% of the overall reaction length, representing a volume fraction of 15.3%.

Figure 6-21 shows the axial average Sauter mean bubble diameters profiles of in the pilot-scale SBCR with and without chemical reactions. As can be seen in this figure incorporating the F-T reaction kinetics into the CFD model decreases the average $d_{32}$ values along the reactor by an average of 17.63%. Similarly, Figure 6-49 shows axial average gas holdup profiles in the pilot-scale SBCR with and without chemical reactions. As can be observed in this figure incorporating the F-T reaction kinetics into the CFD model decreases the average gas holdup along the reactor by an average of 15.4%. Moreover, Figure 6-50 shows the cross sectional contours of the gas holdup in the pilot-scale SBCR. It is important to note that despite the changes of the average $d_{32}$ and gas holdup values along the reactor in the presence of chemical reaction, the liquid
recirculation patterns exhibited in the pilot-scale SBCR under these conditions was similar to that obtained in the absence of chemical reaction as can be observed in Figure 6-51.

Figure 6-48: Effect of coupling kinetics on the average Sauter mean bubble diameter in the Pilot-scale SBCR
Figure 6-49: Effect of incorporating kinetics in the CFD model on the average gas holdup in the pilot-scale SBCR
Figure 6-50: Effect of incorporating kinetics in the CFD model on the gas holdup contours with and without chemical reaction at $t = 60$ s in the pilot-scale SBCR.
Figure 6-51: Effect of incorporating kinetics in the CFD model on the liquid recirculation patterns with and without chemical reaction at \( t = 60 \) s in the pilot-scale SBCR.
6.3.3 Prediction of the Industrial-Scale SBCR Performance

Our CFD model was then used to predict the performance of the industrial-scale SBCR with the design data and operating conditions given in Table 6.8. Due to the huge number of sparger orifices required, 12 concentric-ring spargers were built at the inlet of the reactor. A cross-section view of the geometry and mesh structure of the reactor is shown in Figure 6-52. The mesh consisted of 8.8 million elements, in addition to a mixed-element grid consisting of 71% tetrahedral, 16% prism, 9% pyramid and 4% hexahedral elements. The average element quality was 0.84 and the minimum element quality was 0.167. It should be noted that although a relatively coarse mesh was selected due to the large size of the reactor, this mesh satisfied the convergence criteria set by Patankar [356] for highly non-linear relaxation coefficients, as previously discussed in Section 6.5.

![Figure 6-52: Geometry and mesh details of the industrial scale SBCR: (a) Cross-sectional view, (b) mesh structure](image-url)
The CFD simulations were conducted at four superficial gas velocities of 0.12, 0.24, 0.30 and 0.40 m/s. Figures 6-53 through 6-55 show the simulation results for the CO conversion, H$_2$ conversion and C$_5^+$ products yields, respectively. Under these conditions, the results indicated that the CO conversions are 48%, 59%, 58% and 55% at the superficial gas velocities of 0.12, 0.24, 0.3 and 0.4 m/s, respectively. Similarly, the H$_2$ conversions are 36%, 51%, 56% and 54% at the superficial gas velocities of 0.12, 0.24, 0.3 and 0.4 m/s, respectively. The C$_5^+$ products yields are 275, 576,627 and 654 ton/day at superficial the gas velocities of 0.12, 0.24, 0.3 and 0.4 m/s, respectively.

Figure 6-53: CFD model predictions of the CO conversion for different superficial gas velocities for F-T synthesis in the industrial-scale SBCR
Figure 6-54: CFD model predictions of $\text{H}_2$ conversion for different superficial gas velocities for F-T synthesis in the industrial-scale SBCR

Figure 6-55: CFD model predictions of the C5+ products yield for different superficial gas velocities for F-T synthesis in the industrial-scale SBCR
7.0 CONCLUDING REMARKS

1. A three-phase, 3-D comprehensive CFD model to predict the local hydrodynamics and performance of SBCRs for F-T synthesis was developed. The kinetic theory of granular flow (KTGF) was used to represent the solid-phase behavior, and the model by Gidaspow [242] was used to describe the solid viscosity. The bubbles induced turbulence was considered by introducing two source terms, $S_k$ and $S_\varepsilon$, into the $k$-$\varepsilon$ equation to account for the covariance of the liquid- and dispersed-phase velocities as well as the relative and drift velocity effects. Also, a bubble population balance was included to represent the bubble size distribution. In addition, the model incorporated the breakup and coalescence models by Lou and Svendsen [405] and Prince and Blanch [348], respectively. The CFD model was developed in ANSYS and a first order implicit time stepping was used to advance the solution in time. Moreover, due to the strong non-linear characteristics of the model, relaxation coefficients, as proposed by Patankar [356], were introduced in the momentum conservation equations.

2. The CFD model predictions, in the absence of F-T reactions, were tested against the experimental data by Yu and Kim [3] for air-water-glass beads system and by Chen et al. [4] for N$_2$-Drakeol-glass beads system in order to select the turbulence and drag models. Based on these validations, of inclusion of the RNG $k$-$\varepsilon$ turbulence model coupled with the gas-liquid drag model by Wen-Yu [5], the liquid-solid drag model by Schiller Naumann [6] and the lift
coefficient by Tomiyama [7] in the CFD model, allowed the most accurate predictions of these experimental data.

3. Due to the absence of adequate hydrodynamics and mass transfer data in the literature to validate our CFD model, an experimental program was devised to measure the gas holdup ($\varepsilon_G$), Sauter mean bubble diameter ($d_{32}$), and volumetric mass transfer coefficients ($k_{La}$) for gaseous mixtures of He/N$_2$ as surrogates for H$_2$/CO in F-T reactor wax containing iron catalyst in a pilot-scale (0.3-m ID, 3-m height) SBCR. These data were measured under various operating conditions, pressures (4-31 bar), temperatures (380-500 K), superficial gas velocities (0.1-0.3 m/s) and catalyst concentrations (0-15 vol. %), which are typical to those of the F-T synthesis. The gas distributor used for gas sparging was a 6-arms spider. The F-T reactor wax was provided by the National Institute of Clean and Low-Carbon Energy (NICE), China; and was obtained from a large-scale (5.8-m ID, 30-m height) SBCR operating with iron catalyst under actual F-T industrial conditions. The CFD model predictions, in the absence of F-T chemical reactions, were validated against the gas holdup data obtained in this study under actual F-T conditions, and this validation underscored the importance of including the $k_{La}$ correlation in the CFD model in order to precisely predict the gas holdup data in the pilot-scale SBCR.

4. After validation, the CFD model was used to predict the effect of internals on the local hydrodynamics (local gas hold up, liquid and gas velocity vectors, mixing intensities) inside the pilot-scale SBCR reactor (0.3-m ID, 3-m height) provided with the 6-arms spider for gas sparging. From the simulation results obtained in the absence of F-T reactions, the following remarks can be made:

a. The presence of internals generally increases the gas holdup when compared with the reactor without internals. This behavior could be due to a decrease of the area available for
gas flow. Moreover, there is a significant effect on the radial distribution of the gas holdup, as more even radial distribution can be seen in the presence of internals.

b. The presence of internals does not have a significant effect on the turbulence intensity during the first 40 s, when compared with the case without internals. However, after 40 s, there is a significant increase in the turbulence intensity in the presence of internals, particularly in the upper region of the reactor where the internals are present. This is primarily due to the effect of internals on the longitudinal funneling of the flow, which tends to control the size of large scale eddies, resulting in a more turbulent flow. Moreover, the presence of internals results in a significantly different flow structure throughout the reactor after the 40 s, with smaller and faster liquid recirculation cells in the vicinity of the sparger, and larger liquid recirculation in the upper part of the reactor where the internals are present.

c. Increasing the internals length increases the overall gas holdup and results in less steep radial gas holdup profiles in the vicinity of the internals. Also, there is a general increase of the turbulence intensity, primarily in the upper regions of the reactor. Moreover, there is significant liquid funneling and larger recirculations at the internals zone and smaller, faster recirculations in the vicinity of the sparger.

d. The number of internals does not have a significant effect on the gas holdup, which seems to be governed by the internal cross-sectional areal coverage of the internals. On the other hand, the number of internals appears to have significant effects on enhancing liquid backmixing when compared with that of the cross-sectional area coverage. Thus, the presence of internals and their combination can increase or decrease backmixing depending on their design and arrangement
e. Increasing the number internals for the same cross-sectional areal coverage did not have a significant effect on the overall gas holdup inside the reactor. The internal mixing and the backmixing fraction, nonetheless, increased significantly (about 50% higher) with increasing the number of internals.

f. The local gas holdup and liquid backmixing fraction inside the SBCR provided with internals appeared to increase with increasing the inlet superficial gas velocity and temperature for all internals configurations used.

5. The CFD model was then used to investigate the effect of the gas sparger type and orientation on the gas holdup, Sauter mean bubble diameter, axial concentration profiles, mean axial velocity profiles and the flow structure in the pilot-scale (0.3-m ID, 3-m height), with no internals and no F-T reactions. A 6-arms spider, a concentric ring sparger, with upward and downward facing orifices, and a perforated plate distributor were used in this investigation. The following conclusions can be drawn:

a. The gas holdups obtained using the three spargers vary with the axial and radial positions in the SBCR and the radial gas holdup exhibits a non-linear behavior at any axial position as illustrated by the gradual variation in the color shades of the gas holdup from the center to the wall of the reactor. It should be pointed out that the maximum gas holdup value can be mainly seen near the center of the reactor before it gradually decreases along the radii with various profiles in the axial direction. Also, the 6-arms spider and concentric-rings spargers showed distinctly steeper radial gas holdup profiles, whereas, the perforated plate showed a more uniform gas holdup distribution, which reached the steady-state much sooner than the other two spargers.
b. The CFD model confirmed that the sparger design and configuration have significant impact on the local hydrodynamics. For the 6-arms spider, relatively high liquid turbulence intensities can be observed in the vicinity of the sparger during the startup time, however, after reaching steady-state, the turbulence intensities become more evenly distributed throughout the reactor. For the concentric-rings sparger, the turbulence intensities are more uniform throughout the reactor during the first 40 s, however, their values increase drastically near the walls at 60 s, due to the development of large recirculation cells. On the other hand, the perforated plate exhibits higher turbulence intensities throughout the reactor with higher values near the top after 40 s, which is different from those shown using the other two spargers.

c. For the 6-arms spider sparger, smaller and faster liquid recirculation cells are present in the vicinity of the sparger from the startup until the steady-state. Also, larger and slower liquid recirculation cells appear to develop after around 1.2 time the reactor diameter (measured from the bottom flange). These smaller and faster liquid recirculations in the vicinity of the sparger are primarily due to the geometry of this sparger type because all gas sparging orifices are located on the sides and bottom and none on the top of each sparger arms. For the concentric-rings and perforated plate spargers, only large and slow recirculation cells are present throughout the column above the distributor zone, which is in contrast with liquid velocity vectors observed when using the 6-arms spider.

d. Both the upward and downward 6-arms spider orifice orientations give higher gas holdup values when compared with those of the concentric-rings spargers. The 6-arms spider with upward facing orifices resulted in the highest gas holdups. However, at low superficial gas velocities ($U_g < 0.15$ m/s), the concentric-rings sparger with downward facing orifices
gives higher gas holdup values than those using the sparger provided with upward facing orifices.

e. The concentric-rings spargers resulted in greater $d_{32}$ values when compared with those of the 6-arms spider, which can be attributed to the larger orifice size (7 mm ID) for the concentric-rings sparger versus 5 mm ID for the 6-arms spider. The effect of the superficial gas velocity on the $d_{32}$ obtained with the 6-arms spider was insignificant, which is in agreement with the experimental data.

f. The effect of superficial gas velocity on the $d_{32}$, however, was more significant for the concentric-rings upward facing orifices sparger as a result of the turbulent eddies created, which enhanced the bubbles coalescence. This is because bubbles coalescence and breakup mechanisms is primarily governed by the turbulent eddies, which in turn, are controlled by the liquid and gas velocities [288]. The bubble breakup, however, is governed by the turbulent stresses, which are controlled by the pressure variations within the fluid and subsequently are related to the physical property gradients within the continuous-phase [348].

g. The downward facing orifices spargers give a more uniform axial solids distribution, whereas, the upward facing orifices spargers result in a solid accumulation near the bottom of the reactor. Actually, high solid concentrations (up to 17.2 vol %) can be seen at the bottom of the reactor at superficial gas velocity 0.2 m/s, leading to lower solid concentrations above and far from the sparger.

h. The concentric-rings sparger with upward facing orifices resulted in higher solid concentrations at the bottom of the reactor when compared with those of the 6-arms spider with upward facing orifices. This behavior could be due to the fact that the 6-arms spider
has also nozzles on the sides of each arms, which helped in enhancing mixing around this sparger.

i. The effect of sparger orifices orientation on the axial solids distribution profile at an axial position (z) to the total height (H) ratio (z/H) greater than 0.2 appear to decrease with increasing the superficial gas velocity. Generally, the spargers with downward facing orifices were more effective in solids distribution when compared with those with upward facing orifices. This is due to the increased mixing provided by the gas jets from the downward facing orifices, which increased the solid particles distribution.

6. The CFD model was then used to study the effect of four parallel and four bundled internals configurations on the gas holdup and liquid axial velocity inside a Conceptual SBCR (1-m ID, 10 m high), and in the absence of F-T reactions, the following remarks can be made:

a. For the parallel internals, in the larger Conceptual reactor, faster, larger liquid recirculations were exhibited at a much earlier time, when compared to similar simulations inside the Pilot Scale SBCR. Moreover, the presence of internals significantly enhanced liquid funneling in the Conceptual reactor when compared to pilot-scale SBCR. On the other hand, the gas holdup profiles were found take a longer time to develop in the pilot-scale SBCR when compared to the Conceptual reactor.

b. On the other hand, in the presence of bundled internals, strong liquid recirculations are exhibited for the 1 and 3 bundle configurations, whereas, weaker liquid recirculations were shown for the 4 and 5 bundle configurations. Also, backmixing zones in the bundled arrangements seem to be affected by the presence of wall clearance zones, especially in the configurations which promote large wall clearances, such as the 3 bundle and 5 bundle arrangements, where the large wall clearance zones generated unique backmixing profiles.
Bundled internals also exhibited smoother radial gas holdup profiles, with lower local gas holdup values when compared to the parallel internals. This behavior is primarily due to the increase of the average bubble size for bundled internals when compared with those for parallel internals.

c. The bundled internals result in higher Sauter mean bubble diameter \( d_{32} \) values when compared with those for the parallel internals. This behavior could be due to the fact that the presence of parallel internals enhances bubble breakup and inhibits bubble coalescence, whereas, the presence of bundled internals enhances bubble coalescence. Also, the bubble size appears to increase with decreasing the cross-sectional area for the parallel internals and increasing the number of bundled internals. This behavior could be related to the effect of the distance between the internals in the case of parallel configurations, where lower cross-sectional area coverages result in wider distance between the internals, leading to the formation of large gas bubbles. For bundled internals, on the other hand, this effect is due to the wall clearance, where bigger clearances resulted in increased bubble diameter.

7. The CFD model was also used to simulate the performance of the pilot-scale SBCR reactor available in our laboratory and an industrial-scale SBCR for F-T synthesis using iron catalyst. The kinetic expressions of the F-T synthesis and water-gas-shift provided by NICE were included in the CFD model. The CO and \( \text{H}_2 \) conversions and \( \text{C}_5^+ \) yields were calculated at different operating conditions. The following remarks can be made:

a. The CFD model was used to simulate the performance of the pilot-scale (0.3-m, 3-m height) F-T SBCR, provided with internals in a single bundled arrangement of one, 2.5-inch pipe at the center of the reactor, surrounded by 6, 1.75-inch pipes in a hexagonal pattern and a six arm spider sparger and operating with NICE iron catalyst. The CFD
model was capable of predicting the overall performance and the local hydrodynamics in this pilot-scale SBCR. The simulations were carried out with a catalyst concentrations of 5, 10 and 15 vol% and three H₂/CO ratios of 1, 1.5 and 2, at temperature of 443 K, pressure of 20.5 bar, and a superficial gas velocity of 0.24 m/s. The Simulation results showed that the CO and H₂ conversions increase with increasing the catalyst concentration. Also, the pilot scale SBCR can produce a maximum of 1.87 tons/day of C₅⁺ products when using a catalyst concentration of 15 vol%.

b. The CFD model was also used to simulate the performance of a commercial-scale (5.8-m ID, 42-m height) F-T SBCR, provided with 604 internals and a concentric ring sparger, and operating with NICE iron catalyst. The CFD model was capable of predicting the overall performance and the local hydrodynamics in this commercial-scale SBCR. The simulations were conducted at a catalyst loading of 10 vol% at a temperature of 528 K, pressure of 29 bar and four superficial gas velocities of 0.12, 0.24, 0.3 and 0.4 m/s. Under these conditions, the simulation results indicated that the CO conversions were 48%, 59%, 58% and 55%; the H₂ conversions were 36%, 51%, 56% and 54% and the C₅⁺ products yields were are 275, 576, 627 and 654 ton/day at the superficial gas velocities of 0.12, 0.24, 0.3 and 0.4 m/s, respectively.

c. Thus, the CFD model built and validated in this work could be used to optimize the SBCR design and/or troubleshoot any problems associated with the internal reactor operation.
APPENDIX A

LITERATURE REVIEW TABLES
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fixed Bed</td>
<td>T (°C)</td>
<td>P, MPa</td>
<td>H₂/CO feed</td>
</tr>
<tr>
<td>Reduced Fused Fe/K₂O/MgO</td>
<td>Fixed Bed, Fluidized Bed, Slurry</td>
<td>250-320</td>
<td>2.2-4.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Reduced Nitrided Fe</td>
<td>Fixed Bed</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reduced Nitrided Fused Fe</td>
<td>Fixed Bed</td>
<td>225-240</td>
<td>2.2</td>
<td>0.25-2.0</td>
</tr>
<tr>
<td>Fused Fe &amp; Prec. Fe/Cu/MgO/K₂CO₃</td>
<td>Fixed Bed</td>
<td>200-280</td>
<td>10</td>
<td>3.1²</td>
</tr>
<tr>
<td>Reduced Nitrided Fused Fe/Cr₂O₃/SiO₂/MgO/K₂O</td>
<td>Fixed Bed</td>
<td>225-255</td>
<td>2.2</td>
<td>0.25-2.0</td>
</tr>
<tr>
<td>Reduced Fused Fe/K₂O/Al₂O₃/SiO₂</td>
<td>Fixed Bed</td>
<td>225-265</td>
<td>1.0-1.8</td>
<td>1.2-7.2</td>
</tr>
<tr>
<td>Fe</td>
<td>Fixed Bed, Fluidized Bed</td>
<td>200-340</td>
<td>0.5-4.0</td>
<td>1.0-7.3</td>
</tr>
<tr>
<td>Reduced Nitrided Fused Fe/K₂O/Al₂O₃/SiO₂</td>
<td>Gradientless Fixed Bed</td>
<td>250-315</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table A-1: Kinetics studies for the F-T synthesis on iron catalyst
### Table A-1 (continued)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma Sprayed Fe</td>
<td>Recirculating Reactor</td>
<td>T (°C) 250-300</td>
<td>0.77-3.1 1.5-3.9</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}P_{CO}}{P_{CO} + aP_{H_2}O}$</td>
</tr>
<tr>
<td>Reduced Prec. Fe/Cu/K₂O</td>
<td>Fixed Bed</td>
<td>T (°C) 220-270</td>
<td>1.0-2.0 1.0-6.0</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}}{P_{CO}^{0.25}}$</td>
</tr>
<tr>
<td>Reduced Fused Fe/K₂O/CaO/SiO₂</td>
<td>Slurry</td>
<td>T (°C) 232-263</td>
<td>0.4-1.5 0.5-1.8</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}P_{CO}}{P_{CO}P_{H_2} + aP_{H_2}O}$</td>
</tr>
<tr>
<td>Fe/Cu/K</td>
<td>-</td>
<td>T (°C) 265</td>
<td>- - -</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}P_{CO}}{P_{CO} + aP_{CO_2}}$</td>
</tr>
<tr>
<td>Reduced Prec. Fe/K</td>
<td>Slurry</td>
<td>T (°C) 220-260</td>
<td>1.0 0.5-0.6</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}P_{CO}}{P_{CO} + aP_{CO_2}}$</td>
</tr>
<tr>
<td>Prec. Fe &amp; Fused Fe</td>
<td>Slurry</td>
<td>T (°C) 210-280</td>
<td>0.5-5.5 0.5-3.5</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}P_{CO}}{P_{CO} + aP_{CO_2}}$</td>
</tr>
<tr>
<td>Reduced Prec. Fe/K</td>
<td>Slurry</td>
<td>T (°C) 220-260</td>
<td>- 0.5-2.0</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}P_{CO}}{P_{CO} + aP_{CO_2}}$</td>
</tr>
<tr>
<td>Prec. Fe/Cu/K &amp; Reduced Fe/Cu/K/SiO₂</td>
<td>Slurry</td>
<td>T (°C) 235-265</td>
<td>1.5-3.0 0.6-1.0</td>
<td>$r_{FT} = k_{FT}P_{H_2}$ $r_{FT} = k_{FT}P_{H_2}P_{CO}$</td>
</tr>
<tr>
<td>Prec. Fe/Cu/K</td>
<td>Gradientless</td>
<td>T (°C) 230-264</td>
<td>1.0-2.6 1.1-2.4</td>
<td>$r_{FT} = k_{FT} \frac{P_{H_2}P_{CO}}{P_{CO} + aP_{H_2}O}$</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Reactor</td>
<td>Operating Conditions</td>
<td>Equation</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>----------------------</td>
<td>----------------------</td>
<td>--------------------------------------------------------------------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Reduced Prec. Fe/Cu/K</td>
<td>Fixed Bed</td>
<td>T (°C)</td>
<td>220-300</td>
<td>P, MPa</td>
</tr>
<tr>
<td>Reduced Prec. Fe/Cu/K/SiO₂</td>
<td>Slurry</td>
<td>250</td>
<td>1.2-4.0</td>
<td>0.25-4.0</td>
</tr>
<tr>
<td>Reduced Prec. Fe/CuO/K₂O/Na₂O/SiO₂</td>
<td>Fixed Bed</td>
<td>250-350</td>
<td>0.6-2.1</td>
<td>3.0-6.0</td>
</tr>
<tr>
<td>Precipitated Fe</td>
<td>Slurry</td>
<td>210-250</td>
<td>1.38-4.12</td>
<td>1-7</td>
</tr>
<tr>
<td>Reduced Prec. Fe/Cu/K/SiO₂</td>
<td>Spinning Basket</td>
<td>250</td>
<td>0.8-4.0</td>
<td>0.25-4.0</td>
</tr>
<tr>
<td>Fe</td>
<td>Fixed Bed</td>
<td>220-260</td>
<td>2.4</td>
<td>1.87-2.0</td>
</tr>
<tr>
<td>Fe &amp; Fe/Al₂O₃/Cu/K₂O &amp; Fe/Mn/Cu/K₂O</td>
<td>Slurry</td>
<td>225-275</td>
<td>P_{H_2}=0.26-3.02</td>
<td>P_{CO}=0.02-1.94</td>
</tr>
</tbody>
</table>
Table A-1 (continued)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>T (°C)</th>
<th>P, MPa</th>
<th>H₂/CO feed</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe &amp; Fe/K</td>
<td>Slurry</td>
<td>200-240</td>
<td>1.0</td>
<td>1.0-3.0</td>
<td>$r_{FT} = k_{FT}(P_{H₂})^x(P_{CO})^y$</td>
<td>Eliason and Bartholomew [428]</td>
</tr>
<tr>
<td>Fe/Cu/K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$r_{CH_4} = \frac{k_{SM}P_{H₂}α_1}{1 + (\frac{1}{K_2K_3K_4P_{H₂}^2} + \frac{1}{K_2K_3P_{H₂}^2} + \frac{1}{K_4})\sum_{i=1}^{N}(Π_{j=1}^i α_j)}$, $(n = 1)$</td>
<td>Wang et al. [52, 429]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$r_{CuH_2^{n+2}} = \frac{k_6(1 - β_n)Π_{j=1}^i α_j}{1 + (\frac{1}{K_2K_3K_4P_{H₂}^2} + \frac{1}{K_2K_3P_{H₂}^2} + \frac{1}{K_4})\sum_{i=1}^{N}(Π_{j=1}^i α_j)}$, $(n ≥ 2)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$r_{CuH_2^n} = \frac{k_6P_{Co}P_{H₂} - k_5P_{H₂}P_{H₂}^0}{k_p}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$r_{CO} = \frac{k_1P_{Co} + k_5P_{H₂}}{k_1P_{Co}}$, $(n = 1)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$β_n = \frac{k_{-6}P_{CuH_2^n}}{k_6}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$α_n = \frac{k_1P_{Co} + k_5P_{H₂}}{k_1P_{Co}} + K_p = \frac{5078.0045}{T} - 5.8972089 + 13.958689×10^{-4}T - 27.592844×10^{-8}T^2$</td>
<td></td>
</tr>
</tbody>
</table>

$\sum_{i=1}^{N}(Π_{j=1}^i α_j)$

$\sum_{i=2}^{n}(Π_{j=1}^i α_j)$

$\sum_{i=1}^{N}(Π_{j=1}^i α_j)$
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Reduced Fe/Cu/K | Fixed Bed     | T (°C) 220-269       | \( r_{\text{CH}_4} = \frac{k_{5M}P_{\text{H}_2}^{\alpha_1}}{1 + \left(1 + \frac{1}{K_2K_3K_4} \frac{P_{\text{H}_2}}{P_{\text{H}_2}^{0.5}} + \frac{1}{K_4} \right) \sum_{i=1}^{N} (\prod_{j=1}^{i} \alpha_j)} \), \( r_{\text{CO}_2} = \frac{k_{\text{V}} P_{\text{CO}} P_{\text{H}_2}^{0.5}}{1 + \left(\frac{P_{\text{CO}} P_{\text{H}_2}^{0.5}}{P_{\text{H}_2}^{0.5}} - \frac{P_{\text{CO}} P_{\text{H}_2}^{0.5}}{K_p} \right)} \)  
|                 | P, MPa 1.1-3.1 | H₂/CO feed 1.0-3.0    | \( r_{\text{H}_2n+2} = \frac{k_5P_{\text{H}_2} \prod_{j=1}^{i} \alpha_j}{1 + \left(1 + \frac{1}{K_2K_3K_4} \frac{P_{\text{H}_2}}{P_{\text{H}_2}^{0.5}} + \frac{1}{K_4} \right) \sum_{i=1}^{N} (\prod_{j=1}^{i} \alpha_j)} \), 
|                 |               |                      | \( r_{\text{H}_2n} = \frac{k_5(1 - \beta_n) \prod_{j=1}^{i} \alpha_j}{1 + \left(1 + \frac{1}{K_2K_3K_4} \frac{P_{\text{H}_2}}{P_{\text{H}_2}^{0.5}} + \frac{1}{K_4} \right) \sum_{i=1}^{N} (\prod_{j=1}^{i} \alpha_j)} \)  
| Reduced Fe/Mn   | Fixed Bed     | T (°C) 267-327       | \( r_{\text{CH}_4} = \frac{k_7M K_4 K_6 K_2 P_{\text{CO}} P_{\text{H}_2}^{0.5}}{P_{\text{H}_2}^{0.5}} \), \( r_{\text{CO}_2} = \frac{k_{\text{V}} P_{\text{CO}} P_{\text{H}_2}^{0.5}}{1 + \left(\frac{P_{\text{CO}} P_{\text{H}_2}^{0.5}}{P_{\text{H}_2}^{0.5}} - \frac{P_{\text{CO}} P_{\text{H}_2}^{0.5}}{K_p} \right)} \)  
|                 | P, MPa 1.0-3.0 | H₂/CO feed 1.0-3.0    | \( r_{\text{H}_2n+2} = \frac{k_5 P_{\text{H}_2}^{0.5} \prod_{j=1}^{i} \alpha_j}{1 + \left(1 + \frac{1}{K_2K_3K_4} \frac{P_{\text{H}_2}}{P_{\text{H}_2}^{0.5}} + \frac{1}{K_4} \right) \sum_{i=1}^{N} (\prod_{j=1}^{i} \alpha_j)} \)  

Wang et al. [430] 
Yang et al. [431]
### Table A-1 (continued)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T$ (°C)</td>
<td>$P$, MPa</td>
</tr>
<tr>
<td>Fe/Mn &amp; Fe/Cu/K</td>
<td>Spinning Basket</td>
<td>260-300</td>
<td>1.1-2.6</td>
<td>0.67-2.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Teng et al. [432]
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (°C)</td>
<td>P, MPa</td>
<td>H₂/CO feed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitated Fe</td>
<td>Slurry</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe/Cu/K/SiO₂</td>
<td>Slurry</td>
<td>250-290</td>
<td>1.0-2.5</td>
<td>0.67-1.5</td>
</tr>
<tr>
<td>Reduced Fe</td>
<td>Slurry</td>
<td>260</td>
<td>1-3</td>
<td>0.8-3.2</td>
</tr>
</tbody>
</table>
Table A-2: Kinetics studies for the WGS reaction on iron catalyst

<table>
<thead>
<tr>
<th>Catalyst / Promoter</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fixed Bed, Fluidized Bed</td>
<td>T (°C)</td>
<td>P, MPa</td>
<td>H₂/CO feed</td>
<td>Equation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200-340</td>
<td>0.5-4.0</td>
<td>1.0-7.3</td>
<td></td>
</tr>
<tr>
<td>Reduced Prec. Fe/Cu/K₂O</td>
<td>Fixed Bed</td>
<td>220-270</td>
<td>1.0-2.0</td>
<td>1.0-6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe/Cu/K</td>
<td>-</td>
<td>265</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prec. Fe/Cu/K &amp; Reduced Fe/Cu/K/SiO₂</td>
<td>Slurry</td>
<td>235-265</td>
<td>1.5-3.0</td>
<td>0.6-1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reduced Prec. Fe/CuO/K₂O/Na₂O/SiO₂</td>
<td>Fixed Bed</td>
<td>250-350</td>
<td>0.6-2.1</td>
<td>3.0-6.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prec. Fe/Cu/K</td>
<td>Gradientless</td>
<td>230-264</td>
<td>1.0-2.6</td>
<td>1.1-2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Leib and Kuo [417]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Equation:

- \( \dot{r}_{WGS} = k_{WGS}P_{CO} \)
- \( \dot{r}_{WGS} = k_{WGS}P_{CO} \)
- \( \dot{r}_{WGS} = k_{WGS}\frac{\left(\frac{P_{CO}P_{H_2}O}{K_{eq}} - \frac{P_{CO_2}P_{H_2}}{K_{eq}}\right)}{P_{CO} + aP_{H_2}O} \)
- \( \dot{r}_{WGS} = k_{WGS}\frac{\left(\frac{P_{CO}P_{H_2}O}{K_{eq}} - \frac{P_{CO_2}P_{H_2}}{K_{eq}}\right)}{P_{CO}P_{H_2} + aP_{H_2}O} \)
- \( \dot{r}_{WGS} = k_{WGS}\frac{\left(\frac{P_{CO}P_{H_2}O}{K_{eq}} - \frac{P_{CO_2}P_{H_2}}{K_{eq}}\right)}{P_{CO}P_{H_2} + aP_{H_2}O + bP_{CO_2}} \)

Reference:
- Dry [413]
- Feimer et al. [416]
- Leib and Kuo [417]
- Zimmerman and Bukur [420]
- Lox and Froment [50, 51]
- Shen et al. [436]^2
<table>
<thead>
<tr>
<th>Catalyst / Promoter</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (°C)</td>
<td>P , MPa</td>
<td>H₂/CO feed</td>
</tr>
<tr>
<td>Precipitated Fe</td>
<td>Slurry</td>
<td>210-250</td>
<td>1.38-4.12</td>
<td>1-7</td>
</tr>
<tr>
<td>Reduced Prec. Fe/Cu/K/SiO₂</td>
<td>Spinning Basket</td>
<td>250</td>
<td>0.8-4.0</td>
<td>0.25-4.0</td>
</tr>
<tr>
<td>Reduced Prec. Fe/Cu/K/SiO₂</td>
<td>Slurry</td>
<td>250</td>
<td>1.2-4.0</td>
<td>0.25-4.0</td>
</tr>
<tr>
<td>Fe</td>
<td>Fixed Bed</td>
<td>220-260</td>
<td>2.4</td>
<td>1.87-2.05</td>
</tr>
<tr>
<td>Reduced Prec. Co/MnO</td>
<td>Micro-Fixed Bed</td>
<td>210-250</td>
<td>0.6-2.6</td>
<td>1.6-4.1</td>
</tr>
<tr>
<td>Fe/Cu/K</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table A-2 (continued)

<table>
<thead>
<tr>
<th>Catalyst / Promoter</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (°C)</td>
<td>P, MPa</td>
<td>H₂/CO_feed</td>
</tr>
<tr>
<td>Reduced Fe/Cu/K</td>
<td>Fixed Bed</td>
<td>220-269</td>
<td>1.1-3.1</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>Reduced Fe/Mn</td>
<td>Fixed Bed</td>
<td>267-327</td>
<td>1.0-3.0</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>Fe/Mn &amp; Fe/Cu/K</td>
<td>Spinning Basket</td>
<td>260-300</td>
<td>1.1-2.6</td>
<td>0.67-2.05</td>
</tr>
<tr>
<td>Fe/Cu/K/SiO₂</td>
<td>Slurry</td>
<td>250-290</td>
<td>1.0-2.5</td>
<td>0.67-1.5</td>
</tr>
<tr>
<td>Sasol commercial spray dried precipitated Iron Catalyst</td>
<td>Slurry</td>
<td>240-250</td>
<td>5-40</td>
<td>1.55</td>
</tr>
</tbody>
</table>

¹ as reported in [420]
² as reported in [439]
Table A-3: Kinetics studies for the Fischer-Tropsch synthesis on cobalt-based catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>-</td>
<td>T (°C) 250</td>
<td>$P_{H_2}$ $P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^2}{P_{CO}}$</td>
<td>Brotz [406]</td>
</tr>
<tr>
<td>Co/ThO$_2$/kieselguhr</td>
<td>-</td>
<td>190</td>
<td>$P_{H_2}P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^2}{1 + aP_{CO}P_{H_2}^2}$</td>
<td>Anderson [408]</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>190</td>
<td>$P_{H_2}P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^0.5}{P_{CO}^{0.5}}$</td>
<td>Yang et al. [440]</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>190</td>
<td>$P_{H_2}P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^0.5}{P_{CO}^{0.33}}$</td>
<td>Pannell et al. [441]</td>
</tr>
<tr>
<td>Reduced Prec. Co/Al$_2$O$_3$</td>
<td>Fixed Bed</td>
<td>250</td>
<td>$P_{H_2}P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^0.5}{1 + aP_{CO}P_{H_2}^0.5}$</td>
<td>Outi et al. [47]</td>
</tr>
<tr>
<td>Co/Kieselguhr</td>
<td>Berty internal recycle reactor</td>
<td>190</td>
<td>$P_{H_2}P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^0.5P_{CO}^0.5}{(1 + aP_{CO}P_{H_2}^0.5)^2}$</td>
<td>Sarup and Wojciechowski [427]</td>
</tr>
<tr>
<td>Co/Zr/SiO$_2$</td>
<td>Slurry</td>
<td>220-280</td>
<td>$P_{H_2}P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^0.5}{P_{CO}P_{H_2} + aP_{H_2}^0}$</td>
<td>Withers et al. [402]</td>
</tr>
<tr>
<td>Co/MgO/SiO$_2$</td>
<td>Slurry</td>
<td>220-240</td>
<td>$P_{H_2}P_{CO}$ $P_{CO}$ $P_{H_2}$ $r_{FT} = k_{FT} \frac{P_{H_2}^0.5}{(1 + aP_{CO})^2}$</td>
<td>Yates and Satterfield [69]</td>
</tr>
<tr>
<td>Co/MgO/ThO$_2$/SiO$_2$</td>
<td>Slurry</td>
<td>4.12</td>
<td>$r_{FT} = k_{FT} \frac{P_{CO}P_{H_2}}{(1 + aP_{CO})^2}$</td>
<td>van Berge [424]</td>
</tr>
<tr>
<td>Co/MgO/ThO$_2$/SiO$_2$ &amp; Co/SiO$_2$</td>
<td>Slurry</td>
<td>190-210</td>
<td>$P_{H_2} = 0.01-1.93$ $P_{CO} = 0.05-2.54$ $r_{c,org} = \frac{k_{FT}(P_{H_2}P_{CO}/P_{H_2}^0)}{(1 + a(P_{H_2}P_{CO}/P_{H_2}^0))^2}$</td>
<td>van Steen and Schulz [427]</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Reactor</td>
<td>Operating Conditions</td>
<td>Equation</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------------------</td>
<td>----------------------</td>
<td>--------------------------------------------------------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>CO/TiO₂</td>
<td>Differential fixed bed reactor</td>
<td>T (°C)</td>
<td>P (MPa)</td>
<td>H₂/CO feed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180-240</td>
<td>2.0265</td>
<td>1-3.5</td>
</tr>
<tr>
<td>Reduced Prec. Co/MnO³</td>
<td>Micro-Fixed Bed</td>
<td>210-250</td>
<td>0.6-2.6</td>
<td>1.6-4.1</td>
</tr>
<tr>
<td>Co/Al₂O₃</td>
<td>Fixed Bed (micro)</td>
<td>210-235</td>
<td>0.8-2.5</td>
<td>1.8-2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>2.0</td>
<td>1.6-3.35</td>
</tr>
<tr>
<td>Co-Re/Al₂O₃</td>
<td>Batch</td>
<td>205, 220, 230</td>
<td>1.5, 2.5</td>
<td>1.4, 2.1</td>
</tr>
</tbody>
</table>
Table A-3 (continued)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactor</th>
<th>Operating Conditions</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (°C)</td>
<td>P (MPa)</td>
<td>H₂/CO \text{feed}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>190 - 220</td>
<td>1 - 2.5</td>
<td>1.5 - 3</td>
</tr>
<tr>
<td>Co/Al₂O₃</td>
<td>Tubular fixed bed reactor</td>
<td>190 - 220</td>
<td>1 - 2.5</td>
<td>1.5 - 3</td>
</tr>
</tbody>
</table>

212
<table>
<thead>
<tr>
<th>Reference</th>
<th>Gas-Liquid-Solid System</th>
<th>Reactor Geometry</th>
<th>Operating Conditions</th>
<th>Parameter Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deckwer et al. [75]</td>
<td>N₂ - Paraffin Wax - Al₂O₃</td>
<td>$d_c = 0.04, 0.1 \text{ m}$</td>
<td>P up to 11 bar; $T = 416 \text{ K} &amp; 543 \text{ K}$; $u_g$ up to 0.04 m/s; $C_s$ up to 16 wt.%</td>
<td>$\varepsilon_g, k_{LA}$</td>
</tr>
<tr>
<td>Bukur et al. [76]</td>
<td>N₂ - FT-300 Paraffin Wax - Iron Oxide, Silica</td>
<td>$d_c = 0.05 \text{ m}$; $h_c = 3 \text{ m}$</td>
<td>P atm; $T = 538 \text{ K}$; $u_g$ = 0.02-0.12 m/s; $C_s$ = 10-30 wt.%</td>
<td>$\varepsilon_g$</td>
</tr>
<tr>
<td>Krishna et al. [77]</td>
<td>Air - Paraffin Oil - Silica</td>
<td>$d_c = 0.38 \text{ m}$</td>
<td>P atm; $T_{amb}$; $u_g$ up to 0.5 m/s; $C_s$ up to 36 vol.%</td>
<td>$\varepsilon_g$</td>
</tr>
<tr>
<td>Vandu et al. [366]</td>
<td>Air - C₉-C₁₁ Paraffin Oil - Puralox (Al₂O₃)</td>
<td>$d_c = 0.1 \text{ m}$</td>
<td>P atm; $T_{amb}$; $u_g$ up to 0.4 m/s; $C_s$ up to 25 vol.%</td>
<td>$\varepsilon_g, k_{LA}$</td>
</tr>
<tr>
<td>Behkish et al. [8, 80]</td>
<td>H₂, CO, N₂, He, CH₄ - Isopar-M - Glass Beads, Al₂O₃</td>
<td>$d_c = 0.3 \text{ m}$; $h_c = 3 \text{ m}$</td>
<td>P up to 30 bar; $T$ up to 473 K; $u_g$ up to 0.39 m/s; $C_s$ up to 36 vol.%</td>
<td>$\varepsilon_g, d_{32}, k_{LA}$</td>
</tr>
<tr>
<td>Woo et al. [79]</td>
<td>Actual F-T reactive system with Al₂O₃ supported Co catalyst</td>
<td>$d_c = 0.05 \text{ m}$; $h_c = 1.5 \text{ m}$</td>
<td>P = 10 - 30 bar; $T$ = 480–520 K; $u_g$ = 0.017-0.136 m/s; $C_s$ = 9-27 wt.%</td>
<td>$\varepsilon_g$</td>
</tr>
<tr>
<td>Sehabiague et al. [81]</td>
<td>N₂, He – C₁₂-C₁₃, Paraffins mixture, Light F-T cut, Heavy F-T cut – Alumina, Puralox Alumina, Iron oxide</td>
<td>$d_c = 0.3 \text{ m}$; $h_c = 3 \text{ m}$</td>
<td>P up to 30 bar; $T$ up to 500 K; $u_g$ up to 0.27 m/s; $C_s$ up to 20 vol.%</td>
<td>$\varepsilon_g, d_{32}, k_{LA}$</td>
</tr>
<tr>
<td>System</td>
<td>Conditions</td>
<td>Correlation</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
<td>-------------------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>--------------------</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>$d_c: 0.66 \text{ m}$</td>
<td>$\varepsilon_t = 1.40 \left( \frac{u_t^2}{gd_p} \right)^{0.170} \left( \frac{\mu_t u_t}{\sigma_l} \right)^{0.078}$</td>
<td>Kim et al. [445]</td>
<td></td>
</tr>
<tr>
<td>Sugar solution</td>
<td>$h_c: 2.438 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxymethylcellulose</td>
<td>$u_g: 0.007 - 0.161 \text{ m/s}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$d_p: 1 - 6 \text{ mm}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water-acetone</td>
<td>$\rho_s: 2300 - 2950 \text{ kg/m}^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irregular gravel</td>
<td>$\rho_l: 960 - 1170 \text{ kg/m}^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$\mu_l: 0.001 - 0.07 \text{ Pa} \cdot \text{s}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irregular gravel</td>
<td>$\sigma_l: 0.0398 - 0.0738 \text{ N/m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>$u_g: 0.05 - 4 \text{ m/s}$</td>
<td>$\varepsilon_g = 0.19 \left( \frac{u_t^2 d_p \rho_l}{\sigma_l} \right)^{0.11} \left( \frac{u_t}{\sqrt{gd_p}} \right)^{0.22}$</td>
<td>Kito et al. [446]</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>$d_c: 0.05 - 0.1 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous Glycerol</td>
<td>$d_p: 0.011 - 0.0287 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>$h_c: 0.05 - 0.2 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>$\rho_l: 797 - 1165 \text{ kg/m}^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>$\mu_l: 1.01 - 14.45 \text{ cP}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid</td>
<td>$\sigma_l: 0.0233 - 0.0728 \text{ N/m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>$u_g: 0.02 - 0.12 \text{ m/s}$</td>
<td>$\varepsilon_g = 0.46 \left( \frac{u_t^2}{gd_p} \right)^{0.19} \left( \frac{u_g^2}{gd_p} \right)^{0.01} \left( \frac{u_t d_p \rho_l}{\mu_l} \right)^{0.026}$</td>
<td>Oh and Kim [447]</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>$u_l: 0.03 - 0.14 \text{ m/s}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$\rho_s: 2500 \text{ kg/m}^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$d_p: 1.63 - 7.85 \text{ mm}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$d_c: 0.15 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$h_c: 2.5 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>$u_g: 0 - 0.173 \text{ m/s}$</td>
<td>$\varepsilon_g = 0.26 \left( \frac{u_t^2}{gd_p} \right)^{0.44} \left( \frac{u_g^2}{gd_p} \right)^{-0.032} \left( \frac{u_t d_p \rho_l}{\mu_l} \right)^{-0.006}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>$u_l: 0 - 0.12 \text{ m/s}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina beads</td>
<td>$\rho_l: 100 - 1200 \text{ kg/m}^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$\rho_s: 1720 - 2440 \text{ kg/m}^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina silicate</td>
<td>$d_p: 1.9 - 6.3 \text{ mm}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plexiglas</td>
<td>$d_c: 0.076 - 0.152 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina silicate</td>
<td>$h_c: 0.22 - 0.45 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plexiglas</td>
<td>$d_c: 0.15 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plexiglas</td>
<td>$h_c: 2.5 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plexiglas</td>
<td>$d_c: 0.22 - 0.45 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plexiglas</td>
<td>$h_c: 2.5 \text{ m}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A-5 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$u_g: 0 - 0.0022 \text{ m/s}$</td>
<td>$(1 - \varepsilon_g)u_g + \varepsilon_g u_l = \varepsilon_g(22.67\varepsilon_g + 10.44)$</td>
<td>Koide et al. [107] taken from [450]</td>
</tr>
<tr>
<td>Kerosene Solids</td>
<td>$d_p: 1.1 \text{ mm}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_s: 1330 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_l: 810 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\mu_l: 1.4 \text{ mPa} \cdot \text{s}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>$u_g: 0.03 - 0.15 \text{ m/s}$</td>
<td>$\frac{(1 - \varepsilon_g)^4}{(1 + 4.35(\frac{C_s}{\rho_p})^{0.748}(\frac{\rho_p - \rho_l}{\rho_l})^{0.881}(\frac{d \rho_g \rho_l}{\mu_l})^{0.168}}}$</td>
<td>Koide et al. [107]</td>
</tr>
<tr>
<td>Glycerol Glycol Barium chloride Sodium sulfate Glass spheres Bronze spheres</td>
<td>$d_p: 47.5 - 192 \mu \text{m}$</td>
<td>$A \left(\frac{u_g \mu_l}{\sigma_l}\right)^{0.918} \left(\frac{g \mu_l^4}{p_l \sigma_l^3}\right)^{-0.252}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_s: 2500, 8770 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_l: 0.997 - 1178 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\mu_l: 0.894 - 17.6 \text{ mPa} \cdot \text{s}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_l: 0.0515 - 0.073 \text{ N/m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_c: 0.1 - 0.3 \text{ m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_c: 2.3 - 3 \text{ m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>$u_g: 0.02 - 0.22 \text{ m/s}$</td>
<td>$\varepsilon_g = \left[2.25 + \left(\frac{33.9}{0.01 u_g}\right)^{0.31} \left(1000 \mu_{st}\right)^{0.016}\right]^{-1}$</td>
<td>Smith et al.[451]</td>
</tr>
<tr>
<td>Water</td>
<td>$d_p: 19.4 - 96.5 \mu \text{m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous ethanol (95%)</td>
<td>$\rho_s: 2420, 3990 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicone oil Ethylene glycol Glass beads</td>
<td>$C_v: 2.8 - 5 \text{ vol}%$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_l: 820 - 1100 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\mu_l: 0.82 - 17.1 \text{ mPa} \cdot \text{s}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_l: 17.4 - 71.5 \text{ mN/m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_c: 0.108 \text{ m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_c: 1.94 \text{ m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>$u_g: 0.02 - 0.2 \text{ m/s}$</td>
<td>$\varepsilon_g = 296u_g^{0.44} \mu_l^{0.98} \sigma_l^{-0.16} \rho_g^{0.19} + 0.009$</td>
<td>Reilly et al. [452]</td>
</tr>
<tr>
<td>Water</td>
<td>$d_p: 71 - 745 \mu \text{m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichloroethylene Glass beads</td>
<td>$C_v: \text{ up to 10 vol}%$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_s: 1510 - 4470 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_l: 0.168 - 1.34 \text{ kg/m}^3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A-5 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂, O₂, Water, Na₂SO₄, Activated Carbon, Al₂O₃</td>
<td>$P_{atm}, T_{atm}$, $u_g &lt; 0.07 \text{ms}^{-1}$, $C_v: 0.51 - 15.22 \text{vol}%$, $d_p: 5.4, 6.6 \text{8.1 }\mu\text{m}$, $d_c: 0.095 \text{m}$, $h_c: 0.85 \text{m}$</td>
<td>$\varepsilon_g = F \cdot u_g^{0.87} \cdot \mu_{eff}^{-0.18}$, $F = {0.81$ for salt solution, $0.43$ for tap water, $\mu_{eff} = k(2800u_g)^{n-1}$, $k$ is the fluid consistency index $= 1.97$, $n$ empirical constant $1 \geq n \geq 0.18$</td>
<td>Schumpe et al. [453]</td>
</tr>
<tr>
<td>Air, H₂O, Various Plastics, Sand</td>
<td>$u_g: 0.01 - 0.08 \text{m/s}$, $d_p: 0.11 - 2.8 \text{mm}$, $C_v: 0 - 20 \text{vol}%$, $P_{atm}$, $\rho_s: 1020 - 2780 \text{kg/m}^3$</td>
<td>$\varepsilon_g'''' = K \left( \frac{u_g}{(v_{sl}g u_g)^{1/4}} \right)^{B_1} \left( \frac{v_{sl}}{v_{eff,rad}} \right)^{B_2} \left( \frac{C_s}{C_{so}} \right)^{B_3}$</td>
<td>Sauer and Hempel [186]</td>
</tr>
</tbody>
</table>

The values of constant $K$ and of exponents $B1$-$B3$ are as follows:

**Sieve plate**

- $K = 0.00476$
- $B1 = 0.888$
- $B2 = -0.258$
- $B3 = 0.0407$

**Perforated Plate**

- $K = 0.0277$
- $B1 = 0.844$
- $B2 = -0.136$
- $B3 = 0.0392$

$$v_{sl} = \frac{\mu_L(1 + 2.5\varepsilon_s + 10.05\varepsilon_s^2 + 0.00273e^{16.6\varepsilon_s})}{\rho_s}$$

$$\bar{v}_{eff,rad} = 0.011d_c\sqrt{g\rho_c\left(\frac{u_g^3}{g\eta_i}\right)^{1/8}}$$
Table A-5 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$u_g: 0.0057 - 0.02 , m/s$</td>
<td>$\frac{\bar{c}<em>s}{c</em>{so}} = \frac{u_{ss} h_c}{u_g d_c} \frac{13 Fr_g (1 + 0.09 Re_p Fr_g^{-0.8})}{1 + 8 Fr_g^{0.85}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$u_l: 0.0039 - 0.0195 , m/s$</td>
<td>$\rho_{sl} = \varepsilon_s \rho_s + (1 - \varepsilon_s) \rho_l$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_v: 0.1 - 0.9 , \text{vol.%}$</td>
<td>$\varepsilon_g = 0.794 - 0.04X_1^2 - 0.034X_2^2 - 0.006(u_l)^{0.246}(u_g)^{-0.059}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_p: 250 , \mu m$</td>
<td>$X_1 = 0.409(u_l - 3.01) - 0.913(u_g - 2.12)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_c: 0.2 , m$</td>
<td>$X_2 = 0.973(u_l - 3.01) - 0.229(u_g - 2.12)$</td>
<td>Lee and Lasa</td>
</tr>
<tr>
<td></td>
<td>$h_c: 3.35 , m$</td>
<td></td>
<td>[454]</td>
</tr>
<tr>
<td>Water</td>
<td>$u_g: 0.0057 - 0.02 , m/s$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td>$u_l: 0.0039 - 0.0195 , m/s$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$C_v: 0.1 - 0.9 , \text{vol.%}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_p: 250 , \mu m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_c: 0.2 , m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_c: 3.35 , m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>$P_{atm}$</td>
<td>$\langle \varepsilon_g \rangle_{ij} = 1 - \frac{\Delta P_{ij}/(S_{sl})<em>{ij}}{\Delta h</em>{ij}}$</td>
<td></td>
</tr>
<tr>
<td>FT-300 Paraffin Wax,</td>
<td>$u_g: 0.02 - 0.12$</td>
<td>$i = 1 \text{ to } 5$, $j = i + 1$</td>
<td>Bukur et al.</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>$C_s: 10 - 30 , \text{wt.%}$</td>
<td>$\langle \varepsilon_g \rangle_{ij} = \frac{1}{1/\rho_{water}} \frac{1/\rho_{water}}{W_{sl}^{ij} / \rho_p + (1 - \langle \varepsilon_g \rangle_{ij} / \rho_l) }$</td>
<td>[262]</td>
</tr>
<tr>
<td>Silica</td>
<td>$T: 538$</td>
<td>$\langle \varepsilon_g \rangle_{ij} = \frac{1}{1/\rho_{water}} \frac{1/\rho_{water}}{W_{sl}^{ij} / \rho_p + (1 - \langle \varepsilon_g \rangle_{ij} / \rho_l) }$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_c: 0.05 , m$</td>
<td>$\langle \varepsilon_g \rangle_{ij} = \frac{1}{1/\rho_{water}} \frac{1/\rho_{water}}{W_{sl}^{ij} / \rho_p + (1 - \langle \varepsilon_g \rangle_{ij} / \rho_l) }$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_c: 3 , m$</td>
<td>$\langle \varepsilon_g \rangle_{ij} = \frac{1}{1/\rho_{water}} \frac{1/\rho_{water}}{W_{sl}^{ij} / \rho_p + (1 - \langle \varepsilon_g \rangle_{ij} / \rho_l) }$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S-ON Sparger$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Various Experimental</td>
<td>$\rho_l: 683 - 2965 , \text{kg/m}^3$</td>
<td>$\varepsilon_g = \frac{\sum_{i=1}^{5} \langle \varepsilon_g \rangle_{ij} \Delta h_{ij}}{\sum_{i=1}^{5} \Delta h_{ij}}$</td>
<td></td>
</tr>
<tr>
<td>data for three phase</td>
<td>$\mu_l: 0.29 - 30 , \text{mPa} \cdot \text{s}$</td>
<td></td>
<td>Fan et al.</td>
</tr>
<tr>
<td>systems</td>
<td>$\sigma_l: 0.019 - 0.073 , \text{N/m}$</td>
<td></td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>$\rho_g: 0.2 - 90 , \text{kg/m}^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_s: 0 - 40 , \text{vol%}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_p: 20 - 143 , \mu m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_c: 0.2 , m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_c: 3 , m$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rho_s: 2200 - 5730 , \text{kg/m}^3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table A-5 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$u_g : 0.05 - 0.69 \text{ m/s}$</td>
<td>$Mo = \frac{g(\rho_l - \rho_g)(\mu_l)^4}{\rho_i^2 d_i^3}$ $\alpha = 0.21Mo_m^{0.0079} - Mo_m^{-0.011}$ $\ln \xi = 4.6\xi_s (5.7\xi_s^{0.58} \sinh[-0.71\exp(-5.8\xi_s)\times \ln(Mo)^{0.22} ] + 1)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$u_l : 0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_C : 0.1 - 0.61 \text{ m}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$h_C / d_C &gt; 5$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
|                               | $\varepsilon_g = \varepsilon_{g-large} + \varepsilon_{df}(1 - \varepsilon_{g-large})$ $\varepsilon_{g-large} = \frac{u_g - u_{g-ref}}{u_{b-large}}$ $u_{b-large} = 0.71(d_B)^{0.5}(DF)(SF)(AF)$ \begin{align*} SF : & \begin{cases} 1.13 \left(\frac{d_B}{d_C}\right)^{-0.5} \text{ for } 0.125 < \frac{d_B}{d_C} < 0.6 , \\ 0.496 \left(\frac{d_B}{d_C}\right)^{-0.5} \text{ for } \frac{d_B}{d_C} > 0.6 \end{cases} \\ AF : & \alpha + \beta(u_g - u_{g-ref}) , \quad DF = \left(\frac{129}{\rho_g}\right)^{0.5} \\
|                               |                             |                                                                             | Krishna and Sie [455] |
|                               | $\varepsilon_{df} = \varepsilon_{df,0} \left(\frac{\rho_g}{\rho_{g,ref}}\right)^{0.48} \left(1 - \frac{0.7}{\varepsilon_{df,0}} C_v\right)\left(1 - \frac{0.8}{u_{b-small,0}} C_v\right)$ $u_{b-small} = u_{b-small,0} \left(1 - \frac{0.8}{u_{b-small,0}} C_v\right)$ $\varepsilon_{df,0}, u_{b-small,0} \text{ : function of liquid nature}$ |                       |
| Artic ice                     |                             |                                                                             |                      |
|                              | $u_g : 0.02 - 0.04 \text{ m/s}$ |                                                                             | Chen et al. [456]     |
|                               | $u_l : 0.018 - 0.037 \text{ m/s}$ |                                                                             |                      |
|                               | $C_s : 5.7 \text{ vol\%}$   |                                                                             |                      |
|                               |                             |                                                                             |                      |

| Air                           | $u_g : 0.02 - 0.04 \text{ m/s}$ | $\varepsilon_g = 0.75u_{g,0.78} \exp[8.12 \times 10^{-6} h_C]$ |                      |
| Paraffin oil                  | $u_g : 0.05 - 0.69 m/s$        |                                                                             |                      |
| Tellus oil                    | $u_g : 0.05 - 0.69 m/s$        |                                                                             |                      |
| Nickel Slurry                 | $u_g : 0.05 - 0.69 m/s$        |                                                                             |                      |
Table A-5 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$u_g: 0 - 0.13 \text{ m/s}$</td>
<td>$\varepsilon_g = 0.17 \left( \frac{u_g^2}{g d_p} \right)^{0.33} \left( \frac{d_p u_t \rho_l}{\mu_t} \right)^{-0.065} \left( \frac{d_p^2 \rho_l (\rho_s - \rho_l) g}{\mu_t^2} \right)^{0.125} \left( \frac{\mu_t^4 g}{\rho_l \sigma_t^3} \right)^{0.05}$ for $\frac{d_p u_t \rho_l}{\mu_t} \leq 100$</td>
<td>Ramesh and Murugesan [457]</td>
</tr>
<tr>
<td>55% Glycerol</td>
<td></td>
<td>$0.11 \left( \frac{u_g^2}{g d_p} \right)^{0.35} \left( \frac{d_p u_t \rho_l}{\mu_t} \right)^{0.2} \left( \frac{d_p^2 \rho_l (\rho_s - \rho_l) g}{\mu_t^2} \right)^{0.11} \left( \frac{\mu_t^4 g}{\rho_l \sigma_t^3} \right)^{0.075}$ for $\frac{d_p u_t \rho_l}{\mu_t} &gt; 100$</td>
<td></td>
</tr>
<tr>
<td>25% Glycerol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mono ethanol amine (MEA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solids of various sizes and shapes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>$u_g: 0.0035 - 0.574 \text{ m/s}$</td>
<td>$\varepsilon_g = 4.94 \times 10^{-3} \left( \frac{\rho_l^{0.415} \rho_g^{0.177} g^{0.27}}{\mu_t^{0.174} d_p^{0.053}} \right) \left( \frac{P_T - P_s}{P_T} \right)^{0.203} \left( \frac{d_c}{d_c + 1} \right)^{-0.117} \Gamma^{0.053}$</td>
<td>Behkish et al. [9]</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopar-M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexanes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass beads</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron Oxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\varepsilon_{\text{large}} = \varepsilon_g^{0.84} (F) = \varepsilon_g^{0.84} \left( 1 - 3.04 \times 10^{-6} \frac{\rho_l^{1.97}}{\mu_t^{0.16}} \times \exp[-4.59 C_s] \right)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\varepsilon_{\text{small}} = \begin{cases} \varepsilon_g - \varepsilon_{\text{large}} \text{ for } \varepsilon_g &gt; F^{25/4} \ 0 \text{ for } \varepsilon_g &lt; F^{25/4} \end{cases}$</td>
<td></td>
</tr>
<tr>
<td>System</td>
<td>Conditions</td>
<td>Correlation</td>
<td>Reference</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Air Water CCl4 Glass beads</td>
<td>$u_g: 0 - 0.107 \text{ m/s}$ $u_i: 0.021 - 0.169 \text{ m/s}$ $T: 305 \text{ K}$ $C_s: 13.8 - 24.3 \text{ vol. %}$ $\rho_s: 2216 - 2270 \text{ kg/m}^3$ $d_p: 2.18 - 4.05 \text{ mm}$ $\rho_i: 998.4 - 1600 \text{ kg/m}^3$ $\mu_i: 0.8 - 0.94 \text{ mPa} \cdot \text{s}$ $d_c: 0.1 \text{ m}$ $h_c: 1.24 \text{ m}$</td>
<td>$\varepsilon_g = 5.53 \left( \frac{u_g^2}{gd_c} \right)^{0.4135} \left( \frac{\rho_iu_i}{\mu_i} \right)^{-0.1808} \left( \frac{h_c}{d_c} \right)^{0.0597} \left( \frac{d_p}{d_c} \right)^{0.0873}$</td>
<td>Jena et al. [458]</td>
</tr>
<tr>
<td>Air Water 20% glycerol, 60% glycerol, 90% glycerol, 65% glycerol, 85% glycerol, MEA, Butyric acid, 0.1% Carboxymethylcellulose (CMC), 0.5% CMC, 1% CMC, Spheres, Berl Saddles, Raschig Rings</td>
<td>$u_g: 0.00375 - 0.1375 \text{ m/s}$ $u_i: 0.008 - 0.2487 \text{ m/s}$ $T: 305 \text{ K}$ $C_s: 13.8 - 24.3 \text{ vol. %}$ $\rho_s: 2216 - 2270 \text{ kg/m}^3$ $d_p: 1 - 13.66 \text{ mm}$ $\rho_i: 1245 - 2960 \text{ kg/m}^3$ $\mu_i: 0.85 - 32 \text{ mPa} \cdot \text{s}$ $\sigma_i: 0.025 - 0.072 \text{ N/m}$ $d_c: 0.005 - 0.15 \text{ m}$ $h_c: 1.8 \text{ m}$</td>
<td>$\varepsilon_g = 0.98 \left( \frac{u_g^2}{gd_p} \right)^{0.382} \left( \frac{u_i^2}{gd_p} \right)^{0.0438} \left( \frac{\rho_s}{\rho_i} \right)^{-0.529} \left( \frac{d_p}{d_c} \right)^{0.0339} \left( \frac{g\mu_i^4}{\rho_i\sigma_i^3} \right)^{0.0265} \phi_s^0$</td>
<td>Sivakumar et al. [450]</td>
</tr>
<tr>
<td>He, N2 Paraffins mixture, C12-C13, Light F-T Cut, Heavy F-T Cut, Alumina, Puralox Alumina, Iron oxide</td>
<td>$u_g: 0.14 - 0.26 \text{ m/s}$ $C_v: 0 - 20 \text{ vol. %}$ $T: 330 - 530 \text{ K}$ $P: 8 - 30 \text{ MPa}$ $\rho_s: 3218 - 4000 \text{ kg/m}^3$ $d_p: 1.5 - 140 \mu\text{m}$ $\rho_i: 631.3 - 779.5 \text{ kg/m}^3$ $\mu_i: 0.27 - 9.96 \text{ mPa} \cdot \text{s}$ $\sigma_i: 13 - 27 \text{ mN/m}$ $d_c: 0.3 \text{ m}$ $h_c: 3 \text{ m}$</td>
<td>$\varepsilon_g = 11241.6 \left( \frac{\rho_g^{0.174} u_g^{0.553} \Gamma^{0.053}}{\mu_i^{0.025} \sigma_i^{0.105} \mu_i^{1.59}} \right) \left( \frac{P}{P_p} \right)^{0.203} \left( \frac{d_c}{d_c + 1} \right)^{-0.117} \times \exp \left[ -1.2 \times 10^{-3} C_s - 0.4 \times 10^{-6} C_s^2 - 4339d_p + 0.434X_W \right]$</td>
<td>Sehabiague et al. [81]</td>
</tr>
</tbody>
</table>
Table A-6: Bubbles diameter correlations available in the literature

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{b,o} = 81.18 \frac{\sigma_l}{P_o g}$</td>
<td>Eversole et al. [459]</td>
</tr>
<tr>
<td>$d_b = \left(1.722 \frac{Q^{6/5} 6}{g^{3/5} \pi}\right)^{1/3}$</td>
<td>Van Krevelen and Hoftijzer [460]</td>
</tr>
<tr>
<td>$d_{b,o} = 1.82 \frac{d_o \sigma_l^{0.25}}{g d_o^2 \rho_l}$</td>
<td>Benzing and Mayers [371]</td>
</tr>
<tr>
<td>$d_{b,o} = 0.19d_o^2 Re_b^{0.32}$</td>
<td>Leibson et al. [380, 381]</td>
</tr>
<tr>
<td>$d_b = (l^2 h)^{1/3}$</td>
<td></td>
</tr>
<tr>
<td>$l = \begin{cases} \frac{d_b}{1.147a^{0.176}} \ \frac{d_b}{1.367a^{0.28}} \end{cases}$ &amp; for $2 &lt; Ta &lt; 6$, \text{Nedelchev and Schumpe [461]}</td>
<td></td>
</tr>
<tr>
<td>$h = \begin{cases} 1.3d_b Ta^{-0.352} \ 1.85d_b Ta^{-0.56} \end{cases}$ &amp; for $6 &lt; Ta &lt; 16.5$,</td>
<td></td>
</tr>
<tr>
<td>$Ta = Re_b Mo^{0.23}$</td>
<td></td>
</tr>
<tr>
<td>$Re_b = \frac{d_b u_b \rho_l}{\mu_l}$</td>
<td></td>
</tr>
<tr>
<td>$Mo = \frac{g \mu_l^4}{\rho_l \sigma_l^3}$</td>
<td></td>
</tr>
<tr>
<td><strong>Viscous Liquids:</strong></td>
<td></td>
</tr>
<tr>
<td>$V_b = 1.378 \frac{Q^{6/5}}{g^{3/5}}$</td>
<td>Davidson and Schuler [373]</td>
</tr>
<tr>
<td>$d_b = \left(1.378 \frac{Q^{6/5} 6}{g^{3/5} \pi}\right)^{1/3}$</td>
<td></td>
</tr>
<tr>
<td><strong>Inviscid liquids:</strong></td>
<td></td>
</tr>
<tr>
<td>$d_{b,o} = \frac{32g}{11} \left[\frac{t^2}{4} + \frac{V_o t}{2Q} - \frac{V_o^2}{2Q^2} \ln \left(\frac{Q t + V_o}{V_o}\right)\right]$ &amp;</td>
<td></td>
</tr>
<tr>
<td>$V_o = \frac{\pi d_o^2}{3}$</td>
<td></td>
</tr>
</tbody>
</table>
Table A-6 (continued)

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_b = \left(\frac{4\pi}{2}\right)^{0.25} \left(\frac{15\mu_l Q}{2\rho_l g}\right)^{0.75}$</td>
<td>Kumar and co-workers [378, 385, 462, 463]</td>
</tr>
<tr>
<td>$V_b = 1.09 Q^{6/5} g^{-3/5}$</td>
<td>Wraith [391]</td>
</tr>
<tr>
<td>$V_{b,o} = \frac{\pi d_o \sigma_l}{\Delta \rho g}$</td>
<td>Park et al. [384]</td>
</tr>
<tr>
<td>$V_b = 0.976 \left(\frac{Q^2}{g}\right)^{3/5}$</td>
<td>Acharya et al. [464]</td>
</tr>
<tr>
<td>$d_{b,o} = \left(\frac{3\sigma_l d_o}{\rho_l} + \sqrt{\left(\frac{3\sigma_l d_o}{\rho_l}\right)^2 + \frac{K d_o}{g}}\right)^{1/3}$</td>
<td>Rabiger and Vogelpohl [465]</td>
</tr>
<tr>
<td>$K$: pulsation parameter</td>
<td></td>
</tr>
<tr>
<td>$V_{b,o} = \frac{4\pi \sigma_l d_o}{\rho_l g} + 2 \frac{G^2}{g} \left(\frac{3}{4\pi V_f^2}\right)^{0.33}$</td>
<td>Rice and Lakhani [466]</td>
</tr>
<tr>
<td>$d_{b,o} = \left[\left(\frac{6d_o \sigma_l}{\rho_l g}\right) + \frac{81\eta_l u_b}{\pi g} + \frac{135 u_b^2}{4\pi^2 g}\right]^{0.25}$</td>
<td>Gaddis and Vogelpohl [467]</td>
</tr>
<tr>
<td>$d_b = 6.9 \left(\frac{\sigma_l}{\rho_l}\right)^{0.5} u_g^{0.44}$</td>
<td>Tsuge et al. [386-388, 468]</td>
</tr>
<tr>
<td>$V_b = \frac{\pi d_o \sigma_l}{\Delta \rho g}$</td>
<td></td>
</tr>
<tr>
<td>$d_b = (a^2 b)^{1/3}$</td>
<td>Sada et al. [469]</td>
</tr>
<tr>
<td>$a$: maximum bubble diameter; $b = minimum$ bubble diameter</td>
<td>Wilkinson and van Dierendonck [390]</td>
</tr>
<tr>
<td>$V_{b,o} = \frac{\pi d_o^3}{12}$</td>
<td></td>
</tr>
<tr>
<td>$d_{b,o} = d_o A \frac{W e_l (\rho_l - \rho_g)}{\sqrt{(W e_l - 8)}}$</td>
<td>Pamperin and Rath [383]</td>
</tr>
<tr>
<td>$A = \sqrt{\frac{4}{Re_o}} + \frac{0.124}{\sqrt{Re_o}}$; $Re_o = \frac{2u_b d_o}{\eta_l}$</td>
<td></td>
</tr>
</tbody>
</table>
\begin{table}
\centering
\caption{Table A-6 (continued)}
\begin{tabular}{|c|c|}
\hline
Correlation & Reference \\
\hline
\( \frac{d_{b,o}}{Bd_o} = \left[ \frac{5}{Bd_o^{1.08}} + \frac{9.26Fr_t^{0.36}}{Ga_t^{0.39}} + 2.14Fr_t^{0.51} \right]^{0.33} \) & Jamialahmedi et al. [377] \\
\( Bd_o = 4 \rho_1 g d_b^2 \sigma_l \) & \\
\hline
\( d_b = 26d_c \left( \frac{d_c^2 g \rho_l}{\sigma_l} \right)^{-0.5} \left( \frac{g d_c^3}{\eta_l^2} \right)^{-0.12} \left( \frac{u_g}{\sqrt{g d_c}} \right)^{-0.12} \) & Akita and Yoshida [190] \\
\hline
\( d_{b,o} = \left[ \left( \frac{6d_o \sigma_l}{\rho_l g} \right)^{4/3} + \left( \frac{81Q \eta_l}{\pi g} \right) + \left( \frac{135Q^2}{4\pi^2 g} \right)^{4/5} \right]^{1/4} \) & Gaddis and Vogelpohl [467] \\
\hline
\( d_b = \left( 0.976 \frac{Q^{6/5}}{g^{3/5} \pi} \right)^{1/3} \) & Kumar and Kuloor [462] \\
\hline
\( d_b = 0.725 \frac{\sigma_l^{3/5}}{\rho_l^{1/5} \rho^{2/5}} \) & Hinze [470] \\
\hline
\( d_b = We_c^{3/5} \frac{\sigma_l^{3/5}}{\rho_g^{1/5} \rho^{2/5}} \left( \frac{\mu_l}{\mu_g} \right)^{0.1} \) & Lin et al. [174] \\
\( We_c = \frac{\rho_l \bar{u}_{rms} d_b}{\sigma_l} \); \( \bar{u}_{rms} = \left( \frac{p d_b}{\rho_l} \right)^{2/3} \) & \\
\hline
\( d_b = 1.817 \frac{2\sigma_l}{u_b^{2.3} \rho_g \rho_l^{2}} \) & Levich [471] \\
\hline
\( d_b = k \sqrt{\frac{\sigma_l}{g \rho_g}} \) & Luo et al. [472] \\
\( k = \begin{cases} 
2.53 & \text{Liquid} \\
3.27 & \text{Slurry} 
\end{cases} \) & \\
\hline
\( d_b = \frac{2 \pi^{0.5}}{\sqrt{g \Delta \rho}} \left( \frac{\rho_l}{\rho_g} \right)^{0.5} \frac{u_r^2}{2 \sqrt{\sigma_l g \Delta \rho}} + \left( 1 + \frac{\left( \frac{\rho_l \rho_g u_r^2}{2} \right)^{2}}{\left( \rho_l + \rho_g \right) \sigma_l g \Delta \rho} \right)^{0.5} \) & Wilkinson and van Dierendonck [90] \\
\( u_r: \text{relative velocity between the gas and liquid phase at the interface} \) & \\
\hline
\end{tabular}
\end{table}
Table A-7: Bubbles rise velocity correlations available in the literature

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_b = \frac{g\rho_l d_b^2}{18\mu_l} )</td>
<td>Stokes [473]</td>
</tr>
<tr>
<td>( u_b = 0.35\sqrt{gd_b} )</td>
<td>Dumitrescu [474]</td>
</tr>
<tr>
<td>( u_b = \frac{g\rho_l d_b^2}{18\mu_l} )  ( \text{Re} &lt; 2 )</td>
<td></td>
</tr>
<tr>
<td>( u_b = \frac{0.33g^{0.76}\rho_l^{0.52}r_{b}^{1.28}}{10\mu_l^{0.52}} )  ( 2 &lt; \text{Re} &lt; 4.02 \text{Mo}^{-0.214} )</td>
<td></td>
</tr>
<tr>
<td>( u_b = 1.35 \left( \frac{2\sigma_l G}{d_b \rho_l} \right)^{0.5} )  ( 4.02 \text{Mo}^{-0.214} &lt; \text{Re} &lt; 3.1 \text{Mo}^{-0.25} )</td>
<td>Peebles and Garber [475]</td>
</tr>
<tr>
<td>( u_b = 1.18 \left( \frac{\sigma_l G^2}{\rho_l} \right) )  ( 3.1 \text{Mo}^{-0.25} &lt; \text{Re} )</td>
<td></td>
</tr>
<tr>
<td>( 626 &lt; \rho_l &lt; 1071 \ \frac{kg}{m^3} )</td>
<td></td>
</tr>
<tr>
<td>( 0.016 &lt; \sigma_l &lt; 0.72 \ \frac{N}{m} )</td>
<td></td>
</tr>
<tr>
<td>( 0.22 &lt; \mu_l &lt; 31 \ \text{cP} )</td>
<td></td>
</tr>
<tr>
<td>( u_b = 0.721\sqrt{gd_b} )  ( 782 &lt; \rho_l &lt; 1480 \ \frac{kg}{m^3} )</td>
<td>Haberman and Morton [476]</td>
</tr>
<tr>
<td>( 0.02 &lt; \sigma_l &lt; 0.72 \ \frac{N}{m} )</td>
<td></td>
</tr>
<tr>
<td>( 0.52 &lt; \mu_l &lt; 18000 \ \text{cP} )</td>
<td></td>
</tr>
<tr>
<td>( u_{b\infty} = 1.53 \left[ \frac{g\Delta\rho \sigma_l}{\rho_l^2} \right]^{0.25} )  ( \text{Moderately distorted ellipsoids} )</td>
<td>Harmathy [477]</td>
</tr>
<tr>
<td>( u_{b\infty} = \lambda_i \sqrt{\frac{g\Delta\rho d_b}{\rho_l}} )  ( \text{Cylindrical Slugs} )</td>
<td></td>
</tr>
<tr>
<td>( u_b = K \left( \frac{0.5d_b^3}{6} \right)^{m} )  ( m = 0.167(1 + 0.34\text{Mo}^{0.24}) )</td>
<td>Angelino [478]</td>
</tr>
<tr>
<td>( K = 25/(1 + 0.33\text{Mo}^{0.29}) )</td>
<td></td>
</tr>
<tr>
<td>( u_b = \sqrt{\frac{2\sigma_l}{d_b \rho_l} + 0.5gd_b} )  ( 782 &lt; \rho_l &lt; 1480 \ \frac{kg}{m^3} )</td>
<td>Mendelson [479]</td>
</tr>
<tr>
<td>( 0.02 &lt; \sigma_l &lt; 0.72 \ \frac{N}{m} )</td>
<td></td>
</tr>
<tr>
<td>( 0.52 &lt; \mu_l &lt; 18000 \ \text{cP} )</td>
<td></td>
</tr>
<tr>
<td>( u_b = \left( \frac{\mu_l}{\rho_l d_{b,c}} \right)^{0.149} (J - 0.857) )  ( J = \left{ \begin{array}{ll} 0.94H^{0.757} &amp; (2 &lt; H \leq 59.3) \ 3.24H^{0.441} &amp; (H &gt; 59.3) \end{array} \right. )</td>
<td>Grace et al. [480]</td>
</tr>
<tr>
<td>( H = \frac{4}{3}E\text{Mo}^{-0.149} \left( \frac{\mu_l}{\mu_w} \right)^{-0.14} )</td>
<td></td>
</tr>
<tr>
<td>( u_b = \sqrt{\frac{3\sigma_l}{d_b \rho_l} + \frac{gd_b \Delta\rho}{\rho_l}} )  ( 782 &lt; \rho_l &lt; 1480 \ \frac{kg}{m^3} )</td>
<td>Lehrer [481]</td>
</tr>
<tr>
<td>( 0.02 &lt; \sigma_l &lt; 0.72 \ \frac{N}{m} )</td>
<td></td>
</tr>
<tr>
<td>( 0.52 &lt; \mu_l &lt; 18000 \ \text{cP} )</td>
<td></td>
</tr>
</tbody>
</table>
Table A-7 (continued)

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[u_b = \frac{\mu_i}{\rho_l d_p} M^{-0.149}(J - 0.857)]</td>
<td>Clift et al. [171]</td>
</tr>
<tr>
<td>[M = \frac{g \mu_i^2 (\rho_l - \rho_g)}{\rho_l^2 \sigma_i^2}]</td>
<td></td>
</tr>
<tr>
<td>[J = \begin{cases} 0.94 H^{0.747} &amp; \text{for } 2 &lt; H \leq 59.3 \ 3.42 H^{0.441} &amp; \text{for } H &gt; 59.3 \end{cases}]</td>
<td></td>
</tr>
<tr>
<td>[H = \frac{4}{3} E \delta M^{-0.149} \left( \frac{\mu_L}{\mu_{water}} \right)^{-0.14}]</td>
<td></td>
</tr>
<tr>
<td>[M &lt; 10^{-3}, \quad E \delta &lt; 40, \quad Re &gt; 0.1]</td>
<td></td>
</tr>
<tr>
<td>[u_b = 1.3 (g d_b)^{0.5}]</td>
<td>Fukuma et al. [482]</td>
</tr>
<tr>
<td>[u_b = 0.361 (1 + 4.89/E \delta)^{0.25}]</td>
<td>Nickens et al. [483]</td>
</tr>
<tr>
<td>[u_b \left( \frac{\rho_l}{g \sigma_i} \right)^{0.25} = \left( \frac{Mo^{-0.25}}{K_b} \left( \frac{\rho_l - \rho_g}{\rho_l} \right)^{1.25} \left( \frac{g \rho_l}{d_b \sigma_i} \right)^{-n} \right.]</td>
<td>Fan and Tsuchiya [135]</td>
</tr>
<tr>
<td>[\left. + \left( \frac{2 c}{d_b} \left( \frac{g \rho_l}{\sigma_i} \right)^{-0.5} \left( \frac{\rho_l - \rho_g}{2 \rho_l} d_b \left( \frac{g \rho_l}{\sigma_i} \right)^{0.5} \right)^{-0.5 n} \right)^{-\frac{1}{n}} \right}]</td>
<td></td>
</tr>
<tr>
<td>[n = 0.8 \text{ (contaminated liquid)}, 1.6 \text{ (pure liquid)}]</td>
<td></td>
</tr>
<tr>
<td>[c = 1.2 \text{ (monocomponent liquid)}, 1.4 \text{ (multicomponent liquid)}]</td>
<td></td>
</tr>
<tr>
<td>[K_p = \max(K_{b,0}, Mo^{-0.038}, 12)]</td>
<td></td>
</tr>
<tr>
<td>[K_{b,0} = 14.7 \text{ (aqueous solution)}, 10.2 \text{ (organic)}]</td>
<td></td>
</tr>
<tr>
<td>[u_b = \frac{g d_b^2 (\rho_l - \rho_g)}{18 \mu_l} \left( \frac{3 \mu_u + 3 \mu_g}{2 \mu_u + 3 \mu_g} \right) ; u_{b,wav} = \left( \frac{2 \sigma}{d_b (\rho_l + \rho_g)} + \frac{g d_b}{2} \right)^{0.5}]</td>
<td>Jamialahmedi et al. [194]</td>
</tr>
<tr>
<td>[u_b = 1.16 \left[ \frac{d_b g^{0.5} \rho_l^3 M \gamma_{0.23 b}^{0.5}}{\mu_l^{0.5} C_{0.5}^{0.5}} \right]^{1/(1-b')} \right)^{1/(1-b')} ]</td>
<td>Karamanev [484]</td>
</tr>
<tr>
<td>[C_D = 24 (1 + 0.173 Re^{0.65}) Re + 0.143/(1 + 16300 Re^{-1.089})]</td>
<td></td>
</tr>
<tr>
<td>[u_b = \frac{g (\rho_l - \rho_g) d_b}{2 \rho_l} + \frac{2 c \sigma_i}{d_b \rho_l} \right)^{0.5}]</td>
<td>Maneri [485]</td>
</tr>
<tr>
<td>[c = 0.449 \frac{\mu_{l,0.128}}{\mu_l^{0.019}} \frac{\sigma_i^{0.083}}{\sigma_i^{0.083}}]</td>
<td></td>
</tr>
<tr>
<td>[1301 \leq \rho_l (kg/m^3) \leq 2927]</td>
<td></td>
</tr>
<tr>
<td>[4.23 \leq \mu_l (10^{-4} Pa \cdot s) \leq 83.6]</td>
<td></td>
</tr>
<tr>
<td>[0.024 \leq \sigma_i (N/m) \leq 0.049]</td>
<td></td>
</tr>
<tr>
<td>[u_b = d_B \left[ \frac{(g \mu_l)}{\rho_l} \left( \frac{4 d' M q^{0.46 b'}}{2.85^{0.5 - 2 b'}} \right) \left( \frac{\rho_l^2 g}{\mu_l^2} \right) \right]^{(2 - 2 b')/(2 b' + 1)}]</td>
<td>Nguyen [486]</td>
</tr>
</tbody>
</table>
### Table A-7 (continued)

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$u_{b\text{-large}} = 0.71(gd_b)^{0.5}(DF)(SF)(AF)$</td>
<td>Krishna et al. [487]</td>
</tr>
<tr>
<td>$SF: \begin{cases} 1.13 e^{(-\frac{d_b}{d_c})} &amp; \text{for } 0.125 &lt; \frac{d_b}{d_c} &lt; 0.6 \ 0.496 \left(\frac{d_b}{d_c}\right)^{-0.5} &amp; \text{for } \frac{d_b}{d_c} &gt; 0.6 \end{cases}$</td>
<td></td>
</tr>
<tr>
<td>$AF = \alpha + \beta(u_g - u_{g-df})$: $DF = \left(\frac{\rho_g}{\rho_l}\right)^{0.5}$</td>
<td></td>
</tr>
<tr>
<td>$u_b \left(\frac{\rho_l}{g\sigma_i}\right)^{0.25} = \left{ \left(\frac{Mo^{-0.25}}{K_b} \left(\frac{\rho_l - \rho_g}{\rho_l}\right)^{1.25} g\rho_l d_b^2 \frac{\sigma_i}{\sigma_l}\right)^{\frac{1}{n}} + \left(\frac{2c (g\rho_l)^{-0.5}}{d_b^2 \frac{\sigma_i}{\sigma_l}} + \frac{(\rho_l - \rho_g)g}{2\rho_l} \left(\frac{g\rho_l}{\sigma_l}\right)^{0.5}\right)^{-0.5n} \right}^{-\frac{1}{n}}$</td>
<td>Luo et al. [472]</td>
</tr>
<tr>
<td>$n = 0.8$ (contaminated liquid), $1.6$ (pure liquid)</td>
<td></td>
</tr>
<tr>
<td>$c = 1.2$ (monocomponent liquid), $1.4$ (multicomponent liquid)</td>
<td></td>
</tr>
<tr>
<td>$K_b = \max(K_{b,0}, Mo^{-0.030}, 12)$</td>
<td></td>
</tr>
<tr>
<td>$K_{b,0} = 14.7$ (aqueous solution), $10.2$ (organic)</td>
<td></td>
</tr>
<tr>
<td>$Mo = g \left(\frac{(\rho_l - \rho_g)\mu_l^3}{\rho_l^2 \sigma_l^3}\right)$</td>
<td></td>
</tr>
<tr>
<td>$u_b = \alpha \left[\frac{u_g (1 - \varepsilon_g)^{\frac{1}{2}}}{\varepsilon_g}\right]$</td>
<td>Yang et al. [488]</td>
</tr>
<tr>
<td>$u_b = \sqrt{\frac{2\sigma_l}{\rho_l d_b} + \frac{gd_b}{2}}$</td>
<td>Nedeltchev and Schumpe [461]</td>
</tr>
<tr>
<td>$u_B = \sqrt{\frac{\rho_l^0.33 \sigma_l^0.33}{(d_B)^{2/3} \rho_l^{2/3}}}$</td>
<td>Rodrigue [489]</td>
</tr>
<tr>
<td>$722 &lt; \rho_l &lt; 1380 \frac{kg}{m^3}$</td>
<td></td>
</tr>
<tr>
<td>$0.015 &lt; \sigma_l &lt; 0.091 \frac{N}{m}$</td>
<td></td>
</tr>
<tr>
<td>$0.0022 &lt; \mu_l &lt; 18 \frac{Pa \cdot s}{s}$</td>
<td></td>
</tr>
<tr>
<td>$u_b = 1.95d_c^{1/6}(gd_b)^{0.5}$ for $d_b \geq 0.005$ m</td>
<td>De Swart and Krishna [153]</td>
</tr>
</tbody>
</table>
Table A-8: Gas-Liquid mass transfer correlations applicable to SBCRs

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>135 data sets of 7 different groups</td>
<td></td>
<td>$k_L = 0.00163 u_g^{0.21} \left( \frac{h_C}{d_C} \right)^{-0.261} \left( \frac{\rho_l \sigma_l^3}{g \mu_l^4} \right)^{0.119}$</td>
<td>Gestrich et al. [490]</td>
</tr>
<tr>
<td>N$_2$ – Water, Glycerol, Glycol, BaCl$_2$, Na$_2$SO$_4$ – Glass, Bronze</td>
<td>$P_{atm}$, $u_g &lt; 0.30 m/s$, $C_S$: 0 – 200 kg/m$^3$, $d_C$: 0.1 – 0.3 m, $h_C$: 2.3 – 3 m</td>
<td>$k_L a = \left( \frac{\rho_l d_{AB}}{\sigma_l} \right)^{2.11} \left( \frac{\mu_l}{\rho_l d_{AB}} \right)^{0.5} \left( \frac{g \mu_l^4}{\rho_l \sigma_l^3} \right)^{-0.159} \frac{C_S^{1.18}}{\hat{g}}$</td>
<td>Koide et al. [107]</td>
</tr>
<tr>
<td>N$_2$, O$_2$ – Water, Na$_2$SO$_4$/Activated Carbon – Diatomite, Al$_2$O$_3$</td>
<td>$P_{atm}$, $T_{atm}$, $u_g &lt; 0.07 m/s$, $C_V$: 0.51 – 15.22 vol%, $d_p$: 5.4, 6.6, 8.1 mm, $d_C$: 0.095 m, $h_C$: 0.85 m</td>
<td>$k_L a = K u_g^{0.82} \mu_{eff}^{0.39}$ [ K = { \begin{align*} 0.063 &amp; \text{ for Salt Solutions} \ 0.042 &amp; \text{ for Salt free Systems} \end{align*} ] [ \mu_{eff} = k (2800 u_g)^{n-1} ] [ k \text{ is the fluid consistency index} = 1.97; n: empirical constant 1 [ \geq n \geq 0.18 ]</td>
<td>Schumpe et al. [453]</td>
</tr>
<tr>
<td>Air – Water – 10 different solid particles</td>
<td>$u_g$: 0.01 – 0.08 m/s, $C_V$: 0 – 20 vol%, $d_p$: 0.11 – 2.8 mm, $P_{atm}$, $\rho_g$: 1020 – 2780 kg/m$^3$, PfP, SP Sparger</td>
<td>$k_L a \left( \frac{v_{sl}}{g u_g} \right)^{1/2} = K \left( \frac{u_g}{v_{sl} u_g} \right)^{B_1} \times \left( \frac{v_{sl}}{v_{eff,rad}} \right)^{B_2} \times \left( \frac{C_S}{C_{SO}} \right)^{B_3}$</td>
<td>Sauer and Hempel [491]</td>
</tr>
</tbody>
</table>

The values of constant $K$ and of exponents $B_1$-$B_3$ are as follows:

- **Sieve plate**
  - $K = 0.231 \times 10^4$
  - $B_1 = 0.305$
  - $B_2 = -0.0746$
  - $B_3 = -0.0127$

- **Perforated plate**
  - $K = 0.197 \times 10^4$
  - $B_1 = 0.385$
  - $B_2 = -0.0712$
  - $B_3 = -0.0114$
<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air – Water – Glass beads</td>
<td>$d_p: 0.056 - 2.8 \text{ mm}$ $u_g: up to 0.1 \text{ ms}^{-1}$ $C_V: 9 - 40 \text{ vol%}$</td>
<td>$k_l d_p^2 = 4.5 \times 10^{-4} Sc^{0.5} Ga^{0.8} Bo^{-0.2}$</td>
<td>Fukuma et al. [492]</td>
</tr>
<tr>
<td>Air, N₂ – Water, Alcohols, Calcium alginate, Polystyrene</td>
<td>$P_{atm}$ $u_g$ up to 0.15$\text{ms}^{-1}$ $C_V$ up to 20 vol% $d_C: 0.14, 0.218, 0.3 \text{ m}$ $h_C: 1.5 \text{ m}$</td>
<td>$k_l \alpha = 12.9 Sc^{0.5} Mo^{-0.159} Bo^{-0.184} \varepsilon_3^{1.3} \left( \frac{\rho_l D_{AB}}{\sigma_l} \right) \times \left( 0.47 + 0.53 \exp \left( -41.4 \frac{\Pi_\infty k_l}{\mu_l u_p} Re_B^{-0.5} \right) \right) \left( 1 + 0.62 C_V \right)^{-1}$</td>
<td>Salvacion et al. [203]</td>
</tr>
<tr>
<td>O₂, CO₂ – Glycol, Water, Brine, Aqueous Polyacrylamide</td>
<td>Sieve and Sintered plate</td>
<td>$k_l = \alpha \left( \frac{\rho_l - \rho_g}{\rho_l^2} \right) \frac{1}{\mu_l g} \left( \frac{\mu_l}{\rho_l D_{AB}} \right)^{2/3}$ $\alpha = \begin{cases} 0.31 &amp; \text{for } d_p &lt; 1.0 \text{ mm} \ 0.0031 &amp; \text{for } 1.0 &lt; d_p &lt; 2.5 \text{ mm} \ 0.0042 &amp; \text{for } d_p &gt; 2.5 \text{ mm} \end{cases}$</td>
<td>Calderbank et al. [493]</td>
</tr>
<tr>
<td>CO₂ – NaHCO₃, Na₂CO₃ surfactants</td>
<td>$d_c = 0.113 \text{ m}$ $h_c = 1.086 \text{ m}$ $u_g &lt; 0.002 \text{ ms}^{-1}$</td>
<td>$k_l = K_4 u_g^{0.5} \sigma_l^{1.35}$ $K_4$ is a function of the bubble plate size</td>
<td>Vazquez et al. [494]</td>
</tr>
<tr>
<td>He, N₂, SF₆, Air – 0.8 M Na₂SO₄ – Xanthan gum, Diatomite, Alumina suspensions</td>
<td>$P: 0.1 - 1 \text{ MPa}$ $u_g: 0.01 - 0.08 \text{ ms}^{-1}$ $C_V: Upto 18% \text{ vol}$ $d_p: 7, 22 \mu m$ $d_c: 0.115 \text{ m}$ $h_c: 1.37 \text{ m}$</td>
<td>$k_l = u_g^{0.9} \mu_{eff}^{-0.55} \rho_g^{0.46}$ $K = \begin{cases} 0.063 &amp; \text{for Salt Solutions} \ 0.042 &amp; \text{for Salt free Systems} \end{cases}$ $\mu_{eff} = k \left( 2800 u_g \right)^{n-1}$ $k$ is the fluid consistency index = 1.97; $n$: empirical constant $1 \geq n \geq 0.18$</td>
<td>Dewes et al. [199]</td>
</tr>
<tr>
<td>System</td>
<td>Conditions</td>
<td>Correlation</td>
<td>Reference</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
</tbody>
</table>
| N₂/Fe(CN) - NaOH, CMC, HNaCO₃, Na₂CO₃/glass, diatomite, silicon carbide, alumina | \( u_g : 0.007 - 0.09 \text{ ms}^{-1} \)  
\( C_V : 1.3 - 12.4 \text{ vol\%} \)  
\( d_p : 44 - 105 \mu m \)  
\( \rho_s : 2448 - 3965 \text{ kg/m}^3 \)  
\( \rho_l : 1026 - 1121 \text{ kg/m}^3 \)  
\( \mu_l : 0.99 - 6.27 \text{ mPa} \cdot \text{s} \)  
\( d_C : 0.05 \text{ m} \)  
\( h_C : 0.75 \text{ m} \) | \( \frac{k_L}{u_g} = 0.103(ReFrSc^2)^{0.265} \) | Neme et al. [101] |
| Air – Water – Lexan, PS, Glass | \( u_g : 0.0025 - 0.05 \text{ ms}^{-1} \)  
\( \rho_s : 1170 - 2460 \text{ kg/m}^3 \)  
\( C_V : 0.9 - 2.5 \text{ vol\%} \)  
\( d_p : 2.3 - 3 \text{ mm} \)  
\( d_C : 0.06 \text{ m} \)  
\( h_C/d_C : 22 - 30.2 \) | \( k_La = 4.49u_g^{0.338}C_s^{0.595} \left( 1 - \frac{\rho_l}{\rho_s} \right)^{0.337} \) | Guo et al. [495] |
| Air – Water - Nickel | \( u_g : 0.02 - 0.04 \text{ m/s} \)  
\( \rho_s : 8900 \text{ kg/m}^3 \)  
\( d_p : 177 - 210 \mu m \)  
\( C_V : 5.7 \text{ vol\%} \)  
\( d_C : 0.05 \text{ m} \)  
\( h_C : 0.5 \text{ m} \) | \( k_La = 0.4u_g^{0.625}u_l^{0.26} \times \exp[1.477 \cdot 10^{-5}h_C]\) | Chen et al. [456] |
| H₂/CO – Paraffin oil – Silica gel | \( T: 293 - 523 \text{ K} \)  
\( P: 1 - 5 \text{ MPa} \)  
\( d_p : 134 \mu m \)  
\( C_V : 5 - 20 \text{ vol\%} \)  
\( d_C : 0.037 \text{ m} \)  
\( h_C : 0.48 \text{ m} \) | \( \frac{k_Ld_{32}}{D_{AB}} = 1.546 \times 10^{-2}Eu^{0.052}Re^{0.076}Sc^{-0.231} \)  
\( CO: \frac{k_Ld_{32}}{D_{AB}} = 8.748 \times 10^{-2}Eu^{-0.012}Re^{0.024}Sc^{-0.133} \) | Yang et al. [496] |
<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
</table>
| H₂, CO, N₂ CH₄, Isopar-M. Hexanes – Glass beads, Iron Oxide | $u_g: 0.0035 - 0.574 \text{ m/s}$  
$C_S: 0 - 36 \text{ vol.}\%$  
$T: 275 - 538 \text{ K}$  
$P: 0.1 - 15 \text{ MPa}$  
$\rho_S: 700 - 4000 \text{ kg/m}^3$  
$d_p: 5 - 300 \mu\text{m}$  
$\rho_l: 633.4 - 1583 \text{ kg/m}^3$  
$\mu: 0.189 - 398.8 \text{ mPa} \cdot \text{s}$  
$\sigma_i: 8.4 - 75 \text{ mN/m}$  
$d_C: 0.0382 - 5.5 \text{ m}$ | $\frac{k_L}{(1 - \varepsilon_g)} = 6.14 \times 10^4 \cdot \frac{\rho_l^{0.26} \mu_l^{0.12} \varepsilon_g^{1.21} D_{AB}^{0.5}}{\sigma_i^{0.52} \rho_B^{0.06} u_g^{0.12} d_p^{0.05} T^{0.68} \gamma^{0.11}} \left( \frac{d_C}{d_C + 1} \right)^{0.4}$ | Lemoine et al. [179] |
| Semi-Theoretical approach based on Kolmogorov theory of isotropic turbulence | - | $k_L a = f_c \sqrt{\frac{4 D_{AB} R_{sf} f_B S_B}{\pi S_B A_c u_b}}$  
$R_{sf} = \pi \sqrt{\frac{l^2 + h^2}{2} - \frac{(l_b - h_b)^2}{8} u_b}$  
$S_B = \pi \frac{l^2}{2} \left[ 1 + \left( \frac{h}{l} \right)^2 \frac{1}{2e} \ln \left( \frac{1 + e}{1 - e} \right) \right]$  
$e = \sqrt{1 - \left( \frac{h}{l} \right)^2}$ | Nedeltchev and Schumpe [461] |

\[ l = \begin{cases} 
\frac{d_b}{1.14 T_a^{-0.176}} & \text{for } 2 < T_a < 6; \\
\frac{d_b}{1.36 T_a^{-0.28}} & \text{for } 6 < T_a < 16.5 
\end{cases} \]

\[ h = \begin{cases} 
1.3 d_b T_a^{-0.352} & \text{for } 2 < T_a < 6; \\
1.85 d_b T_a^{-0.56} & \text{for } 6 < T_a < 16.5 
\end{cases} \]

\[ T_a = R e_b M o^{0.23}; R e_b = \frac{d_b u_b \rho_l}{\mu_l}; M o = \frac{g \mu_l^4}{\rho_l \sigma_i^3} \]
Table A-8 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Conditions</th>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
</table>
| H₂, CO, N₂ CH₄, Isopar-M. Hexanes – Glass beads, Iron Oxide | \( u_g: 0.0035 – 0.574 \text{ m/s} \)  
\( C_V: 0 – 36 \text{ vol.\%} \)  
\( T: 275 – 538 K \)  
\( P: 0.1 – 15 \text{ MPa} \)  
\( \rho_s: 700 – 4000 \text{ kg/m}^3 \)  
\( d_p: 5 – 300 \mu\text{m} \)  
\( \rho_l: 633.4 – 1583 \text{ kg/m}^3 \)  
\( \mu_l: 0.189 – 398.8 \text{ mPa} \cdot \text{s} \)  
\( \sigma_l: 8.4 – 75 \text{ mN/m} \)  
\( d_C: 0.0382 – 5.5 \text{ m} \) | \( f_c = 0.124E^{0.94} \left( \frac{\rho_g}{\rho_{g_{ref}}} \right)^{0.15} = 0.124 \left( \frac{g(\rho_l – \rho_g)d_p^2}{\sigma_l} \right)^{0.94} \left( \frac{\rho_g}{1.2} \right)^{0.15} \)  
\( f_B = \frac{u_gA_c}{V_b} \);  
\( V_b = \frac{\pi d_p^3}{6} = \frac{4}{3} \pi \left( \frac{l}{2} \right)^2 \frac{h}{2} \) | Behkish et al. [9] |
| He, N₂ – Paraffins mixture, C₁₂-C₁₃, Light F-T Cut, Heavy F-T Cut – Alumina, Puralox Alumina, Iron oxide | \( u_g: 0.14 – 0.26 \text{ m/s} \)  
\( C_V: 0 – 20 \text{ vol.\%} \)  
\( T: 330 – 530 K \)  
\( P: 8 – 30 \text{ MPa} \)  
\( \rho_s: 3218 – 4000 \text{ kg/m}^3 \)  
\( d_p: 1.5 – 140 \mu\text{m} \)  
\( \rho_l: 631.3 – 779.5 \text{ kg/m}^3 \)  
\( \mu_l: 0.27 – 9.96 \text{ mPa} \cdot \text{s} \)  
\( \sigma_l: 13 – 27 \text{ mN/m} \)  
\( d_C: 0.3 \text{ m}; \ h_C: 3 \text{ m} \) | \( k_La = 0.185S_e^{0.6} \left( \frac{\rho_l\eta_l}{M_w_l} \right)^{-2.84} \left( \rho_g u_g \right)^{0.49} \times \exp\left[ -2.66C_V \right] \) | Sehabiague et al. [81] |
Table A-9: Heat transfer correlations applicable to SBCRs

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Nu_{(d_R)} = 34.7Re_{G,d_R}^{0.22}$ for $Re_{G,d_R} &gt; 150$</td>
<td>Köbel et al. [497]</td>
</tr>
<tr>
<td>$Nu_{(d_R)} = 22.4Re_{G,d_R}^{0.36}$ for $Re_{G,d_R} &gt; 150$</td>
<td></td>
</tr>
<tr>
<td>$St_{Sus} = 0.124 \left[ \left( Re_{G}Fr_{G}Pr_{Sus}^{2.5} \right)^{1/3} \right]^{-0.66}$</td>
<td>Köbel and Langemann [498]</td>
</tr>
<tr>
<td>$\alpha_W = 8850u_G^{0.22}$</td>
<td>Fair et al. [118]</td>
</tr>
<tr>
<td>$St = 0.1 \left[ \left( Re_{G}Fr_{G}Pr_{L}^{2} \right)^{1/3} \right]^{-2/3}$</td>
<td>Kast [499]</td>
</tr>
<tr>
<td>$St = 0.11 \left[ \left( Re_{G}Fr_{G}Pr_{L}^{2.48} \right)^{1/3} \right]^{-0.69}$</td>
<td>Burkel [500]</td>
</tr>
<tr>
<td>$St = 0.11 \times 1.25 \left[ \left( Re_{G}Fr_{G}Pr_{L}^{2.5} \right)^{1/3} \right]^{-0.667}$</td>
<td>Shaykhutdinov et al. [501]</td>
</tr>
<tr>
<td>$St = 0.418(Re_{G}Fr_{G}Pr_{L}^{2})^{-1/3}u_G^{1/4} \left( \frac{\rho_l - \rho_g}{\rho_l} \right)^{1/3} \left( \frac{\eta_L}{\eta_{L,W}} \right)^{-0.05}$</td>
<td>Nishikawa et al. [502]</td>
</tr>
<tr>
<td>$St = 0.3(Re_{G}Fr_{G}Pr_{L}^{2})^{-1/3}u_G^{1/4} \left( \frac{\rho_l - \rho_g}{\rho_l} \right)^{1/3} \left( \frac{\eta_L}{\eta_{L,W}} \right)^{-0.05}$</td>
<td></td>
</tr>
<tr>
<td>$St = 1.2(Re_{G}Fr_{G}Pr_{L}^{2})^{-1/3}(u_Gu_L)^{1/4} \left( \frac{\rho_l - \rho_g}{\rho_l} \right)^{1/3} \left( \frac{\eta_L}{\eta_{L,W}} \right)^{-0.05}$</td>
<td></td>
</tr>
<tr>
<td>$h = 1977u_G^{0.079}u_g^{0.059}d_p^{0.106}$</td>
<td>Baker et al. [503]</td>
</tr>
<tr>
<td>$St = 0.136 \left[ \left( Re_{G}Fr_{G}Pr_{L}^{1.94} \right)^{1/3} \right]^{-0.81}$</td>
<td>Louisi [504]</td>
</tr>
<tr>
<td>$St = 0.1 \left[ \left( Re_{G}Fr_{G}Pr_{L}^{1.94} \right)^{1/3} \right]^{-0.75}$</td>
<td>Deckwer et al. [367, 505]</td>
</tr>
<tr>
<td>$\frac{hd_G}{k_l} = 0.4 \left( \frac{d_G}{\eta_l} \right)^{2} \left( \frac{\mu_l}{\mu_{l,w}} \right) \left( \frac{C_p\mu_l}{k_l} \right)^{1/3}$</td>
<td>Joshi and Sharma [506]</td>
</tr>
<tr>
<td>$v_c = 1.31 \left[ gd_G(u_G - \varepsilon_Gv_{b,ao}) \right]^{1/3}$</td>
<td></td>
</tr>
<tr>
<td>$Nu' = 0.044(Re'Pr)^{0.78} + 2.0Fr_{G}^{0.17}$</td>
<td>Kato et al. [507]</td>
</tr>
</tbody>
</table>
Table A-9 (continued)

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Nu' = \frac{h d_p \varepsilon_l}{K_l (1 - \varepsilon_l)}$, $Re' = \frac{\rho_i d_p u_l \varepsilon_l}{\mu_l (1 - \varepsilon_l)}$</td>
<td></td>
</tr>
<tr>
<td>$Pr = \frac{\mu_i C p_l}{K_l}$, $Fr_g = \frac{u_g^2}{g d_p}$</td>
<td></td>
</tr>
<tr>
<td>$\frac{hl_B}{k_L} = 0.18 (1 - \varepsilon_G) \left( \frac{v_c l_B}{\eta_L} \right)^\frac{2}{3} \left( \frac{C_p l \mu_l}{k_l} \right)^\frac{1}{3}$</td>
<td>Zehner [255, 508]</td>
</tr>
<tr>
<td>$v_c = \sqrt{\frac{1}{2.5} \left( \frac{\rho_l - \rho_G}{\rho_l} \right) g d_c u_G}$; $l_B = d_B \frac{3}{2} \sqrt{\frac{\pi}{6 \varepsilon_G}}$</td>
<td></td>
</tr>
<tr>
<td>$St = 0.0371 Re_G^{0.17} Fr_G^{0.32} Pr_L^{-0.46}$</td>
<td>Wendt [509]</td>
</tr>
<tr>
<td>$St = 0.11 \left[ (Re_G Fr_G Pr_L^2)^{1/3} \right]^{-0.75}$</td>
<td>Michael [510]</td>
</tr>
<tr>
<td>$St_{Sus} = 0.12 \left[ (Re_{G,Sus} Fr_G Pr_{Sus}^2)^{1/3} \right]^{-0.75}$</td>
<td></td>
</tr>
<tr>
<td>$St_{m3} = St_{m2} = 0.1234 Re_m^{0.305} Pr_r^{-2/3}$</td>
<td>Chiu and Ziegler [511]</td>
</tr>
<tr>
<td>$h = 2290 u_g^{0.1} u_l^{0.05} \mu_i^{-0.18} d_p^{0.04}$</td>
<td>Kang et al. [512]</td>
</tr>
<tr>
<td>$h_3 = 1 + 0.0413 \left( \frac{u_g}{u_l} \right)^{0.3} \left( \frac{d_p / D_c}{\rho_s - \rho_l} \right)^{0.61}$</td>
<td>Muroyama et al. [513]</td>
</tr>
<tr>
<td>$Nu = 0.762 Re_m^{0.646} Pr_r^{0.638} U_R^{0.266} \phi_s^{-1} \left( \frac{1 - \varepsilon_{l,2}}{\varepsilon_{l,3}} \right)$</td>
<td>Chiu and Ziegler [514]</td>
</tr>
<tr>
<td>$Nu = 0.036 Re_l^{0.81} Pr_l^{0.65}$</td>
<td>Kang et al. [515]</td>
</tr>
<tr>
<td>$h = 2.13 \left( 10^{-4} \right) u_g^{0.338} u_l^{0.54} \rho_i^{1.235} \mu_i^{0.162} K_l^{0.04} C_{p, l}^{1.04} d_l^{0.930} \left( \rho_s - \rho_l \right)^{-0.357}$</td>
<td>Saberian-Broudjenni et al. [516]</td>
</tr>
</tbody>
</table>
Table A-9 (continued)

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ h = 0.0647 \left( \frac{K_l \rho_l C_{p,l}}{\varepsilon_i \mu_l} \right) \left( \frac{(u_l + u_g)(\varepsilon_i \rho_l + \varepsilon_g \rho_g + \varepsilon_r \rho_s) - u_l \rho_l)}{\varepsilon_i \mu_l} \right)^{0.5} \right]^{0.5} ]</td>
<td>Suh et al. [517]</td>
</tr>
<tr>
<td>[ h = 0.0722 \left( \frac{K_l \rho_l C_{p,l}}{\varepsilon_i \mu_l} \right) \left( \frac{(u_l + u_g)(\varepsilon_i \rho_l + \varepsilon_g \rho_g + \varepsilon_r \rho_s) - u_l \rho_l)}{\varepsilon_i \mu_l} \right)^{0.5} \right]^{0.5} ]</td>
<td>Kim et al. [518]</td>
</tr>
<tr>
<td>[ j''<em>H = 0.137 Re</em>{l,g}^{-0.271} ]</td>
<td>Muroyama et al. [519, 520]</td>
</tr>
<tr>
<td>[ NuPr_l^{-1/3} \left( \frac{\mu_b}{\mu_w} \right)^{-0.14} Re_l^{0.2} Re_g^{0.055} = 10.5e^{-3.18(10^{-4})(C_s-22)^2} ]</td>
<td>Hatate et al. [521]</td>
</tr>
<tr>
<td>[ St = 0.12 \left( \left( Re_l Fr_g Pr_l^{2.2} \right)^{1/3} \right)^{-0.83} \left( \frac{D_R}{d_R} \right)^{0.15} \left( \frac{\eta_L}{\eta_{L,W}} \right)^{0.3} ]</td>
<td>Korte [222, 522]</td>
</tr>
<tr>
<td>[ h = 0.1 \left( \frac{K_l \rho_l C_{p,l}}{V_l} \right)^{0.5} + 0.285 \left( \frac{K_l \rho_l C_{p,l} \varepsilon_r^{1/3} (u_l - u_{mf})}{\varphi_s d_{eq}} \right) ]</td>
<td>Magiliotou et al. [523]</td>
</tr>
<tr>
<td>[ h = 0.0685 \left( \frac{(u_l + u_g)}{\varepsilon_i \mu_l} \right) \left( \frac{1 - \left( \frac{V_f}{V_s} \right)}{\left( 1 + \frac{V_f}{V_s} \right)} \right)^{0.5} ]</td>
<td>Kim et al. [524]</td>
</tr>
<tr>
<td>[ 0.02 \leq u_g \leq 0.14 \text{ m/s}, \quad 0.02 \leq u_l \leq 0.09 \text{ m/s} ]</td>
<td></td>
</tr>
<tr>
<td>[ 1 \leq d_p \leq 6 \text{ mm}, \quad 0 \leq \frac{V_f}{V_s} \leq 0.2, \quad 1500 \leq \rho_f \leq 1800 \text{ kg/m}^3 ]</td>
<td></td>
</tr>
<tr>
<td>[ Nu = 0.042 Re_l^{0.72} Pr_l^{0.86} Fr_g^{0.067} ]</td>
<td>Zaidi et al. [525]</td>
</tr>
<tr>
<td>[ 0.01 \leq u_g \leq 0.14 \text{ m/s}, \quad 1.27 \leq u_l \leq 9 \text{ cm/s} ]</td>
<td></td>
</tr>
<tr>
<td>[ 3.7 \leq \mu_l \leq 300 \text{ Pa}, \quad d_p = 3.5 \text{ mm} ]</td>
<td></td>
</tr>
</tbody>
</table>
Table A-9 (continued)

<table>
<thead>
<tr>
<th>Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h = 1800 \eta_g^{0.11} \mu_{eff}^{-0.14} u_i^{1.03(0.65-\varepsilon_t)} \delta_p^{0.58(\varepsilon_t-0.68)}$</td>
<td>Saxena [526]</td>
</tr>
<tr>
<td>$0.01 \leq \eta_g \leq 0.14 \text{ ms}^{-1}, \quad 0.013 \leq u_i \leq 0.09 \text{ ms}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$h_w = 0.0035(k_s \rho_{sl} C_{p,sl})^{0.5} \left( \frac{\rho_{sl} \delta_p}{\mu_{sl}} \right)^{0.47} u_G^{0.25}$</td>
<td></td>
</tr>
<tr>
<td>$Nu' = 5.56(10)^2(Re'Pr)^{0.709} \left( \frac{\rho_s - \rho_l}{\rho_s} \right)^{0.156}$</td>
<td>Kumar et al. [527]</td>
</tr>
<tr>
<td>$Nu' = \frac{h_{av,2} d_p \varepsilon_i}{K_L (1-\varepsilon_i)} \quad Re'Pr = \frac{d_p u_i \rho_l C_p}{K_L (1-\varepsilon_i)}$</td>
<td></td>
</tr>
<tr>
<td>$59.96 \leq Re'Pr \leq 15,472.7 \quad (\text{for } Pr = 5.83) \quad 1.04 \leq \rho_s \leq 2.5 \text{ g cm}^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$St = 0.037 \left( \left[ Re_{sl} Fr_{sl} 1.87 \left( \frac{\varepsilon_g}{1-\varepsilon_g} \right) \right]^{-0.22} \right)$</td>
<td>Yang et al. [488]</td>
</tr>
<tr>
<td>$St = A(ReFr)^B Pr^C \left( \frac{x}{H} \right)^D \left( \frac{r}{R} \right)^E$</td>
<td>Kantarci et al. [528]</td>
</tr>
<tr>
<td>$St = 0.1 \left[ Pr^2 ReFr \frac{\mu_b}{\mu_l g \rho_l u_l} \right]^{0.25}$</td>
<td>Kskrao [529]</td>
</tr>
<tr>
<td>$\frac{h d_c}{k_l} = 0.084 \left( \frac{d_c v_c \rho_l}{\eta_L} \right)^{0.8} \left( \frac{C_{p,sl} H_{sl}}{k_l} \right)^{1/3} \left( \frac{\mu_l}{\mu_{l,w}} \right)^{0.14}$</td>
<td>Jhawar and Prakash [530]</td>
</tr>
<tr>
<td>$v_c = 0.21 \sqrt{g d_c} \left( \frac{u_G^3}{g \eta_l} \right)^{0.125}$</td>
<td></td>
</tr>
<tr>
<td>$h(r) = h \left( 1 - \left( \frac{n-1}{n} \right) \left( \frac{r}{R} \right)^n \right)$</td>
<td></td>
</tr>
<tr>
<td>Where recommended value of $n = 1.4$</td>
<td></td>
</tr>
</tbody>
</table>
Table A-10: Liquid-phase axial dispersion coefficient models

<table>
<thead>
<tr>
<th>Model</th>
<th>Conditions</th>
<th>$u_g$ (cm/s)</th>
<th>$u_l$ (cm/s)</th>
<th>$d_c$ (cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_L = \frac{d_c(2u_g + u_{b\infty})}{Pe_l}$</td>
<td>Air-tap water systems. Concentrated NaCl was injected via 20 holes in a spiral tube, tracer concentrations were measured using a conductivity meter.</td>
<td>45</td>
<td>0.88-2.18</td>
<td>5.08,14, 29</td>
<td>Reith et al. [129]</td>
</tr>
<tr>
<td>$D_L = \begin{cases} 75.4d_c^2u_g^{12} + 17000d_o &amp; 0 \leq u_g \leq 0.07 m/s \ 0.14d_c &amp; u_g \geq 0.1 m/s \end{cases}$</td>
<td>Air-tap water systems. The tracer, 4 N aqueous solution of potassium chloride, was poured instantaneously and uniformly on the liquid surface at the top of column from the tracer injector.</td>
<td>2-26</td>
<td>0</td>
<td>4-16</td>
<td>Ohki and Inoue [531]</td>
</tr>
<tr>
<td>$D_L = \frac{g^{0.5}d_c^{1.5}}{13} \left[ 1 + 6.5 \left( \frac{u_g}{gd_c} \right)^{0.8} \right]$</td>
<td>Used zero order reaction analysis under continuous flow conditions of the liquid.</td>
<td>4-20</td>
<td>0.52</td>
<td>3, 4.5, 6.6, 12.2</td>
<td>Kato and Nishiwaki [268]</td>
</tr>
<tr>
<td>$D_L = 1.23d_c^{1.5}u_g^{0.5}$</td>
<td>Steady-state experiments with large diameter bubble columns.</td>
<td>0.9-8.92</td>
<td>0.6-1.5</td>
<td>40.64, 106.68</td>
<td>Towell and Ackerman [279]</td>
</tr>
<tr>
<td>$D_L = g^{0.5}d_c^{1.5} \left[ 0.06 + 0.55 \left( \frac{u_g}{gd_c} \right)^{0.7} \right]$</td>
<td>Various gas-liquid systems, liquids were water, glycol, methanol and aqueous NaCl, gases were air, oxygen, helium and CO$_2$.</td>
<td>0.53-41.9</td>
<td>3.5</td>
<td>15.2, 30.1, 60</td>
<td>Akita and Yoshida [83]</td>
</tr>
<tr>
<td>$D_L = 0.692d_c^{1.4}u_g^{1/3}$</td>
<td>Air-Water system. The dispersion coefficient was measured using the stationary method using both a dye and a heat source.</td>
<td>0.5-15</td>
<td>0.2-0.8</td>
<td>15</td>
<td>Badura [532]</td>
</tr>
<tr>
<td>$D_L = d_c^{1.25} \left( 0.15 + 0.69u_g^{0.77} \right) \left( \frac{10^{-3}}{\eta_l} \right)^{0.12}$</td>
<td>Impulse injection with KCl solution as tracer. Two bubble columns (19 and 10 cm diameter, 240 and 150 cm high). Air was used for the gas phase, water, aqueous methanol and aqueous cane sugar solutions used for the liquid phase. Temperature range of 12.5 – 20 °C.</td>
<td>4.3-33.8</td>
<td>0</td>
<td>10, 19</td>
<td>Hikita and Kikukawa [533]</td>
</tr>
</tbody>
</table>
Table A-10 (continued)

<table>
<thead>
<tr>
<th>Model</th>
<th>Conditions</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_L = 0.678 d_c^{1.4} u_g^{0.3}$</td>
<td>Different gas distributors. Liquid phases investigated were tap water, aqueous solutions of sodium sulfate and sodium chloride, as well as aqueous solutions of molasses with various concentrations. Gas phase was oxygen. Steady and impulse injection with NaCl solution as tracer.</td>
<td>5-12</td>
<td>0.71</td>
</tr>
<tr>
<td>$D_L = 0.33 d_c^{4/3} (g u_g)^{1/3}$</td>
<td>Semi theoretical model based on isotropic turbulence model for eddy diffusivity, correlated to experimental data from literature.</td>
<td>0.3-45</td>
<td>-</td>
</tr>
<tr>
<td>$D_L = 0.9 d_c^{1.5} \left[ h_c (u_g - \varepsilon_g V_s) \right]^{1/3}$ $V_s = 0.164 \left(1 - \varepsilon_g\right)^{1.39} \left(1 + 2.25 \varepsilon_g^3\right)$</td>
<td></td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>$D_L = 0.33 (V_c + u_t) d_c$ $V_c = 1.31 \left[ g d_c \left( u_g - \frac{\varepsilon_g}{1 - \varepsilon_g} u_t \right.$ $\left. - \varepsilon_g u_b \right) \right]^{1/3}$</td>
<td>Theoretical derivation based on the multiple circulation cell model of a bubble column. The height to diameter ratio of the circulation cell and the column was taken to be 0.8 rather than 1.0.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$D_L = d_c^{1.5} u_g^{0.25} \left(0.291 + \frac{0.341}{1 - 0.5 u_g^{0.5}}\right)^2$</td>
<td>Theoretical derivation.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$D_L = 0.068 (g u_g)^{3/8} d_c^{1.5} u_t^{-1/8}$</td>
<td>Theoretical derivation based on the assumption of the validity of the $Pe = 2$ analogy, developed for fixed bed, to bubble columns.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$D_L \propto D_c^{1.5}$ $D_L \propto u_g^{1/3}$</td>
<td>Steady injection, heat tracer method. Systems investigated were air/water/CO$_2$, N$_2$/n-propanol/CO$_2$ and air/glycol.</td>
<td>0.5-18</td>
<td>0-6</td>
</tr>
<tr>
<td>Model</td>
<td>Conditions</td>
<td>( u_g ) (cm/s)</td>
<td>( u_l ) (cm/s)</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>( D_L = 0.5 \times 0.368 g^{1/3} d_c^{4/3} u_g^{1/3} )</td>
<td>Theoretical calculation based on the multiple circulation cell model of a bubble column.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( D_L = 0.606 d_c \left( \frac{g u_g h_{l0}}{4 + \frac{70}{Re^{0.25}} h_{l0}} \right)^{1/3} )</td>
<td>Theoretical calculation using microscopic and macroscopic balances.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( Re &gt; 1000, \frac{h_{l0}}{d_c} &gt; 3 )</td>
<td>Steady injection method using both heat and NaCl as tracers.</td>
<td>1.5-30</td>
<td>0.2-4.5</td>
</tr>
<tr>
<td>( D_L \propto d_c^{1.4} )</td>
<td>Measured dispersion coefficients in several Newtonian and non-Newtonian liquids (water, MC, CMC-1, CMC-2, and Separan) in a 0.23 m diameter, 1.22 m high bubble column. Solid tracer particles suspended freely in the liquid were used to determine the dispersion coefficient.</td>
<td>0.01-5</td>
<td>-</td>
</tr>
<tr>
<td>( D_L = 0.343 n^{-8/3} g^{1/3} d_c^{4/3} u_g^{1/3} )</td>
<td>Measured dispersion coefficients in several Newtonian and non-Newtonian liquids (water, MC, CMC-1, CMC-2, and Separan) in a 0.23 m diameter, 1.22 m high bubble column. Solid tracer particles suspended freely in the liquid were used to determine the dispersion coefficient.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( D_L = 0.208 u_g^{0.4} (d_c + n_l d_l)^{1.48} A_f^{1.8} u_l^{-0.12} )</td>
<td>Measured dispersion coefficients in several Newtonian and non-Newtonian liquids (water, MC, CMC-1, CMC-2, and Separan) in a 0.23 m diameter, 1.22 m high bubble column. Solid tracer particles suspended freely in the liquid were used to determine the dispersion coefficient.</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>( D_L = 0.632 d_c^{1.25} \frac{u_g}{\varepsilon_g} )</td>
<td>Tap water, aqueous alcohol and CMC solutions of lower concentrations were used as the liquid phase. Dispersion coefficients were measured by detecting tracer gas concentration in the quadrupole mass spectrometer. Helium, argon and carbon dioxide were used as the tracer gases.</td>
<td>1-18</td>
<td>15, 25</td>
</tr>
<tr>
<td>( D_L \propto d_c^n; \frac{n}{n_o} = 1 - 0.11ln \left( \frac{\rho_g}{\rho_g,o} \right) )</td>
<td>Thermal dispersion, water and hydrocarbon as the liquid phase, air as the gas phase.</td>
<td>2-20</td>
<td>0.34-1.0</td>
</tr>
</tbody>
</table>
Table A-11: Liquid-phase radial dispersion coefficient investigations

<table>
<thead>
<tr>
<th>Description</th>
<th>( u_g ) (cm/s)</th>
<th>( u_l ) (cm/s)</th>
<th>( d_c ) (cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-tap water systems. A steady tracer stream was introduced by a single tube at the axis of the column; radial dispersion was obtained by measuring the concentration downstream of the injection point at several distances from the axis of the column. The radial dispersion coefficient was found to be a factor 10 smaller than the axial dispersion coefficient at the same superficial gas velocity.</td>
<td>45</td>
<td>0.88-2.18</td>
<td>14, 29</td>
<td>Reith et al. [129]</td>
</tr>
<tr>
<td>Air-tap water system in a 5-cm co-current air-water bubble column were investigated using the steady-state, point-source tracer injection technique. Radial dispersion coefficients were found to be a factor of 10 times smaller than the axial dispersion coefficient for the same gas and liquid velocities.</td>
<td>1.41 - 6.72</td>
<td>0.748 - 1.275</td>
<td>5</td>
<td>Eissa et al. [128]</td>
</tr>
<tr>
<td>Air-tap water and air/sea water systems were used. Measured radial dispersion in a 2.3 m tall, 0.193 m diameter bubble column bioreactor. For otherwise equal conditions, the radial dispersion coefficient value was typically only about 1% of the axial value</td>
<td>0.062 -5.1</td>
<td>0</td>
<td>19.3</td>
<td>Rubio et al. [131]</td>
</tr>
<tr>
<td>Model</td>
<td>Conditions</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Pe_s = \frac{u_g d_c}{d_p}$</td>
<td>For low Froude number and large particle diameters. Glass beads, $\rho_p = 2520 \text{ kg/m}^3$, $75.5 &lt; d_p &lt; 163 \mu\text{m}$ $C_s = 48 - 202 \text{ kg/m}^3$</td>
<td>Kato and Nishiwaki [268]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{u_g d_c}{d_p} = \left[ 1 + 0.009 \text{Re}_s \left( \frac{u_g}{g d_c} \right)^{-0.8} \right] \frac{13 \left( u_g / \sqrt{g d_c} \right)}{1 + 8 \left( u_g / \sqrt{g d_c} \right)^{0.05}}$</td>
<td>Glass beads, $1 &lt; d_p &lt; 125 \mu\text{m}$, $C_s = 3.1 - 62 \text{ kg/m}^3$</td>
<td>Kojima et al. [108]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{u_g d_c}{d_p} = 10 \left( \frac{u_g}{g d_c} \right)^{0.76}$</td>
<td>Glass beads, $\rho_p = 2420 \text{ kg/m}^3$, $88 &lt; d_p &lt; 105 \mu\text{m}$ $C_s = \text{up to} 420 \text{ kg/m}^3$</td>
<td>O’Dowd et al. [208]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{u_g d_c}{d_p} = 7.7 \left( \frac{Fr_g^6}{Re_g} \right)^{0.098} + 0.019 \text{Re}_p^{1.1}$</td>
<td>Glass beads, $\rho_p = 2420, 3990 \text{ kg/m}^3$, $48.5 &lt; d_p &lt; 164 \mu\text{m}$ $C_s = \text{up to} 420 \text{ kg/m}^3$</td>
<td>Smith and Reuther [538]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A-13: Literature F-T SBCR empirical models [46, 126]

<table>
<thead>
<tr>
<th>Authors/Ref.</th>
<th>Kinetics</th>
<th>Species involved in MB</th>
<th>Gas Phase</th>
<th>Liquid/Slurry Phase</th>
<th>Solid Phase</th>
<th>Energy</th>
<th>Gas Consumption</th>
<th>Steady-State or Transient?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calderbank et al. [539]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>PF</td>
<td>Uniform</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Satterfield and Huff [540]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>No</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Deckwer et al. [541]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Deckwer et al. [542]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ADM</td>
<td>ADM</td>
<td>SDM</td>
<td>ADM</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Bukur [148]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>PM; PF</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Kuo [543]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>PF; PM; ADM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Stern et al. [176]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>No</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Leib and Kuo [417]</td>
<td>F-T, L-H WGS, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>Unmixed</td>
<td>SDM</td>
<td>-</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Stern et al. [267]</td>
<td>F-T, L-H WGS, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;, C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;m&lt;/sub&gt;</td>
<td>ADM</td>
<td>ADM</td>
<td>SDM</td>
<td>Isothermal</td>
<td>Overall gas MB</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Bukur and Zimmerman [262]</td>
<td>F-T, L-H WGS, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;, C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;m&lt;/sub&gt;</td>
<td>PF</td>
<td>Unmixed</td>
<td>SDM</td>
<td>Isothermal</td>
<td>Overall gas MB</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Turner and Mills [270]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>MCM; PF</td>
<td>MCM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Authors/Ref.</td>
<td>Kinetics</td>
<td>Species involved in MB</td>
<td>Gas Phase</td>
<td>Solid Phase</td>
<td>Energy</td>
<td>Gas Consumption</td>
<td>Steady-State or Transient?</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>----------</td>
<td>------------------------</td>
<td>-----------</td>
<td>-------------</td>
<td>--------</td>
<td>-----------------</td>
<td>---------------------------</td>
<td></td>
</tr>
<tr>
<td>Leib et al. [544]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>MCM</td>
<td>MCM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Inga and Morsi [181]</td>
<td>F-T, L-H WGS, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PF</td>
<td>MCM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>No</td>
<td>Steady-State</td>
</tr>
<tr>
<td>Mills et al. [261]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ADM</td>
<td>ADM</td>
<td>SDM</td>
<td>ADM</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
<tr>
<td>van der Laan et al. [56]</td>
<td>F-T, L-H WGS, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;, n-products</td>
<td>PF</td>
<td>PM</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Linear f(X)</td>
</tr>
<tr>
<td>de Swart and Krishna [153]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ADM</td>
<td>AD M</td>
<td>ADM</td>
<td>SDM</td>
<td>ADM</td>
<td>Linear f(X)</td>
</tr>
<tr>
<td>Rados et al. [150, 265]</td>
<td>F-T, 1&lt;sup&gt;st&lt;/sup&gt; order</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, pseudo-product</td>
<td>ADM</td>
<td>AD M</td>
<td>ADM</td>
<td>Uniform</td>
<td>ADM</td>
<td>Overall gas MB</td>
</tr>
<tr>
<td>Song et al. [266]</td>
<td>F-T, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, pseudo-product</td>
<td>PF</td>
<td>PM</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Overall gas MB</td>
</tr>
<tr>
<td>Song et al. [545]</td>
<td>F-T, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PM</td>
<td>PM</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>No</td>
</tr>
<tr>
<td>Fernandes [258]</td>
<td>F-T, L-H WGS, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;, n-products</td>
<td>PF</td>
<td>PM</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Linear f(X)</td>
</tr>
<tr>
<td>Iliuta et al. [160, 263]</td>
<td>F-T, L-H WGS, L-H</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;, CO, H&lt;sub&gt;2&lt;/sub&gt;O, CO&lt;sub&gt;2&lt;/sub&gt;, n-pseudo-products</td>
<td>Core &amp; Annulus ADM</td>
<td>ADM</td>
<td>Overall gas MB</td>
<td>Steady-State</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Authors/Ref.</td>
<td>Kinetics</td>
<td>Species involved in MB</td>
<td>Gas Phase</td>
<td>Liquid/Slurry Phase</td>
<td>Solid Phase</td>
<td>Energy</td>
<td>Gas Consumption</td>
<td>Steady-State or Transient?</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------</td>
<td>------------------------</td>
<td>-----------</td>
<td>---------------------</td>
<td>-------------</td>
<td>--------</td>
<td>----------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>Sehabiague et al. [151]</td>
<td>F-T, L-H</td>
<td>H₂, CO, H₂O, CO₂, N₂, n-products</td>
<td>ADM</td>
<td>AD M</td>
<td>ADM</td>
<td>SDM</td>
<td>ADM</td>
<td>Overall gas MB</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>LB</td>
<td>SB</td>
<td></td>
<td></td>
<td></td>
<td>Steady-State</td>
</tr>
<tr>
<td>Wang et al. [158]</td>
<td>F-T, L-H</td>
<td>H₂, CO, H₂O, CO₂, N₂, n-products</td>
<td>PF</td>
<td>PM</td>
<td>PM</td>
<td>Uniform</td>
<td>Isothermal</td>
<td>Overall gas MB</td>
</tr>
<tr>
<td></td>
<td>WGS, L-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Steady-State</td>
</tr>
<tr>
<td>Guettel and Turek [546]</td>
<td>F-T, 1st order</td>
<td>H₂</td>
<td>PF</td>
<td>PM</td>
<td>Uniform</td>
<td>PF</td>
<td>Linear f(X)</td>
<td>Steady-State</td>
</tr>
</tbody>
</table>

L-H: Overall reaction rate based on Langmuir-Hinshelwood kinetics.
ADM: Axial-Dispersion Model
MCM: Mixing-Cell Model
SDM: Sedimentation-Dispersion Model
PF: Plug-Flow
PM: Perfectly Mixed
MB: Mass Balance

1 as reported by Mills et al. [261]
2 as reported by Bukur and Zimmerman [262]
Table A-14: Summary of multiple cell circulation models [285]

<table>
<thead>
<tr>
<th>Reference</th>
<th>Numerical method for the continuous phase</th>
<th>Numerical method for the dispersed phase</th>
<th>Height of circulation cells</th>
<th>Liquid circulation driving force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freedman [547]</td>
<td>Vortex function equation</td>
<td>Bubble path calculated in the known velocity field</td>
<td>Equal to the column height</td>
<td>Gas distribution partially covering cross section</td>
</tr>
<tr>
<td>Rietema and Ottengraf [548, 549]</td>
<td>Laminar, viscous</td>
<td>Maximum of the energy dissipation function</td>
<td>Only one circulation cell</td>
<td>N/A</td>
</tr>
<tr>
<td>Whalley and Davidson [550]</td>
<td>Equation for the vortex function</td>
<td>Bubble path calculated in the known velocity field</td>
<td>Equal to the column diameter</td>
<td>Gas distribution partially covering cross section</td>
</tr>
<tr>
<td>Ueyama and Miyauchi [140]</td>
<td>Analytical with constant apparent liquid viscosity</td>
<td>Assumed distribution profile</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Joshi and Sharma [256, 551]</td>
<td>Equation for the vortex function</td>
<td>Bubble path calculated in the known velocity field</td>
<td>Equal to the column diameter</td>
<td>Gas distribution partially covering cross section</td>
</tr>
<tr>
<td>Zehner [127, 255]</td>
<td>Circulation velocity calculated from the drag coefficient</td>
<td>Algebraic equation derived using mass balance</td>
<td>Equal to the column diameter</td>
<td>N/A</td>
</tr>
<tr>
<td>Clark et al. [286, 552]</td>
<td>Difference method, mixing lengths</td>
<td>Bubble path integrated</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Anderson and Rice [287]</td>
<td>Von Karman</td>
<td>Assumed distribution profile</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Gasche et al. [553]</td>
<td>Finite volume, k-ε</td>
<td>Finite volume</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Geary and Rice [141, 290, 554]</td>
<td>Mixing lengths</td>
<td>Assumed distribution profile</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Grienberger and Hoffmann [315]</td>
<td>Finite volume, k-ε</td>
<td>Finite volume</td>
<td>Only one circulation cell along column</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Table A-14 (continued)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Numerical method for the continuous phase</th>
<th>Numerical method for the dispersed phase</th>
<th>Height of circulation cells</th>
<th>Liquid circulation driving force</th>
</tr>
</thead>
<tbody>
<tr>
<td>Svendsen et al. [405]</td>
<td>Finite volume, $k$-$\varepsilon$</td>
<td>Finite volume</td>
<td>Only one circulation cell along column height</td>
<td>N/A</td>
</tr>
<tr>
<td>Ranade [555]</td>
<td>Finite volume, $k$-$\varepsilon$</td>
<td>Finite volume</td>
<td>Only one circulation cell along column diameter</td>
<td>N/A</td>
</tr>
<tr>
<td>Sokolichin et al. [556]</td>
<td>Finite volume, Laminar flow</td>
<td>Finite volume</td>
<td>Only one circulation cell along column height</td>
<td>Gas distribution partially covering cross section</td>
</tr>
<tr>
<td>Millies et al. [285, 557]</td>
<td>Explicit difference method, mixing length</td>
<td>Transient assumptive functions, integrated along the characteristics</td>
<td>Calculated</td>
<td>Small disturbances of the gas distribution</td>
</tr>
<tr>
<td>Delnoij et al. [283, 284]</td>
<td>Finite elements, Volume averaged mass and momentum balance equations</td>
<td>Individual Bubble path integrated by accounting for force balance</td>
<td>20 circulation cell per L/D along column height</td>
<td>Gas distribution partially covering cross section</td>
</tr>
</tbody>
</table>
Table A-15: CFD modeling of three-phase reactors

<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-fluid Eulerian approach for three phase fluidized bed</td>
<td>- Both symmetric and axisymmetric&lt;br&gt;- Kinetic theory granular flow model applied for solid phase&lt;br&gt;- Gas phase treated as a particulate phase with 4 mm diameter</td>
<td>- Compared time averaged axial solid velocity with experimental data&lt;br&gt;- Verified different flow regimes in fluidized beds.</td>
<td>Bahary et al. [558]</td>
</tr>
<tr>
<td>Two fluid Eulerian-Eulerian model for three phase bubble column</td>
<td>- 3-D&lt;br&gt;- Liquid phase and solid particles modelled as pseudo-homogeneous phase by modifying the viscosity and density.&lt;br&gt;- Included bubble size distribution based on the bubble induced turbulent length scale and the local turbulent kinetic energy level.</td>
<td>- Liquid circulation&lt;br&gt;- Solid movement&lt;br&gt;- Studied variation of bubble size distribution</td>
<td>Grevskot et al. [243]</td>
</tr>
<tr>
<td>Multi fluid Eulerian approach for three phase bubble column</td>
<td>- 2-D axisymmetric&lt;br&gt;- Modified drag correlation between liquid and gas phase to account for effect of solid particles.&lt;br&gt;- Modified drag correlation between solid and liquid phase to account for the effect of gas bubbles.&lt;br&gt;- Standard k-ε turbulence model&lt;br&gt;- Accounted for effect of bubbles on liquid phase turbulence</td>
<td>- Studied axial variation of gas holdup and solid holdup profiles for a wide range of superficial gas velocities and solid circulation velocities.</td>
<td>Mitra-Majumdar et al. [244]</td>
</tr>
<tr>
<td>Eulerian-Eulerian approach for three phase bubble column</td>
<td>- 2-D&lt;br&gt;- Pseudo two phase fluid dynamics model based on the time averaged Navier-Stokes equation.&lt;br&gt;- $k_{sus}$-$\varepsilon_{sus}$-$k_b$-$\varepsilon_b$ turbulence model used to describe and calculate the local flow ($sus$: suspension phase, $b$: gas phase).</td>
<td>- Studied effects of:&lt;br&gt;  o Solid loading&lt;br&gt;  o Superficial liquid velocity&lt;br&gt;  o Superficial gas velocity&lt;br&gt;  - On local flow characteristics such as axial liquid velocity and gas holdup.&lt;br&gt;  - Validated local axial liquid velocity and local gas holdup with experimental data from tap water-compressed air-resin particles system.</td>
<td>Jianping and Shonglin [201]</td>
</tr>
</tbody>
</table>
Table A-15 (continued)

<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
</table>
| Eulerian-Lagrangian model for three phase fluidization | - 2-D CFD-VOF-DPM  
- Eulerian fluid dynamics method to account for liquid phase flow.  
- Dispersed particle method (DPM) to account for solid particles behavior.  
- Volume of fluid (VOF) method to account for gas phases.  
- Continuum surface force (CSF) model to account for gas-liquid coupling.  
- Surface tension force model to account for particle-bubble coupling  
- Newton’s third law to account for particle liquid coupling.  
- Included a close distance interaction model in the particle-particle collision analysis to account for the liquid interstitial effects between colliding particles. | Studied:  
- Single bubble rise velocity in a liquid solid fluidized bed.  
- Bubble wake structure and bubble rise velocity in liquid and liquid-solid mediums. | Li et al. [294] |
| Multi fluid Eulerian approach for three phase draft tube bubble column | - 3-D  
- Extended multiphase $k$-$\varepsilon$ turbulence model as developed by Kashiwa [559]  
- Drag between solid grains and the gas bubbles was modelled identically to drag between liquid and gas bubbles – based on the notion that solid particles in the vicinity of gas bubbles tend to follow the liquid. | - Simulated gas volume fractions and liquid circulation in draft tube bubble column.  
- Validated simulation results with experimental measurements of gas holdups for three and two fluid flow systems (tap water-air-siliceous sand) in an air lift draft tube by Pironti et al. [560] | Padial et al. [561] |
| Eulerian-Lagrangian model for three phase fluidized bed | - 2-D  
- Eulerian volume averaged method to describe the liquid phase  
- Lagrangian dispersed particle method (DPM) to describe the solid particles  
- Volume of fluid (VOF) method to describe the gas bubbles. | - Studied the effect of pressure and solid holdup on the bubble size rise characteristics such as the bubble rise velocity, bubble shape and bubble trajectory. | Zhang et al. [313] |
<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
</table>
| **Eulerian-Lagrangian model for three phase fluidized bed** | - 2-D  
- Eulerian volume averaged method to describe the liquid phase  
- Lagrangian dispersed particle method (DPM) to describe the solid particles  
- Volume of fluid (VOF) method to describe the gas bubbles.  
- Bubble induced force model to describe the particle –bubble coupling interaction  
- Continuum surface force (CSF) model to describe the gas liquid coupling interaction  
- Newton’s third law to describe the particle-liquid coupling interaction | - Validated simulation results with experimental measurements of bubble rise velocities of a gas-liquid system. | **Zhang et al.** [563] |
| **Multi fluid Eulerian approach for slurry bubble column** | - 3-D  
- Kinetic theory granular flow (KTGF) model for describing particulate phase  
- Standard $k$-$ε$ turbulence model for liquid phase turbulence | - Studied:  
- Single bubble rise behavior in a liquid solid suspension.  
- Bubble entrainment by a bubble on the surface of the bed.  
- Validated simulation results with experimental measurements of bed expansion and pressure drop in a water-air-Piolite particles fluidized bed by Lin et al. [562] | **Matonis et al.** [297] |
Table A-15 (continued)

<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
</table>
| Multi fluid Eulerian approach for slurry bubble column | - Standard $k$-$\varepsilon$ turbulence model for liquid phase turbulence  
- Accounted for the momentum transfer between the dispersed phases (gas-solid) through the modified drag model of Padial et al. [561]  
- Used a very coarse grid with average grid length of 0.059 m to limit computational load | - Studied gas and solid holdups throughout the SBCR at different superficial gas velocities.  
- Validated gas holdup simulations against the data of Dziallas [564] | Michele ad Hempel [565] |
| Multi-phase Eulerian-Eulerian model for three phase flow in a bubble column | - 2-D  
- Standard $k$-$\varepsilon$ turbulence model for liquid phase turbulence.  
- Kinetic theory granular flow (KTGF) model for describing particulate phase | - Studied the effect of solid loading and superficial gas velocity on solid distribution.  
- Qualitatively validated simulation results with experimental values from an air-water-glass beads system | Rampure et al. [566] |
| Multi-phase Eulerian-Eulerian model for three phase flow in a slurry bubble column | - 2-D  
- Used the kinetic theory of granular flow with a measured restitution coefficient to model particulate viscosity  
- Simplified kinetics to incorporate the reaction between carbon monoxide and hydrogen to produce methanol  
- Operating conditions are based on the Air Products/DOE La Porte’s slurry reactor for methanol synthesis | - Solids distribution  
- Reactor performance | Gamwo et al. [567] |
| Eulerian-Lagrangian model for three phase fluidized bed | - 3-D  
- Locally averaged Navier-Stokes equations are used to describe the liquid phase flow outside the gas bubble and the gas phase floe inside the gas bubble.  
- Employed a Sub-Grid Scale (SGS) stress model with modified coefficients to account for the effect of the bubble induced turbulence.  
- Level set method to describe the motion and topological variation of the gas bubbles.  
- | - Studied air bubble formation from an orifice and bubble rise velocity  
- Validated simulation results with experimental measurements of bubble rise velocity for air-water and air-heat transfer fluid (Paratherm NF)-solid systems. | Chen and Fan [372] |
<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified transport equation approach for three phase bubble column</td>
<td>- Lagrangian dispersed particle method (DPM) to describe the solid particles</td>
<td>- Investigated the time averaged vertical mixture velocity and the volume fraction of the gas and solid phases.</td>
<td>Glover and Generalis [568]</td>
</tr>
<tr>
<td>Multi fluid Eulerian approach for three phase bubble column</td>
<td>- Modified mixture model for the volume fraction of the dispersed phase - Ignored particle interactions - Implemented Reynolds stress turbulence model.</td>
<td>- Compared the local time averaged liquid velocity and gas holdup profiles along the radial position</td>
<td>Feng et al. [296]</td>
</tr>
<tr>
<td>Multi fluid Eulerian approach for three phase bubble column</td>
<td>- Liquid and solid phases modelled as a pseudo homogenous phase because of ultrafine nanoparticles. - Interface model used for drag, lift and virtual mass. - Standard k-ε turbulence model</td>
<td>- Studied back mixing in the liquid and gas phase - Presented an alternate approach to the modeling of three phase floe for an L/D ratio of 5.</td>
<td>Wieman and Mewes [569]</td>
</tr>
<tr>
<td>Multi fluid Eulerian approach for three phase bubble column</td>
<td>- Multi fluid Eulerian model coupled with a population balance equation. (Solid and gas phases considered Eulerian) - Accounted for bubble breakup and coalescence using source terms in the mass balance - Modified k-ε turbulence model for the liquid phase - Kinetic theory granular flow (KTGF) model for describing particulate phase pressure and stress tensor.</td>
<td>- Validated simulation results with experimental measurements of local gas and liquid holdup, and liquid velocities for a three phase air-water-solid particles system by Dziallas et al. [564]</td>
<td>Schallenberg et al. [299]</td>
</tr>
<tr>
<td>Multiphase model</td>
<td>Supporting models/ Simulation conditions</td>
<td>Parameters investigated</td>
<td>Author</td>
</tr>
<tr>
<td>--------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| Multi scale Eulerian Lagrangian model for thee phase flow                      | - 3-D  
- Combined front tracking approach for gas bubbles  
- Discrete particle (DP) approach for solid particles  
- Staggered rectangular 3-D grid using a two-step projection-correction method with explicit treatment of the convection and diffusion terms and implicit treatment of the pressure gradient. | - Studied bubble rise behavior and bubble-particle interaction for single and multiple bubble scenarios                                                                                                                                   | Annaland and Kuipers [570]                                                                     |
| Eulerian- Lagrangian model for three phase slurry reactor                      | - Liquid flow modeled using a volume averaged system of governing equations  
- Bubbles and particles modelled using a Lagrangian trajectory analysis procedure  
- Bubble-bubble and particle-particle collision are included using a hard sphere collision model.  
- Two way phase coupling. Coupling between fluid and dispersed phases is implemented using a momentum interaction term from the discrete phase to the fluid phase.  
- Accounted for drag, lift, buoyancy and virtual mass forces.  
- Bubble coalescence included in the model using a critical Webber number approach. | Studied:  
- Transient characteristics of the gas, liquid and solid phase flows in terms of flow structure and instantaneous velocities.  
- Effect of bubble size on variation of flow patterns.                                                                 | Zhang and Ahmadi [298]                                                                         |
| Multi fluid Eulerian approach for three phase fluidized bed                    | - 2-D  
- Gidaspow model for drag  
- Isothermal, reaction free model for mass and momentum balances                                                                                                                                                             | Studied:  
- Phase holdups and velocity profiles  
- Effect of liquid velocity on pressure drop  
- Effect of liquid velocity on bed porosity  
- Validated simulation results with experimental measurements of solid phase mean and turbulent velocities for a three phase air/tap water/ solid (glass, PVC and | Nguyen et al. [571]                                                                                   |
| Multi fluid Eulerian approach for three phase fluidized bed reactor            | - 2-D and 3-D  
- Pressure field is assumed to be shared by all three phases, in proportion to their volume fraction.                                                                                                                                                  | - Validated simulation results with experimental measurements of solid phase mean and turbulent velocities for a three phase air/tap water/ solid (glass, PVC and | Punneerselva m et al. [293]                                                                   |
<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
</table>
| **Multi fluid Eulerian-Lagrangian approach for a three phase circulating fluidized bed** | - Momentum of each phase is governed by respective mass and momentum conservation equations.  
- Applied closure law to model liquid turbulence, solid pressure and interphase momentum exchange  
- Modelled gas-solid interphase drag in the same way as that between the continuous and dispersed phase using the model developed by Wang et al. [572] | acetate) bead system by Kiared et al. [573], and with experimental measurements of gas and liquid phase velocities and holdups for a three phase air-water-glass beads system by Yu and Kim [3, 574] |                                                                                                                                  |
| **Two fluid Eulerian approach for a three phase slurry reactor for petroleum hydrosulfurization** | - 2-D  
- Two fluid model used for coupling between gas and liquid phases.  
- Lagrangian Distinct element method (DEM) used to describe solid particle motion.  
- Standard $k$-$\varepsilon$ turbulence model | - Studied:  
  ○ Radial distribution of local liquid velocity at various liquid viscosities and at various superficial gas velocities.  
  ○ Variation of local solid hold-up in radial direction for various superficial gas velocities  
- Qualitatively validated simulation results with experimental values from an air-water-styrene resin beads system | Cao et al. [575]                                                             |
|                                                                                          | - 2-D  
- Axisymmetric  
- Solid and Liquid combined into a pseudo-liquid phase  
- Difference in density between the catalyst and the slurry phase is so small that the catalyst does not settle and the fluid velocity is sufficiently small to assume axial symmetry.  
- Mass balance for the two phases (pseudo-liquid and gas) is coupled by an overall mass balance.  
- Friction terms used to couple the momentum balance of both phases.  
- Standard $k$-$\varepsilon$ turbulence model | - Validated simulation results with experimental measurements of the radial variation of the gas and liquid holdups for a two phase air-water system by Grienberger and Hofmann [315]  
- Studied effect of grid size and simulation time on kinetics results | Matos et al. [301]                                                             |
<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
</table>
| **Multi fluid Eulerian approach for three phase fluidized bed contactor** | - Implemented hydro-sulfurization reaction kinetics into the mass balance  
- Axial velocities at the entrance of the reactor set using experimental results by Torvik and Svendsen [314] | - Investigated the effect of various drag force models on phase velocities  
- Studied the effect of:  
  ○ Liquid superficial velocity on the axial solid velocity  
  ○ Particle size and density on the axial solid velocity  
  ○ Gas velocity and liquid viscosity on bed porosity  
  ○ Column diameter on gas holdup, liquid holdup and bed porosity. | Muthiah et al. [576] |
| **Multiphase Eulerian approach for three phase fluidized bed** | - 3-D  
- Isothermal energy conditions, no energy equations  
- Neglected momentum transfer between dispersed phases  
- Bubbles are assumed as rigid spheres with a constant diameter  
- \( k-\varepsilon \) turbulence model for liquid phase | Studied:  
- Mass averaged velocities of solid and liquid phases  
- Particle velocity fluctuations  
- Collision time  
- Liquid droplet distribution | O’Rourke et al. [577] |
| **Two fluid Eulerian approach for a three phase slurry reactor for Fischer Tropsch synthesis** | - 2-D  
- Introduced the Multiphase particle-in-cell (MP-PIC) method for modeling particle dynamics and collisional exchange. Solved the solid phase particle distribution function.  
- 2-D/3-D  
- Bubble size distribution predicted using a population balance model.  
- Incorporated heterogeneous and homogenous reaction rates representing simplified F-T synthesis from Yates and Satterfield [317]  
- Turbulence is described by the two equation RNG \( k-\varepsilon \) model | Studied:  
- Time averaged Sauter diameter at different elevations from inlet  
- Gas holdup at different catalyst concentrations  
- Inlet velocity on syngas conversion and reactor productivity | Troshko and Zdarvistch [316] |
<table>
<thead>
<tr>
<th>Multiphase model</th>
<th>Supporting models/ Simulation conditions</th>
<th>Parameters investigated</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-phase mixture approach for three phase fluidized bed reactor</td>
<td>- Interphase drag exchange coefficient from Ishii and Mishima [272]</td>
<td>- Axial variation of time averaged Sauter diameter along the reactor axis for different catalyst concentrations</td>
<td>Silva Jr. et al. [302]</td>
</tr>
<tr>
<td></td>
<td>- Discrete phase method (DPM) to account for gas phase behavior.</td>
<td>- Studied effect of different porous models (porous jump vs porous zone) on liquid and solid phase velocities.</td>
<td>Sivaguru et al. [300]</td>
</tr>
<tr>
<td></td>
<td>- Solid and liquid phases modelled using a simplified mixture model in: phases move at different velocities, but assume local equilibrium over short spatial length scales</td>
<td>- Validated simulation results with experimental measurements of pressure drop for a three phase air/water/solid system.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Second order upwind scheme for discretization of the momentum equations.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multi fluid Eulerian approach for three phase fluidized bed reactor</td>
<td>- 3-D pressure based solver</td>
<td>- Studied: o Significance of implementing different numerical schemes.</td>
<td>Hamidipour et al. [292]</td>
</tr>
<tr>
<td></td>
<td>- Triple Euler model</td>
<td>o Accuracy of different k-ε turbulence models (standard, RNG, realizable)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Applied closure law to model liquid turbulence, solid pressure and interphase momentum exchange</td>
<td>o Solid wall boundary conditions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Isothermal, reaction free model for mass and momentum balances</td>
<td>o Granular temperature models</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Accounted for liquid-solid, gas-liquid and gas–solid drag forces.</td>
<td>- Validated simulation results with experimental measurements of axial solid velocity and gas holdup for a three phase air-tap water-glass bead system by Kiared et al. [573], and Yu and Kim [3]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- k-ε turbulence model</td>
<td>- Disregarded heat and mass transfer effects.</td>
<td></td>
</tr>
<tr>
<td>Multi fluid Eulerian approach for three phase slurry bubble column</td>
<td>- 3-D transient simulation</td>
<td>- Validated simulation results using different drag models with experimental measurements of axial gas velocity and holdup for a three phase air-water-catalyst system by Wu et al. [144]</td>
<td>Silva Jr. et al. [302]</td>
</tr>
<tr>
<td></td>
<td>- Wen-Yu and Gidaspow models used for liquid-solid drag force correlations [578].</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Schallenberg and Syamlal-O’Brien models used for gas-solid drag force correlations [299]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Turbulence is described by the two equation RNG k-ε model.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Disregarded heat and mass transfer effects.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>System</td>
<td>Drag Coefficient Correlation</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>Various experimental data for air-water</td>
<td>$C_D = \begin{cases} 29.1667 - \frac{3.8889}{Re_b^{2}} + 1.222 &amp; 1 &lt; Re_b &lt; 10 \ \frac{24}{Re_b} (1 + 0.15Re_b^{0.687}) &amp; 10 &lt; Re_b &lt; 200 \end{cases}$</td>
<td>Clift et al. [171]</td>
<td></td>
</tr>
<tr>
<td>Ambient air-water, air-dilute NO$_2$SO$_3$</td>
<td>$C_D = \begin{cases} \frac{24}{Re_b} (1 + 0.1Re_b^{0.75}) &amp; N_\mu &lt; 36\sqrt{2} \frac{(1 + 0.1Re_b^{0.75})}{Re_b^2} \ \frac{2}{3} \sqrt{E\bar{o}<em>b} &amp; N</em>\mu \geq 36\sqrt{2} \frac{(1 + 0.1Re_b^{0.75})}{Re_b^2} \end{cases}$</td>
<td>Ishii and Zuber [319]</td>
<td></td>
</tr>
<tr>
<td>Derivation for spherical bubble in an unbounded shear flow</td>
<td>$C_D = \left(\frac{16}{Re_b}\right) \left{1 + \left[ \frac{8}{Re_b} + 0.5 \left(1 + \frac{3.315}{\sqrt{Re_b}}\right) \right]^{-1}\right}$</td>
<td>Mei and Klausner [323]</td>
<td></td>
</tr>
<tr>
<td>Ambient air-tap water-glass beads/non-spherical silica</td>
<td>$C_D = \max \left[ \min \left(\frac{16}{Re_b} (1 + 0.15Re_b^{0.687}), \frac{48}{Re_b} \frac{E\bar{o}_b}{3 E\bar{o}_b + 4} \left(1 + \frac{17.67a_s^{9/3}}{18.67a_s^{2}}\right)\right)^2 \right]$</td>
<td>Tomiyama et al. [322]</td>
<td></td>
</tr>
<tr>
<td>For a slightly contaminated liquid:</td>
<td>$C_D = \max \left[ \min \left(\frac{24}{Re_b} (1 + 0.15Re_b^{0.687}), \frac{72}{Re_b} \frac{E\bar{o}_b}{3 E\bar{o}_b + 4} \left(1 + \frac{17.67a_s^{9/3}}{18.67a_s^{2}}\right)\right)^2 \right]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>For contaminated systems:</td>
<td>$C_D = \max \left[ \frac{24}{Re_b} (1 + 0.15Re_b^{0.687}), \frac{8}{3 E\bar{o}_b + 4} \right]$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air-water system at 12-70 °C</td>
<td>$C_D = \frac{5.645}{E\bar{o}_b^{-1} + 2.835}$</td>
<td>Grevskott et al. [243]</td>
<td></td>
</tr>
</tbody>
</table>
### Table A-16 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Drag Coefficient Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron particle in glycerin/water shear flow</td>
<td>[ C_D = \begin{cases} 16 \ Re_b \ 16 \frac{Re_b}{Re_b} \ (1 + 0.15Re_b^{0.5}) &amp; \text{Re}_b &lt; 1 \ \frac{Re_b}{Re_b} \end{cases} ]</td>
<td>Kurose et al. [320]</td>
</tr>
<tr>
<td>Air-tap water/ propanol</td>
<td>[ C_D = \begin{cases} \frac{16}{Re_b} &amp; \text{Re}_b \leq 1.5 \ 1.49 \frac{Re_b^{0.78}}{Re_b} &amp; 1.5 \leq \text{Re}_b \leq 80 \ 48 \frac{Re_b}{Re_b} \left(1 - \frac{2.21}{\sqrt{Re_b}}\right) + (1.86 \times 10^{-15})Re_b^{4.756} &amp; 80 \leq \text{Re}_b \leq 1500 \ 2.61 &amp; \text{Re}_b \geq 1500 \end{cases} ]</td>
<td>Lain et al. [321]</td>
</tr>
<tr>
<td>Statistical analysis of small bubbles in isotropic turbulence</td>
<td>[ C_D = \begin{cases} \frac{24}{Re_b} &amp; \text{Re}_b \leq 1 \ \frac{24}{Re_b} \left(1 + \frac{3.6}{Re_b^{0.313}} \left(\frac{Re - 1}{19}\right)^2\right) &amp; 1 \leq \text{Re}_b \leq 20 \ \frac{24}{Re_b} \left(1 + 0.15Re_b^{0.687}\right) &amp; \text{Re}_b &gt; 20 \end{cases} ]</td>
<td>Snyder et al. [324]</td>
</tr>
</tbody>
</table>
### Table A-17: Commonly used liquid-solid and gas-solid drag models

<table>
<thead>
<tr>
<th>System</th>
<th>Drag Coefficient Correlation</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Smooth spherical particle in stagnant fluid | $C_D = \begin{cases} 
\frac{24}{Re_p} & Re_p < 1000 \\
0.44 & Re_p \geq 1000 
\end{cases}$ | Schiller and Naumann [6] |
| Sand/silt-Water system, $dp = 0.001 - 0.01$ m | $C_D = \left(0.63 + \frac{4.8}{\sqrt{Re_p}}\right)^2$ | Dalla Ville [579] |
| Smooth spherical particle in stagnant fluid, $dp = 0.0025$ m | $C_D = \begin{cases} 
\frac{24}{Re_p} & Re_p < 0.1 \\
22.73 + \frac{0.0903}{Re_p} + 3.69 & 0.1 < Re_p < 1 \\
29.1667 - 3.8889 & 1 < Re_p < 10 \\
46.5 - 116.67 + 0.6167 & 10 < Re_p < 100 \\
98.33 - 2778 + 0.3644 & 100 < Re_p < 1000 \\
148.62 - 4.75 \times 10^4 + 0.357 & 1000 < Re_p < 5000 \\
-490.546 + 57.87 \times 10^4 & 5000 < Re_p < 10000 \\
-1662.5 + 5.4167 \times 10^6 & 10000 < Re_p < 50000 
\end{cases}$ | Morsi and Alexander [580] |
### Table A-17 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Drag Coefficient Correlation</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Various published experimental data for glass beads/spheres-water/glycol/glycerol systems $d_p = 0.006 \text{ m}$ | $C_D = \frac{1}{f^2} \left(0.63 + \frac{4.8}{\sqrt{Re_p / f}}\right)^2$  
$f = 0.5 \left[ A - 0.06Re_p + \sqrt{0.036Re_p^2 + 0.12Re_p(2B - A) + A^2} \right]$  
$A = \alpha_s^{4.34}$   ;   $B = \begin{cases} 0.8\alpha_s^{1.28} & \alpha_s \leq 0.85 \\ \alpha_s^{2.65} & \alpha_s > 0.85 \end{cases}$ | Garside and Al-Dibouni [581] |
| Various published experimental data for glass beads/spheres-water/glycol/glycerol systems $d_p = 0.006 \text{ m}$ | $C_D = \frac{0.44}{\alpha_s^{2(n-1)}}$  ;   $n = \frac{5.1 + 0.27Re_p^{0.9}}{1 + 0.1Re_p^{0.9}}$ (Richardson and Zaki) | Garside and Al-Dibouni [581] |
| 478 points from various published experimental data for a wide range of Reynolds $[395, 582-604]$ | $C_D = \frac{24}{Re_p} + \frac{3}{16}$                                                                                                  $Re_p < 0.01$  
$C_D = \frac{24}{Re_p} \left[1 + 0.1315Re_p^{(0.82 - 0.05w)}\right]$  
$0.01 \leq Re_p \leq 20$  
$C_D = \frac{24}{Re_p} \left[1 + 0.195Re_p^{0.6305}\right]$  
$20 \leq Re_p \leq 260$  
$log(C_D) = 1.6435 - 1.1242w + 0.1558w^2$  
$260 \leq Re_p \leq 1500$  
$log(C_D) = -2.4571 + 2.5558w - 0.929w^2 + 0.1049w^3$  
$1500 \leq Re_p \leq 1.2 \times 10^4$  
$log(C_D) = -1.9181 + 0.6370w - 0.0636w^2$  
$1.2 \times 10^4 \leq Re_p \leq 4.4 \times 10^4$  
$log(C_D) = -4.3390 + 1.5809w - 0.1546w^2$  
$4.4 \times 10^4 \leq Re_p \leq 3.8 \times 10^5$  
$w = log(Re_p)$ | Clift et al.[171] |
### Table A-17 (continued)

<table>
<thead>
<tr>
<th>System</th>
<th>Drag Coefficient Correlation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass spheres - Ethylene glycol glass spheres - water</td>
<td>[ C_D = \left( \frac{24}{R_e_p} \right) \left( 1 + 0.347 \frac{\tau_0}{\delta} + \frac{1}{2} \left( \frac{\tau_0}{\delta} \right)^2 \right) ]</td>
<td>Molerus [605]</td>
</tr>
<tr>
<td>Glass Spheres in Glycerin-Water 10 cm ID column ( d_p = 0.036 )</td>
<td>[ C_D = \begin{cases} \left( \frac{24}{R_e_p} \right) (1 + 0.1R_e_p^{0.75}) &amp; R_e_p &lt; 1000 \ 0.45 &amp; 1000 \leq R_e_p \leq 2 \times 10^5 \end{cases} ]</td>
<td>Ishii and Zuber [319]</td>
</tr>
<tr>
<td>Derived using the experimental data from Heywood [606, 607] and Lapple and Shepherd [608] for a wide range of spherical particles in Newtonian fluids</td>
<td>[ C_D = \frac{24}{R_e_p} 10^6 ] [ E = 0.261R_e_p^{0.369} - 0.105R_e_p^{0.431} - \frac{0.124}{1 + \left( \log(R_e_p) \right)^2} ]</td>
<td>Flemmer and Banks [609]</td>
</tr>
<tr>
<td>Derived using the same experimental data used by Clift et al. [171]</td>
<td>[ C_D = \frac{24}{R_e_p} (1 + 0.173R_e_p^{0.657}) + \frac{0.413}{1 + 16300R_e_p^{-1.09}} ] ( R_e_p &lt; 2.6 \times 10^5 )</td>
<td>Turton and Levenspiel [610]</td>
</tr>
<tr>
<td>Fitted experimental data [599, 602, 608, 611]1-5 using the modified Rosenbrock method [612]</td>
<td>[ C_D = (2.25R_e_p^{-0.31} + 0.36R_e_p^{0.06})^{3.45} ] ( 0.01 \leq R_e_p \leq 3 \times 10^5 )</td>
<td>Khan and Richardson [613]</td>
</tr>
<tr>
<td>Derived using the same experimental data used by Clift et al. [171]</td>
<td>[ C_D = \frac{24}{R_e_p} (1 + 0.1806R_e_p^{0.6459}) + \frac{0.4251}{1 + 6880.95R_e_p^{-1}} ] ( R_e_p &lt; 2.6 \times 10^5 )</td>
<td>Haider and Levenspiel [357]</td>
</tr>
<tr>
<td>Thermodynamic derivation for multiphase turbulent flows</td>
<td>[ C_D = \left( \frac{24}{R_e_p} \right) (1 + 0.1R_e_p^{0.75}) \left[ \frac{1}{\left( 1 - \left( \frac{1 - \alpha_s}{0.64356} \right) \right)^{1.6089}} \right] ]</td>
<td>Ma and Ahmadi [326]</td>
</tr>
<tr>
<td>System</td>
<td>Drag Coefficient Correlation</td>
<td>Reference</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------</td>
<td>-----------</td>
</tr>
</tbody>
</table>
| Theoretical derivation | $\varepsilon_g < 0.8$ (Derived using the Wen and Yu [5] Fluidization model) \[
\beta = 150 \frac{(1 - \alpha_g)^2 \mu_g}{\alpha_g d_p^2} + 1.75 \rho_g (1 - \alpha_g) |v_g - v_s| d_p \]
| | $\varepsilon_g \geq 0.8$ (Derived using the Ergun Pressure Drop correlation [614]) \[
\beta = \frac{3}{4} C_D \frac{\alpha_g |v_g - v_s| \rho_g (1 - \alpha_g)}{d_p} \]
| | \[C_D = \begin{cases} 
\left( \frac{24}{\alpha_g Re_b} \right) \left( 1 + 0.15 (\alpha_g Re_b)^{0.687} \right) \alpha_g^{-2.65} & \alpha_g Re_p < 1000 \\
0.44\alpha_g^{-2.65} & \alpha_g Re_p \geq 1000 
\end{cases} \]
| Glass ballotini/ Lead shot-bromoform 0.062 m ID column  
$d_p = 0.031754$ m | $C_D = 0.44\alpha_s^{-2.65}$ | Richardson and Zaki [615] |
| Numerical simulation for two phase gas-solid flows | $C_D = 0.44 + \frac{24}{Re_p} + \frac{6}{1 + \sqrt{Re_p}}$ | Zhang and van der Heyden [327] |
APPENDIX B

EXPERIMENTAL PROCEDURES AND CALCULATION METHODS

B.1 EXPERIMENTAL PROCEDURES

The experimental procedures to obtain the volumetric liquid-side mass transfer coefficients ($k_{L,a}$), gas holdup ($\varepsilon_G$), and the Sauter-mean bubble diameter ($d_{32}$) are detailed in the following.

B.1.1 $\varepsilon_G$ Measurement

The hydrostatic method, known also as the manometric method, was used to obtain the gas holdup. Once the system reaches thermodynamic equilibrium (steady state), the following procedure for obtaining the gas holdup was followed:

1. The dP cells legs were purged of liquid or slurry and pressurized with the gas which was being used.
2. The hydrostatic pressure was measured at different positions along the height of the reactor by opening and closing the corresponding valves.
3. The computer collected the dP cell readings and calculates the gas holdup at any given position along the reactor.
B.1.2 \( d_{32} \) Measurement

The Dynamic Gas Disengagement (DGD) technique was employed to obtain the bubble size and the bubble size distribution. Once \( k_{La} \) and \( \varepsilon_G \) measurements were successfully completed at given temperature, the following procedure was followed:

1. The dP cell legs at given positions were opened.
2. Using the pneumatically actuated valves, the inlet valve for the gas flow at the bottom of the reactor was closed, while the valve located at the top of the reactor was opened, directing the gas from the bottom to the top of the reactor, and as a result the gas retained in the liquid disengaged.
3. The dP cell readings were recorded until all the gas bubbles were completely disengaged from the liquid or slurry and the pressure leveled off.
4. The computer collected the dP cell readings and calculated the gas holdup.
5. The bubble sizes were then calculated using the gas holdup versus time data.

B.1.3 \( k_{La} \) Measurement

The Transient Physical Gas Absorption technique (TPGA) was employed to obtain \( k_{La} \) for the gases into the liquid phase or slurry phase under the operating conditions used. The experimental procedure is described below:

1. A predetermined amount of liquid or slurry was charged into the reactor (95 liters).
2. The entire system was vacuumed to remove any gases which might be dissolved in the liquid-phase. Once the pressure in the reactor reaches the vapor pressure of the liquid phase, the vacuum was stopped.
3. The reactor content was heated to the desired temperature.

4. The gas was charged into the supply vessel and an initial mass balance was built.

5. The gas was then charged to the reactor until the desired pressure was reached.

6. The cooling water and the drain valves for the compressor were opened.

7. Once the gas was charged, the compressor was turned on and the gas was being recirculated only through the top of the reactor with valve AV-2 open and valve AV-1 closed. The gas velocity was adjusted to the desired flow rate, regulated by the gas bypass valve.

8. The top valve AV-2 was closed while simultaneously opening the bottom gas valve AV-1 allowing the gas to flow through the liquid or slurry. The reactor pressure was recorded as a function of time during the gas absorption in the liquid or slurry phase until thermodynamic equilibrium is reached.

9. Once the system reaches thermodynamic equilibrium, data collection was stopped.

10. $k_La$ was then calculated from the transient part of the pressure-time data and the gas solubility ($C^*$) is obtained from the equilibrium part.

In order to obtain different $k_La$ at various conditions, Steps 2–8 are repeated.
The equilibrium solubility \( C^* \) for each gas used in the molten reactor wax was calculated from the steady-state portion of the pressure decline (Pressure-Time) curve, whereas the volumetric liquid-side mass transfer coefficient \( k_{L,a} \) was obtained from the transient portion of the same curve. The calculations were performed by building mass balances on the supply vessel of the SBCR and the reactor, coupled with the Peng-Robinson Equation of State (PR-EOS).

The following assumptions were made in order to calculate \( C^* \) and \( k_{L,a} \):

1. The gas-phase in the preheater (or supply vessel) and reactor behaves as non-ideal gas and the Peng-Robinson Equation-of-State (PR-EOS) is applicable.
2. The gas and liquid phases are well mixed, resulting in homogeneous concentrations for each phase.
3. No gas absorption prior to mixing.
4. The liquid volume is constant during the absorption process, which is true, if the gas has low solubility in liquid-phase.

### B.2.1 Peng-Robinson EOS

The PR-EOS was used to calculate the number of moles of gas in the feed tank before and after charging the reactor, and to calculate the number of moles remaining in the reactor after gas absorption. A general form of the PR-EOS can be written as:

\[
P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2}
\]

This equation can be expressed in terms of the compressibility factor, \( Z \) as:
\[ Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \]  \hspace{1cm} (B-2)

Where:

\[ A = \frac{aP}{R^2T^2} \]  \hspace{1cm} (B-3)

\[ B = \frac{bP}{RT} \]  \hspace{1cm} (B-4)

\[ z = \frac{P\nu}{RT} \]  \hspace{1cm} (B-5)

For a multi-component, one-phase system, the solution of Equation (B-2) results in three real roots or one real (single-phase) and two imaginary roots. The coefficients in Equations (B-3) and (B-4) are listed below.

\[ a = \sum_i \sum_j y_i y_j a_{ij} \]  \hspace{1cm} (B-6)

\[ b = \sum_i y_i b_i \]  \hspace{1cm} (B-7)

\[ a_{ij} = (1 - \delta_{ij})\sqrt{a_i a_j} \]  \hspace{1cm} (B-8)

\[ a_i = 0.45724 \frac{R^2T_c^2}{P_c^2} \left[ 1 + \kappa [1 - T_R^{0.5}] \right] \]  \hspace{1cm} (B-9)

\[ b_i = 0.0778 \frac{RT_c}{P_c} \]  \hspace{1cm} (B-10)

\[ \kappa = 0.37464 + 1.5422\omega - 0.26992\omega^2 \]  \hspace{1cm} (B-11)

Equation (B-1) was used to calculate the number of moles before and after absorption in the gas-phase in order to calculate the gas solubility.
B.2.2 Equilibrium Solubility, C*

The equilibrium solubility ($C^*$) is defined as the number of moles of gas absorbed into the liquid at equilibrium and can be defined by:

$$C_i^* = \frac{N_{i,I} - N_{i,F}}{V_L} \quad (B-12)$$

Where $N_{i,I}$ is the initial number of moles of the gaseous species ($i$) in the reactor prior to absorption and $N_{i,F}$ is the number of moles of the gaseous species ($i$) remaining in the reactor at thermodynamic equilibrium. $N_{i,I}$ and $N_{i,F}$ are calculated as follows:

$$N_{i,I} = \frac{V_G}{Z_{i,I} R T_I} (P_{i,I} - P^S) \quad (B-13)$$

$$N_{i,F} = \frac{V_G}{Z_{i,F} R T_{F,avg}} (P_{F,i,I} - P^S) \quad (B-14)$$

Where $T_I$ is the initial temperature before the start of the absorption and $T_{F,avg}$ is the average temperature of the gas phase during the absorption. The volume of the gas phase, $V_G$, is calculated by subtracting the reactor volume and the liquid volume as follow:

$$V_G = V_{reactor} - \left( \frac{m_{\text{liquid}}}{\rho_{\text{liquid}}} \right) \quad (B-15)$$

In the above equation, $m_{\text{liquid}}$ and $\rho_{\text{liquid}}$ are the mass and density of the liquid-phase, respectively. The solubility, $C^*$ is then obtained by substituting Equations (B-13) or (B-14) into Equation (B-15).

B.2.3 Gas Holdup, $\varepsilon_G$

The gas holdup was determined using the manometric method (also known as the hydrostatic head method) with the following assumptions: (1) the reactor is operating under steady-state condition;
(2) the liquid or slurry and gas phases are well mixed in the volume between the 2 dP cell legs; and (3) the impact of the frictional effects on the pressure drop is negligible [616, 617].

The passage of gas bubbles throughout the slurry phase alters the pressure drop along the column which can be expressed by the following expression:

\[
\frac{dP}{dh} = -\rho_D g \tag{B-16}
\]

Where \( \rho_D \) is the density of the dispersed phase containing gas, liquid and solid and can be derived as:

\[
\rho_D = \varepsilon_G \rho_G + \varepsilon_L \rho_L + \varepsilon_S \rho_S \tag{B-17}
\]

Introducing \( c_V \) as the volumetric concentration of catalyst in the slurry-phase, the equation above becomes:

\[
\rho_D = \varepsilon_G \rho_G + (1 - \varepsilon_G)[c_V \rho_S + (1 - c_V)\rho_L] \tag{B-18}
\]

Replacing this expression of \( \rho_D \) in Equation (B-17), the latter can be integrated as follows:

\[
\int_{P_B}^{P_T} dP = -\int_{h_B}^{h_T} (\varepsilon_G \rho_G + (1 - \varepsilon_G)[c_V \rho_S + (1 - c_V)\rho_L])g dh \tag{B-19}
\]

The lower and higher limits are defined by the position of the dP cell legs on the column. If assumption #2 is used, the gas holdup and the catalyst concentration can be considered constant between the two dP cell legs leading to:

\[
P_T - P_B = -[\varepsilon_G \rho_G + (1 - \varepsilon_G)[c_V \rho_S + (1 - c_V)\rho_L]]g(H_T - H_B) \tag{B-20}
\]

The pressure difference between the lower and the upper legs is directly measured by the dP cell and since the distance between the legs is known, the following expression for gas holdup can be written:
\[
\varepsilon_G = \frac{c_V \rho_S + (1 - c_V) \rho_L}{c_V \rho_S + (1 - c_V) \rho_L - \rho_G} \left(1 - \frac{\Delta P_{cell}}{(c_V \rho_S + (1 - c_V) \rho_L) g \Delta H_{cell}}\right)
\]

(B-21)

**B.2.4 Gas Bubbles Size (d_b) and the Sauter Mean Bubble Diameter (d_{32})**

The Dynamic Gas Disengagement (DGD) technique was used to obtain the Sauter-mean bubble diameter. The corresponding gas holdups of the small and large gas bubbles in the SBCR were calculated using the technique introduced by Inga and Morsi [369] and successfully used by Behkish et al. [618, 619] and Lemoine et al. [620]. This technique relies on the assumption that large gas bubbles have greater rise velocity and therefore disengage first, whereas small gas bubbles, retained within the slurry or entrained in the wakes created by the flow of the large gas bubbles, have smaller rise velocity and therefore they disengage in a later stage.

The following assumptions were made in order to derive the equations needed for calculating the gas bubble sizes: (1) the rate of gas disengagement of each bubble is constant under given experimental conditions; (2) once the gas flow is stopped, there is no coalescence or breakup of gas bubbles, meaning that the bubbles sizes remain constant as they disengage; and (3) the liquid internal circulation does not affect the bubble rise velocity. [621]

The assessment of the \(\varepsilon_G\) with time after the gas flow inside the SBCR has been stopped using Equation (B-21) can lead to the estimation of the rate of disengagement of each bubble size. An example of the behavior of \(\varepsilon_G\) with time is shown in Figure B-1. From \(t = 0\) to \(t_1\), the dP cell shows no decline in \(\varepsilon_G\), however, no more gas is entering the bottom of the reactor. This means that the amount of gas that leaves the dP cell section (from \(H_B\) to \(H_T\)) is the same as the one which leaves the lower section (from \(H_0\) to \(H_B\)). From \(t_1\) to \(t_2\), the large gas bubbles having a bubble rise velocity (\(U_b\)) ranging from \(\Delta H_{cell}/t_1 = (H_T-H_B)/t_1\) to \(\Delta H_{cell}/t_2\) disengage from the cell region and
during this period, the small gas bubbles present in the lower section (H₀ to Hₐ) do not affect the dP cell reading. From t₂ to t₃, the small gas bubbles are disengaging from the cell region (Hₐ to Hₜ) and the dP cell reflects the small gas bubbles with \( U_b \) ranging from \( \Delta H_{cell}/t₂ \) to \( \Delta H_{cell}/t₃ \).

The volume of the gas bubbles that leaves the dP cell region (\( \Delta H_{cell} = Hₜ - Hₐ \)) can therefore be represented by the decrease of the total gas holdup as follows:

\[
\Delta \varepsilon_{G,i} = \int_{t_{i-1}}^{t_i} \frac{d\varepsilon_G}{dt} \, dt
\]

Consequently the total gas holdup is:

\[
\varepsilon_G = \sum_{i=1}^{n} \Delta \varepsilon_{G,i}
\]  \hspace{1cm} (B-22)

The rise velocity of each size of the bubbles can then be calculated at any time (t) from:

\[
U_{b,i} = \frac{\Delta H_{cell}}{t}
\]  \hspace{1cm} (B-23)

This method is valid when dealing with gas-liquid system, however, the presence of solids should be accounted for, due to the settling velocity of the solid particles. In this study, the correlation proposed by Fukuma et al. [622], who used up to 50 vol.% glass beads, was used to calculate the bubble size \( d_{b,i} \):

\[
d_{b,i} = \frac{U_{b,i}^2}{1.69g}
\]  \hspace{1cm} (B-24)

The Sauter-mean bubble diameter (\( d_{32} \) or \( d₃ \)) was then calculated using the following equation:

\[
d_{32} = \frac{\sum_{i} n_i d_{b,i}^3}{\sum_{i} n_i d_{b,i}^2}
\]  \hspace{1cm} (B-25)
Figure B-1: Dynamic Gas Disengagement in SBCR [619]
B.2.5 Volumetric Liquid-Side Mass Transfer Coefficient, $k_{La}$

The volumetric mass transfer coefficient, $k_{La}$, was calculated using the Transient Physical Gas Absorption technique. During the absorption of the gas into the liquid, the decline of reactor pressure was recorded as a function of time until the equilibrium was reached.

The rate of mass transfer of the solute gas into the liquid phase can be calculated using the two-film model as:

$$\frac{dn_L}{dt} = k_L a (C^* - C_L) V_L$$  \hspace{1cm} (B-27)

The interface gas concentration ($C^*$) at a given gas partial pressure was estimated assuming the validity of Henry’s law. At any time (t), the gas concentration in the liquid-phase ($C_L$) was calculated by building a mass balance on the gas-phase inside the reactor with the Peng-Robinson Equation of State (P-R EOS), which uses the experimental pressure decline data and the temperature recorded during the gas absorption. The $k_{La}$ values were then calculated by numerically solving Equation (B-27), i.e., by fitting the $C_L/C^*$ values as function of time.
APPENDIX C

EFFECT OF OPERATING CONDITIONS ON THE GAS BUBBLES DISTRIBUTION

The dynamic gas disengagement (DGD) technique was used to calculate the bubble size and distribution using the data obtained in this study as presented in Section 6.1. The bubble size was determined using the bubble rise velocity, which is dependent on the positions of the pressure transducers or on the liquid height, as shown in Equation (C-1), and a correlation relating the bubble rise velocity to the bubble diameter, such as that by Fukuma et al. [622] (Equation (C-2)).

\[ U_{b,i} = \frac{\Delta H_{cell}}{\Delta t} \quad (C-1) \]

\[ d_{b,i} = \frac{U_{b,i}^2}{1.69(g)} \quad (C-2) \]

Eight different classes were identified in the SBCR based on the bubble diameter as follows: < 1 mm, 1-3 mm, 3-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, 20-30 mm and > 30 mm. The volume fraction and relative frequency of each bubble-class were calculated using Equations (C-3) and (C-4), respectively.

\[
Volume\ fraction_{i} = \frac{\sum_{d_{b,i}-upper\ bound}^{d_{b,i}-lower\ bound} V_{G,i}}{V_{G,total}} \quad (C-3)
\]
\[
Relative frequency_i = \frac{\sum_{d_{b,i}-\text{upper bound}}^{d_{b,i}-\text{lower bound}} n_i}{n_{\text{total}}}
\]  

(C-4)

The volume fraction represents the ratio between the volume of a certain bubble-class and the total volume of the bubbles in the reactor, whereas, the relative frequency represents the ratio between the number of bubbles in a certain bubble-class and the total number of bubbles in the reactor. Although the relative frequency may not have a direct effect on gas holdup, it is an important factor in characterizing the fluid flow and turbulent behavior within the reactor, where the bubbles induced turbulences play a significant role.

C.1 EFFECT OF PRESSURE ON GAS BUBBLES DISTRIBUTION

Figure C-1 shows that increasing pressure increases the volume fraction of larger gas bubble sizes (> 30 mm) and decreases the volume fraction of the intermediate and small gas bubble sizes. Figure C-2 also shows that increasing pressure significantly decreases the relative frequency of small gas bubbles (< 1 mm) and increases those of the intermediate and large gas bubbles. This behavior can be attributed to the fact that increasing pressures decreases the gas bubbles size at the distributor, resulting in the formation of more frequent smaller gas bubbles. Also, increasing pressure increases the gas momentum, which imparts a greater upward force on the bubbles, thus enhancing their departure from the sparger zone. Thus, increasing pressure increases the frequency and momentum of gas bubbles, which enhance their coalescence and interaction in the vicinity of the gas sparger, resulting in significantly high frequency of the 1-3 mm bubbles. It is important to note that the relative frequency of bubbles has a significant effect on the hydrodynamics and flow regimes within the reactor.
At low pressures, however, the high frequency of small gas bubbles results in low interphase pressure gradients and weak turbulence forces, leading to strong tendencies of gas bubbles movement towards the reactor walls with low liquid-backmixing.

Figure C-1: Effect of pressure on bubble volume fraction

(a) $C_s = 15\, \text{vol}\%$, $P = 2.89\, \text{MPa}$, $T = 460\, \text{K}$, $u_g = 0.15\, \text{m/s}$

(b) $C_s = 15\, \text{vol}\%$, $P = 2.97\, \text{MPa}$, $T = 437\, \text{K}$, $u_g = 0.20\, \text{m/s}$
C.2 EFFECT OF SOLID CONCENTRATION

Figures C-3 and 10-4 show that increasing solids concentration increases the volume fraction of the larger gas bubbles and decreases the relative frequency of smaller gas bubbles. This behavior is primarily due to the fact that increasing solid concentration increases the slurry viscosity and density, which enhance the gas bubbles coalescence and accordingly the formation of large gas bubbles.

It should be noted that the effect of solid particle-bubble interaction in the SBCR was insignificant due to the small particle sizes used in this study (100 µm), which are an order of magnitude smaller than that of the lowest bubble-class size present in the reactor. When using
large solid particle sizes, however, the effect of particle-bubble interactions on enhancing the gas bubbles breakup becomes significant [623].

Figure C-3: Effect of solid concentration on bubble relative frequency

(a) T = 432 K
P = 1.53 MPa
u_g = 0.15 m/s
C_s = 5 vol%.
C_s = 15 vol%.

(b) T = 427 K
P = 2.08 MPa
u_g = 0.19 m/s
C_s = 10 vol%.
C_s = 15 vol%.
C.3 EFFECT OF TEMPERATURE

Figure C-5 (a) shows that increasing temperature at low solid concentration increases the volume fractions of the small gas bubbles, and decreases that of the large gas bubbles, however, Figure C-5 (b) shows that increasing temperature at high solid concentrations increases the volume fraction of the large gas bubbles (> 30 mm) and decreases that of the small gas bubbles.

Similarly, Figure C-6 show that increasing temperature at low solid concentrations slightly increases the relative frequency of the smallest gas bubble-class and slightly decreases the relative frequency of the rest of the gas bubble classes. Increasing temperature at high solid concentrations, however, significantly decreases the relative frequency of the smallest bubble-class and increases the relative frequency of the other gas bubble classes. These results are supported by Figures 5-18.
to 5-20, where increasing temperature at low solid concentrations increased the Sauter mean bubble diameter ($d_{32}$), while increasing temperature at high solid concentrations did not have clear effect on $d_{32}$.

At high temperatures and high solid concentrations, the change of the gas bubbles behavior is primarily due to the competing effects of both temperature and solid concentration on the slurry physical properties. Increasing temperature decreases the liquid surface tension and viscosity, whereas, increasing solid concentration increases the slurry viscosity. It should be pointed out, however, that at high temperatures, the effect of solid concentrations on the slurry viscosity decreases significantly as shown in Figure C-7.

![Figure C-5: Effect of temperature on bubble volume fraction](image-url)
Figure C-6: Effect of temperature on bubble relative frequency

(a) $C_s = 5 \text{ vol}\%$. $P = 1.58 \text{ MPa}$ $u_g = 0.15 \text{ m/s}$ $T = 461 \text{ K}$ $T = 433 \text{ K}$

(b) $C_s = 15 \text{ vol}\%$. $P = 2.13 \text{ MPa}$ $u_g = 0.20 \text{ m/s}$ $T = 460 \text{ K}$ $T = 432 \text{ K}$

Figure C-7: Temperature on the slurry density (a) and viscosity (b) at different solid concentrations

(a) $C_s = 0 \text{ vol}\%$. $C_s = 5 \text{ vol}\%$. $C_s = 10 \text{ vol}\%$. $C_s = 15 \text{ vol}\%$

(b) $C_s = 0 \text{ vol}\%$. $C_s = 5 \text{ vol}\%$. $C_s = 10 \text{ vol}\%$. $C_s = 15 \text{ vol}\%$
C.4 EFFECT OF SUPERFICIAL GAS VELOCITY

Figures C-8 and C-9 show that increasing the superficial gas velocity does not have a significant effect on either the bubble size volume fraction or the relative bubble frequency, which is an agreement with Figure 5-22, which indicated that the superficial gas velocity did not have a noticeable effect on the gas bubbles size within the experimental conditions used.

(a) Figure C-8: Effect of superficial gas velocity on bubble volume fraction

(b) Figure C-9: Effect of superficial gas velocity on relative bubble frequency
C.5 EFFECT OF GAS DENSITY

Figure C-10 shows that increasing gas density increases the volume fraction of the large (> 30 mm) and small (< 5 mm) gas bubbles, and decreases the volume fraction of the intermediate gas bubbles. Also, Figure C-11 shows that increasing gas density increases the relative frequency of the smallest gas bubbles and decreases the relative frequency of the remaining gas bubble classes. This behavior is primarily due to the effect of gas density on the bubble momentum, where at high gas densities the increased bubble momentum enhances bubble breakup and accordingly the frequency of the large gas bubbles dramatically decreases as shown in Figure C-11.
Figure C-10: Effect of gas density on bubble volume fraction

Figure C-11: Effect of gas density on bubble relative frequency
APPENDIX D

COMPARISON WITH LITERATURE GAS HOLDUP AND SAUTER BUBBLE DIAMETER DATA

Figure 7 shows a comparison between our gas holdup data and available experimental values obtained by numerous investigators under different operating conditions as given in Table 7. As can be observed, the gas holdup data obtained in this work are notably greater than all other data depicted in the figure. This behavior can be attributed to the high pressure values used in this work (15.6 and 20.5 bar), which increased the gas density, momentum, and thus the gas holdup [121]. This behavior is further supported by the behavior of data sets 5 and 6 obtained at lower pressures of 11.7 and 7.5 bar by Behkish et al. [8, 80]. Also, the relatively high gas holdup (data set 8) by Deckwer et al. [75] obtained at 8 bar and 523 K were measured at low gas velocities (0.005-0.03 m/s) and no direct comparison with our data could be made.

The gas holdup (data sets 9 and 15) by Bukur et al. [624-627] obtained at ambient pressure (1 bar) and high temperature (538 K) in 0.05 and 0.21 m ID reactors are greater than those (data set 7) by Behkish et al. [8, 80] and those (data sets 16 and 17) by Krishna et al. [77] obtained under about 1 bar at 298 K. This behavior was expected since increasing temperature decreases the liquid properties (viscosity, surface tension and density), which enhance the gas bubbles breakup, leading
to the formation of numerous small bubbles, thus increasing the gas holdup. As a matter of fact, under 1 bar, Bukur et al. [624-627] reported small bubble diameters between 0.9 to 1.4 mm at 538 K, whereas Behkish et al. [8, 80] reported bubble diameters between 2-3 mm at 400 K. On the other hand, increasing temperature decreases the gas density and its momentum, thus decreasing the gas holdup. It appears that the effect of decreasing liquid properties on the gas holdup was more significant than that of decreasing the gas momentum, since the gas holdup was found to increase with temperature.

Figure 8 shows a comparison between our Sauter mean bubble diameter (d32) and experimental values obtained by Patel et al.[628, 629] and Bukur et al. [624-627, 629] under different conditions as given in Table 8. It should be emphasized that their data were measured under ambient pressure (1 bar) and high temperature (538 K) in different waxes using the Dynamic Gas Disengagement technique in the absence of solid particles. As can be observed in this figure, our (d32) values (data sets 1-6) vary between 0.18 and 6 mm; and the values (data sets 7-10) by Patel et al.,[628, 629] obtained at superficial gas velocities (< 0.12 m/s) in a small diameter column (0.05 m), varied from 0.37 to 5.6 mm. However, d32 vales (data set 11) by Patel et al. [628, 629] and (data set 12) by Bukur et al. [624-627, 629] measured in a 0.23 and 0.21 m diameter columns, respectively, at gas velocities (< 0.12 m/s) were between 0.27 and 1.7 mm. As mentioned above, increasing temperature enhances gas bubbles breakup, leading to the formation of numerous small bubbles; and increasing pressure shrinks further these gas bubbles, leading to small values of d32. On the other hand, increasing solid concentration, increases the slurry viscosity thereby increasing the bubble coalescence and the formation of large bubbles, resulting in high values of d32. Thus, these two opposing effects should dictate the resultant value of the Sauter mean bubble diameter. Based only on the temperature effect, our d32 values were supposed to be greater than those by
Patel et al.[628, 629] and Bukur et al.[624-627, 629] in the large column since our temperature is lower. Also, based on the presence of solids in addition to the higher viscosity of the reactor wax used in this work, our d32 were supposed to be greater than those by these authors. However, the much greater pressure used in this work appeared to suppress the bubble growth and reduce the bubble size, leading to d32 in the range of from 0.18 to 6 mm, which is in agreement with previous findings.[46]
Figure D-1: Comparison of measured gas holdup data with published data sets in the literature
Table D-1: Gas holdup data sets used in the comparison in Figure D-1

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Operating Conditions</th>
<th>Reactor Dimensions</th>
<th>Liquid</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (K)</td>
<td>P (bar)</td>
<td>C_v (wt%)</td>
<td>D_C (m)</td>
</tr>
<tr>
<td>1</td>
<td>This work</td>
<td>461</td>
<td>15.6</td>
<td>20</td>
<td>0.29</td>
</tr>
<tr>
<td>2</td>
<td>This work</td>
<td>443</td>
<td>20.5</td>
<td>34</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>This work</td>
<td>445.9</td>
<td>25.9</td>
<td>20</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td>This work</td>
<td>459.5</td>
<td>20.7</td>
<td>45</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>Behkish et al. [8, 80]</td>
<td>400</td>
<td>11.7</td>
<td>32.8</td>
<td>0.29</td>
</tr>
<tr>
<td>6</td>
<td>Behkish et al. [8, 80]</td>
<td>400</td>
<td>7.5</td>
<td>32.8</td>
<td>0.29</td>
</tr>
<tr>
<td>7</td>
<td>Behkish et al. [8, 80]</td>
<td>298</td>
<td>1.75</td>
<td>41.2</td>
<td>0.316</td>
</tr>
<tr>
<td>8</td>
<td>Deckwer et al. [75]</td>
<td>523</td>
<td>8</td>
<td>16</td>
<td>0.1</td>
</tr>
<tr>
<td>9</td>
<td>Bukur et al. [624-627, 629]</td>
<td>538</td>
<td>1</td>
<td>20</td>
<td>0.21</td>
</tr>
<tr>
<td>10</td>
<td>Bukur et al. [624-627, 629]</td>
<td>538</td>
<td>1</td>
<td>20</td>
<td>0.21</td>
</tr>
<tr>
<td>11</td>
<td>Bukur et al. [624-627, 629]</td>
<td>538</td>
<td>1</td>
<td>20</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Table D-1 (continued)

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Operating Conditions</th>
<th>Reactor Dimensions</th>
<th>Liquid</th>
<th>Solid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T (K)</td>
<td>P (bar)</td>
<td>C_v (wt%)</td>
<td>D_L (m)</td>
<td>H_L (m)</td>
</tr>
<tr>
<td>12</td>
<td>Bukur et al. [624-627, 629]²</td>
<td>538</td>
<td>1</td>
<td>20</td>
<td>0.21</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td>Bukur et al. [624-627, 629]²</td>
<td>538</td>
<td>1</td>
<td>20</td>
<td>0.05</td>
<td>3</td>
</tr>
<tr>
<td>14</td>
<td>Bukur et al. [624-627, 629]</td>
<td>538</td>
<td>1</td>
<td>20</td>
<td>0.05</td>
<td>3</td>
</tr>
<tr>
<td>15</td>
<td>Bukur et al. [624-627, 629]</td>
<td>538</td>
<td>1</td>
<td>20</td>
<td>0.05</td>
<td>3</td>
</tr>
<tr>
<td>16</td>
<td>Krishna et al. [77]</td>
<td>298</td>
<td>1</td>
<td>58.9</td>
<td>0.38</td>
<td>4</td>
</tr>
<tr>
<td>17</td>
<td>Krishna et al. [77]</td>
<td>298</td>
<td>1</td>
<td>59.9</td>
<td>0.38</td>
<td>4</td>
</tr>
</tbody>
</table>

¹Suspension height
²Liquid velocity = 0.005 m/s
Figure D-2: Comparison of measured Sauter bubble diameter data with published data sets in the literature
Table D-2: Sauter bubble diameter data sets used in the comparison in Figure D-2

<table>
<thead>
<tr>
<th>#</th>
<th>Reference</th>
<th>Operating Conditions</th>
<th>Reactor Dimensions</th>
<th>Liquid</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T  (K)</td>
<td>P  (bar)</td>
<td>C_v  (wt%)</td>
<td>D_L  (m)</td>
</tr>
<tr>
<td>1</td>
<td>This work</td>
<td>429.1</td>
<td>14.29</td>
<td>34</td>
<td>0.29</td>
</tr>
<tr>
<td>2</td>
<td>This work</td>
<td>455.9</td>
<td>27.63</td>
<td>45</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>This work</td>
<td>414</td>
<td>14.95</td>
<td>34</td>
<td>0.29</td>
</tr>
<tr>
<td>4</td>
<td>This work</td>
<td>443</td>
<td>27.85</td>
<td>34</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>This work</td>
<td>444.3</td>
<td>21.07</td>
<td>34</td>
<td>0.29</td>
</tr>
<tr>
<td>6</td>
<td>This work</td>
<td>470.8</td>
<td>24.66</td>
<td>20</td>
<td>0.29</td>
</tr>
<tr>
<td>7</td>
<td>Patel et al. [628, 629]</td>
<td>538</td>
<td>1</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>8</td>
<td>Patel et al. [628, 629]</td>
<td>538</td>
<td>1</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td>Patel et al. [628, 629]</td>
<td>538</td>
<td>1</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>10</td>
<td>Patel et al. [628, 629]</td>
<td>538</td>
<td>1</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>Patel et al. [628, 629]</td>
<td>538</td>
<td>1</td>
<td>0</td>
<td>0.23</td>
</tr>
<tr>
<td>12</td>
<td>Bukur et al. [624-627, 629]</td>
<td>538</td>
<td>1</td>
<td>0</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Using the experimental data obtained in the pilot scale SBCR operating with the molten reactor wax, the following parameters can be estimated: (1) overall gas holdup; (2) large and small gas bubble holdups; (3) Sauter mean bubble diameters of large and small gas bubbles; and (4) gases volumetric gas-liquid mass transfer coefficients. The hydrodynamic and mass transfer data obtained in the reactor wax were compared with the predictions of different correlations available in the literature by calculating the average relative error (ARE), the absolute average relative error (AARE) and their associated standard deviations (SD).

### E.1 OVERALL GAS HOLDUP CORRELATION

The overall gas holdup data were compared with the predictions of the available literature correlations are shown in Table E-1. As can be observed in this table, the correlation by Sehabiague and Morsi [81] gives the best prediction closely followed by that of Hammer et al., [630] Joshi et al., [631] Wilkinson et al., [102] and Urseanu et al. [632] The correlation by Sehabiague and Morsi
was further modified as shown in Equation (E-1) in order to enhance the accuracy of the gas holdup predictions as given in Table E-1 and Figure E-1 (a).

\[
\begin{align*}
\varepsilon_g &= 1.235 \times 10^4 \frac{\rho_g^{0.174} u_g^{0.53} \Gamma^{0.053} \left( \frac{P}{P - P_v} \right)^{0.203}}{\rho_L^{1.59} \mu_L^{0.025} \sigma_L^{0.105}} \left( \frac{1 + D_c}{D_c} \right)^{0.117} \\
&\times \exp(-1.5 \times 10^{-4} C_p - 1.78 \times 10^{-6} C_p^2 - 433.9 d_p + 0.434 X)
\end{align*}
\]

(E-1)

<table>
<thead>
<tr>
<th>Reference</th>
<th>ARE</th>
<th>SD (ARE)</th>
<th>AARE</th>
<th>SD(AARE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation (E-1)</td>
<td>-0.9%</td>
<td>9.5%</td>
<td>7.3%</td>
<td>6.1%</td>
</tr>
<tr>
<td>Sehabiague and Morsi [81]</td>
<td>-17.9%</td>
<td>10.1%</td>
<td>18.9%</td>
<td>8.1%</td>
</tr>
<tr>
<td>Hammer et al. (1984) as reported in [630]</td>
<td>-3.0%</td>
<td>20.4%</td>
<td>17.9%</td>
<td>10.2%</td>
</tr>
<tr>
<td>Joshi et al. (1998) as reported in [631]</td>
<td>-9.9%</td>
<td>18.9%</td>
<td>18.9%</td>
<td>9.9%</td>
</tr>
<tr>
<td>Wilkinson et al. [102]</td>
<td>-13.9%</td>
<td>18.5%</td>
<td>20.7%</td>
<td>10.3%</td>
</tr>
<tr>
<td>Urseanu et al. [632]</td>
<td>6.5%</td>
<td>22.9%</td>
<td>19.1%</td>
<td>14.2%</td>
</tr>
<tr>
<td>Krishna et al. [87, 110, 455, 487]</td>
<td>23.6%</td>
<td>19.0%</td>
<td>25.5%</td>
<td>16.4%</td>
</tr>
<tr>
<td>Koide et al. [107]</td>
<td>-56.4%</td>
<td>7.3%</td>
<td>56.4%</td>
<td>7.3%</td>
</tr>
<tr>
<td>Gandhi et al. [631]</td>
<td>-53.7%</td>
<td>11.6%</td>
<td>53.7%</td>
<td>11.6%</td>
</tr>
<tr>
<td>Dharwadkar et al. [633]</td>
<td>66.2%</td>
<td>35.9%</td>
<td>66.2%</td>
<td>35.8%</td>
</tr>
<tr>
<td>Reilly et al. [634]</td>
<td>71.8%</td>
<td>35.4%</td>
<td>71.8%</td>
<td>35.4%</td>
</tr>
<tr>
<td>Akita and Yoshida [83]</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>79.3%</td>
<td>4.7%</td>
</tr>
<tr>
<td>Nedeltchev and Schumpe [461]</td>
<td>85.8%</td>
<td>47.6%</td>
<td>85.9%</td>
<td>47.5%</td>
</tr>
</tbody>
</table>
Figure E-1: Comparison between experimental data and predicted gas holdup values using Equation (E-1)

E.2 SAUTER MEAN DIAMETER OF GAS BUBBLES CORRELATION

Table E-2 shows that the correlations by Fukuma et al. [492] and Wilkinson et al., [635] which were developed for gas-liquid systems, are unable to predict the experimental data in the presence of solids which was not surprising. Similarly, the correlation by Lemoine et al. [179] could not predict the data with acceptable accuracy. Therefore, a more accurate correlation, based on the that of Lemoine et al., [179] is developed to predict the gas Sauter mean bubble diameter for catalyst volumetric concentrations less or greater than 5 vol.% as shown in Equation (E-2).
If $C_v < 5 \text{ vol.}\%$ \quad $d_{32} = 0.213e^{2.81C_v}F$

If $C_v \geq 5 \text{ vol.}\%$ \quad $d_{32} = 0.0574e^{2.9C_v}F$

\[ F = \frac{\mu_L^{0.08} \sigma_L^{1.22} \rho_G^{0.02} T^{1.66} U_G^{0.14}}{\rho_L^{1.52} M \omega_G^{0.12}} \left( \frac{D_C}{D_C + 1} \right) (1 - \epsilon_G)^{1.56} \Gamma^{-0.02} \]  \quad (E-2)

Table E-2: Comparison among predictions of the gas bubbles Sauter mean diameter correlations

<table>
<thead>
<tr>
<th>Reference</th>
<th>ARE</th>
<th>SD(ARE)</th>
<th>AARE</th>
<th>SD(AARE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation (E-2)</td>
<td>-34.9%</td>
<td>22.2%</td>
<td>37.4%</td>
<td>17.7%</td>
</tr>
<tr>
<td>Lemoine et al. [636]</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>Fukuma et al. [492]</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
</tr>
<tr>
<td>Wilkinson et al. [635]</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
</tr>
</tbody>
</table>

E.3 HOLDUP OF LARGE GAS BUBBLES CORRELATION

The data for the holdup of large gas bubbles were compared with the correlations by Behkish et al. [9] and by Krishna et al. [87, 110, 455, 487]. The correlation of Behkish et al. [9] was able to predict the experimental data with reasonable accuracy as shown in Table E-3.

Table E-3: Comparison among predictions of the large gas bubbles holdup correlations

<table>
<thead>
<tr>
<th>Reference</th>
<th>ARE</th>
<th>SD (ARE)</th>
<th>AARE</th>
<th>SD(AARE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Behkish et al. [9]</td>
<td>3.0%</td>
<td>24.8%</td>
<td>15.1%</td>
<td>19.9%</td>
</tr>
<tr>
<td>Krishna et al. [87, 110, 455, 487]</td>
<td>-41.9%</td>
<td>24.5%</td>
<td>42.6%</td>
<td>23.3%</td>
</tr>
</tbody>
</table>
E.4 DIAMETER OF LARGE GAS BUBBLES CORRELATION

The correlation by Krishna et al. [487] proposed for gas-liquid systems could not predict the size of the large gas bubbles, whereas that by Lemoine et al. [636] under predicted the size of large gas bubbles by an average of 93%. The latter correlation was then modified as shown in Equation (E-3) to predict the experimental data with better accuracy as shown in Table E-4.

\[ d_{LB} = d_{32}^{0.78} \left( 1 - 10^{-5} \rho_L^{0.22} \mu_L^{0.03} \sigma_L^{8.6} U_g^{0.04} \varepsilon_G^{2.37} \varepsilon_{LB}^{2.74} \right) \]  \hspace{1cm} \text{(E-3)}

Table E-4: Comparison among predictions of the large gas bubble diameter correlations

<table>
<thead>
<tr>
<th>Reference</th>
<th>ARE</th>
<th>SD (ARE)</th>
<th>AARE</th>
<th>SD(AARE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation (E-3)</td>
<td>0.0%</td>
<td>51.9%</td>
<td>44.2%</td>
<td>27.0%</td>
</tr>
<tr>
<td>Lemoine et al. [637]</td>
<td>-93.0%</td>
<td>5.8%</td>
<td>93.0%</td>
<td>5.8%</td>
</tr>
<tr>
<td>Krishna et al. [487]</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
</tr>
</tbody>
</table>

E.5 VOLUMETRIC MASS TRANSFER COEFFICIENT CORRELATION

The experimental \( k_{L\alpha} \) data obtained in this study were compared with the predictions of different literature correlations shown in Table A-8; and as can be observed in Table E-5, the best prediction was obtained using the correlation by Sehabiague and Morsi,[81] which could predict the experimental data with an ARE of 9.9%. This correlation was further modified in order to increase the prediction accuracy as show in Equation (E-4) and Figure E-1 (b).
\[ k_{La} = 9.34 \times 10^{-6} \frac{\rho_L^{1.82} \rho_g^{0.27} U_g^{0.387}}{M_g^{0.02} \mu_L^{0.25} \sigma_L^{0.976}} \left( \frac{P}{P - P_v} \right)^{0.242} \left( \frac{D_C}{0.3 + D_C} \right)^{0.1} \times \exp \left( -8 \times 10^{-9} C_p^3 - 1.6 \times 10^{-6} C_p^2 - 0.8 C_p + 1675.7 d_p + 0.176 X \right) \] 

(E-4)

Figure E-2: Comparison between experimental data and predicted \( k_{La} \) values using Equation (E-4)

Table E-5: Comparison among predictions of \( k_{La} \) correlations

<table>
<thead>
<tr>
<th>Reference</th>
<th>ARE</th>
<th>SD (ARE)</th>
<th>AARE</th>
<th>SD(AARE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation (E-4)</td>
<td>0.0%</td>
<td>14.0%</td>
<td>11.1%</td>
<td>8.5%</td>
</tr>
<tr>
<td>Sehabiague and Morsi [81]</td>
<td>-9.9%</td>
<td>22.0%</td>
<td>20.7%</td>
<td>12.4%</td>
</tr>
<tr>
<td>Koide et al. [107]</td>
<td>-16.2%</td>
<td>27.4%</td>
<td>28.2%</td>
<td>14.6%</td>
</tr>
<tr>
<td>Nedeltchev and Schumpe [461]</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
<td>&gt;100%</td>
</tr>
</tbody>
</table>
E.6 NOVEL APPROACH AND CORRELATION FOR BUBBLE SIZE DISTRIBUTION IN THE SBCR OPERATING IN THE CHURN- TURBULENT FLOW REGIME

Over the past four decades, significant work has been done to investigate the hydrodynamics in bubble columns and SBCRs, and numerous correlations were developed for predicting the gas holdup, average bubble size, bubble rise velocity and axial dispersion coefficients, as recently summarized by Basha et al. [2]. However, investigating the bubble size distribution in bubble columns and SBCRs has been limited, despite its importance in developing proper closure models for numerical modeling as well as CFD simulation.

Previous 1-D and 2-D modeling efforts investigating bubble columns and SBCRs have frequently used the “two-bubble” or bimodal class model, which is based on convective and dispersive mechanisms [244, 638], in order to account for gas bubbles representation [155, 301, 350]. This model represents an oversimplification of the complex hydrodynamics inside the two-phase and three-phase reactors. In this model, the gas bubbles are classified into small bubbles, which are primarily controlled by the liquid- or slurry-phase motion, and large bubbles, which are independent of the liquid or slurry motion as they flow upwards in a plug-flow manner. The demarcation size of the gas bubbles classified as small has been always arbitrary.

The validity of two-bubble class model in describing the gas bubbles behavior, however, appeared to be questionable due to the fact that actual results for gas bubbles did not follow a bimodal size distribution, as demonstrated by numerous investigators [144, 145, 243, 639-642]. Also, the bimodal gas bubble distribution fails to explain the enhanced gas-phase mixing with increasing the superficial gas velocity. This is because this model assumes that the increase of the volume fraction of large gas bubbles leads the gas mixing to approach a plug-flow, which
contradicts the reported experimental data [266, 643, 644]. Therefore, there is a great need to
develop a novel model for bubble size distribution, which should enable more accurate
representation of the different gas bubble classes inside the SBCR.

The current practice to determine the size of gas bubbles in bubble column and SBCRs is
to employ the DGD technique coupled with the correlation relating the bubble rise velocity to the
bubble diameter by Fukuma et al. [622]. In this DGD technique, the disengagement profiles, which
have been studied by various authors [8, 111, 645, 646], have been characterized by two straight
lines, where the first line represents the disengagements of the large gas bubbles and some of the
small bubbles, and the second line represents the disengagement of the small gas bubbles. It should
be pointed out, however, some of the small gas bubbles disengage within the fast bubble flow
region and some are hindered by the disengagement of the large bubbles; and the bubble rise
velocity obtained from DGD is actually the swarm rise velocity associated with the class of gas
bubbles disengaging during a given period. Thus, it is important to differentiate between the swarm
properties and the gas bubble properties in order to accurately determine the bubble size
distribution in the DGD process.

Schumpe and Grund [185, 453] reported some of the uncertainties and problems associated
with the DGD technique. These included: (1) the subjectivity involved in obtaining an accurate
disengagement profile during large gas bubbles disengagement, (2) the waterfall effect or the
downward flow of liquid during bubble disengagement and its impact on the rise velocities of the
small gas bubbles, which are still in the liquid-phase, and (3) the errors introduced by the bubbles
entering the dispersion zone as the pressure in the plenum chamber equilibrates with the
hydrostatic pressure in the reactor after the interruption of the feed gas. In addition, in a strongly
coalescing or highly turbulent flow regime, the assumptions that there are no bubble-bubble
interactions and that the dispersion is axially homogenous at the moment when the gas flow is
interrupted are not entirely accurate. It is important to note that in the coalescing flow regime, the bubble-bubble interactions play a significant role in bubbles formation, a behavior which is oversimplified with the assumption of a bimodal bubble size distribution. Furthermore, it should be mentioned that the correlation by Fukuma et al. [622] was developed using an air-tap water system in the presence of glass beads at ambient conditions. The glass beads used had diameters from 0.056 to 0.46 mm and exhibited solid concentrations between 13 and 50 vol.%. This brings into question the extrapolation of such a correlation to predict the bubble rise velocity and consequently the bubble diameters in SBCRs, operating under high-pressures and high-temperatures.

In this study, in order to delineate the bubble size distributions from the DGD technique, we define a minimum stable bubble size based on the assumptions that turbulences are isotropic and that bubble breakup mainly occurs due to the collision of eddies with the gas bubbles in the turbulent flow regime. We also assume that only eddies of length-scale ≥ the bubble diameter would contribute to the bubbles breakup, while small eddies would transport the bubbles without breakup. This latter assumption is based on the statistical derivation of Prince and Blanch [348], which indicated that smaller eddies are unlikely to significantly contribute to the bubble breakup, due to their comparatively insignificant momentum when compared with that of large bubbles.

The smallest hydrodynamic eddy length-scale at which the energy is dissipated in turbulent flow, referred to as the Kolmogorov’s length-scale, is used to represent the minimum stable bubble size, which is expressed by Equation (E-5):

\[ l_{min} = d_{b, min} = \left( \frac{D_c H_{sturr}^3}{\rho_{sturr}^3 U_G^3} \right)^{0.25} \]  \hspace{1cm} (E-5)

Also, the semi-empirical correlation by Luo et al. [472] for high-pressure SBCRs is used to represent the maximum stable bubble size as shown in Equation (E-6):
\[ d_{b,\text{max}} = 2.53 \left( \frac{\sigma_{\text{liquid}}}{g \rho_G} \right)^{0.5} \] 

(A-E-6)

A typical DGD pressure-drop-time relationship, corresponding to the gas bubbles leaving the DGD cell (length), is shown in Figure E-3 for three different runs. The increase of the pressure drop at any time \( t \) is due to the disengagement of bubbles from the DGD cell.

![Figure E-3: Pressure drop change with time as obtained from three DGD experiments](image)

Our novel approach considers the overall energy balance within the gas disengagement cell. During the DGD process, the pressure drop measured is primarily due to the change in the overall density within the DGD cell. In order to write the energy balance on the DGD cell, the following assumptions are made:
1. There is no dissipation of mechanical energy.

2. The bubble rise velocities, which is dependent on the bubble diameter, will determine which bubbles will disengage first. This means that at a given time \( t \), only a single bubble class will disengage from the DGD cell, with the largest bubbles disengaging first.

3. The gas bubbles disengage from the top of the DGD cell in the axial direction at a 0° angle.

Considering these assumptions, the energy balance on the DGD cell requires that the energy lost from the cell should be equivalent to that gained by the bubbles leaving the cell, as expressed in Equation (E-7).

\[
dP \cdot (V_{DGD-cell}) = (\Delta H_{DGD-cell}) \sum n_{b,i} F_{b,i} \tag{E-7}
\]

Where \( F_{b,i} \) refers to the force applied on the number of disengaging bubbles of class \( i \) \( (n_{b,i}) \).

The overall force balance on one spherical bubble (assuming no bubble deformation) with a constant bubble rise velocity \( (U_{b,i}) \) throughout the disengagement cell, is expressed using Equation (E-8):

\[
\sum F_{b,i} = F_{Buoyancy} + F_M - F_D - F_{VM} - F_{Basset} - F_C - F_G \tag{E-8}
\]

Where \( F_D \) is the liquid drag; \( F_{Basset} \) is the Basset force, \( F_{Buoyancy} \) is the buoyancy force; \( F_C \) is the particle collision; \( F_{VM} \) is the virtual mass force, \( F_M \) is the force due to bubble momentum and \( F_G \) is the gravity. The description of each force is given in Table E-6.
Table E-6: Forces involved in the overall energy balance for the gas bubble [272, 323, 336, 351, 372, 647]

<table>
<thead>
<tr>
<th>Force</th>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_D$: Drag</td>
<td>$C_D = \begin{cases} \left( \frac{24}{Re_b} \right) (1 + 0.15 Re_b^{0.687}) &amp; \text{Re}_b &lt; 10^3 \ 0.44 &amp; \text{Re}_b \geq 10^3 \end{cases}$</td>
<td>Force accounting for the fluid resistance, acting opposite to the relative motion of the bubbles. The drag coefficient of Schiller and Naumann was used [6].</td>
</tr>
<tr>
<td>$F_{VM}$: Virtual Mass</td>
<td>$\frac{\pi}{12} \rho_{slurry} d_b^3 \frac{U_G}{\Delta t}$</td>
<td>Accounts for the resistance of the fluid mass that is moving at the same acceleration as the particle. It is assumed that the liquid velocity is insignificant compared to the gas velocity, $\Delta t$ was taken to be 0.05 s.</td>
</tr>
<tr>
<td>$F_{Basset}$: Basset</td>
<td>$3 \frac{d_b^3}{2} (\pi \rho_{slurry} \mu_{slurry})^{0.5} \frac{U_b}{(\Delta t)^{0.5}}$</td>
<td>Additional drag due to vortices formed by bubble acceleration [648], $\Delta t$ was taken to be 0.05 s.</td>
</tr>
<tr>
<td>$F_{Buoyancy}$: Buoyancy</td>
<td>$\frac{\pi}{6} d_b^3 (\rho_{slurry} - \rho_G) g$</td>
<td>Upward force exerted by the slurry on the bubble.</td>
</tr>
<tr>
<td>$F_G$: Gravity</td>
<td>$\frac{\pi}{6} d_b^3 \rho_G g$</td>
<td>Force due to gravity</td>
</tr>
<tr>
<td>$F_C$: Particle Collision</td>
<td>$\frac{\pi}{4} d_b^2 \varepsilon_s U_G^2 \rho_s$</td>
<td>Force imparted due to collision with solid particles [242]</td>
</tr>
<tr>
<td>$F_M$: Bubble Momentum</td>
<td>$\frac{\pi}{4} d_b^2 \rho_G U_b^2$</td>
<td>Accounts for the bubble momentum as it rises throughout the column.</td>
</tr>
</tbody>
</table>

The solution of Equation (E-8) was carried out under the constraints given in Equations (E-9) through (E-12).

$$\sum F_{b,i} = \mu_G \left( \frac{\pi d_{b,i}^3}{6} \right) \frac{U_{b,i}}{\Delta t}$$ (E-9)
\[ V_{G,i} = \varepsilon_{G,i} V_{DGD-cell} = n_{b,i} \left( \frac{\pi d_{b,i}^3}{6} \right) \] (E-10)

\[ d_{b,\text{min}} \leq d_b \leq d_{b,\text{max}} \] (E-11)

\[ d_{b,i} \big|_t > d_{b,i} \big|_{t+\Delta t} \] (E-12)

It is important to note that in order to successfully use this novel method, the gas holdup for each bubble class is required, which can be simultaneously determined from the gas disengagement profile while performing the DGD experiments, as described in Sections 5.3 and 5.4.

When substituting the forces given in Table E-6 into the right-hand-side of Equation (E-8) and inserting it into Equation (E-7), the energy balance leads to a cubic equation of \( d_{b,i} \), which can be used to identify the single bubble size and the number of bubbles for every bubble class disengaging at any time \( (t) \).

In this study, this novel method was followed to calculate the number of bubbles for every bubble diameter between the minimum and maximum stable sizes calculated using Equations (E-5) and (E-6), with increments of 0.5 mm. It should be mentioned that a single bubble diameter \( (d_{b,i}) \) and number of bubbles \( (n_{b,i}) \) were obtained for the majority of the experimental data. In a few cases, however, multiple solutions were found and the values, which were more in line with the rest of the data at similar operating conditions, were selected. The volume fraction of each bubble size was then calculated using Equations (E-13) and (E-14), whereas the relative frequency of each bubble size was determined using Equation (C-4).

\[ Volume \ space \ fraction_{b,i} = \frac{\sum_{d_{b,\text{min}}}^{d_{b,\text{max}}} n_{b,i} V_{b,i}}{V_{G,\text{total}}} \] (E-13)

\[ V_{b,i} = \frac{\pi (d_{b,i} - 0.5 \cdot \Delta d_b)^3}{6} \] (E-14)

Where \( \Delta d_b = 0.5 \text{ mm} \) in this work.
Figures 5-22 and 6-14 show the calculated volume fraction and relative frequency as a function of the bubble diameter at different operating conditions, respectively.

Figure E-4: Bubbles volume fraction distributions from the DGD under different operating conditions.
As can be seen in these figures, the bubbles volume fraction and relative frequency distributions at each set of operating conditions (T, P, C_s, and ρ_g) can be represented using a probability distribution function, as shown in Equation (E-15).

\[
f(d_{b,i}|d_{b,avg},\beta^2)|_{T,P,u_G} = \frac{1}{\sqrt{2\beta^2\pi}} e^{-\left(\frac{(d_{b,i}-d_{b,avg})^2}{2\beta^2}\right)}
\]  

(E-15)
Where \( f(d_{b,i}|d_{b,avg}, \beta^2) \bigg|_{T,P,u_g} \) is the relative frequency of a bubble class \( i \) with a diameter \( (d_{b,i}) \) at a certain set of operating conditions \((T, P, u_g)\); \( d_{b,avg} \) is the arithmetic mean of the bubble sizes obtained from a given DGD data set at fixed pressure, temperature and gas velocity; and \( \beta^2 \) is the variance. It should be remembered that the variance represents the spread of the distribution, where a small variance indicates that the bubble distribution is close to the arithmetic mean, whereas a large variance indicates that the bubble distribution spreads far away from the arithmetic mean.

The experimental DGD data obtained in the pilot-scale SBCR for the gas-liquid solid systems discussed in Sections 6.1.1 to 6.1.3 along with those for paraffins mixture-Puralox alumina, reactor wax-iron oxide, and reactor wax-alumina obtained also in the SBCR [8, 46, 81, 637, 649] were used to correlate the arithmetic mean bubble size and the variance as a function of the operating conditions used in each run. A total of 772 DGD experiments were used to develop the correlations of the arithmetic mean bubble size and the bubble size variance, which are given in Equations (E-16) and (E-17), respectively.

\[
d_{b,avg} = 2.03\times10^{-3}\frac{\mu_{slurry}U_G^{0.885}(\rho_{slurry} - \rho_G)^{2.05}}{\rho_{slurry}^{1.13}\sigma_{liquid}^{4.07}} \quad (E-16)
\]

\[
\beta^2 = 1.27\times10^{-3}\left(\frac{Re^{0.0358}Eö^{0.494}}{We^{0.0198}}\right) \quad (E-17)
\]

The definition of the dimensionless numbers, \( Re \), \( We \) and \( Eö \) used in these correlations are given in Equations (E-18) through (E-20).

\[
Re_b = \frac{\rho_{slurry}U_G d_b}{\mu_{slurry}} \quad (E-18)
\]

\[
We = \frac{\rho_{slurry} d_b U_G^2}{\sigma_{liquid}} \quad (E-19)
\]
\[ \text{Eö} = \frac{g(\rho_{\text{slurry}} - \rho_G)d_B^2}{\sigma_{\text{liquid}}} \]  \hspace{1cm} (E-20)

It should be mentioned that these correlations can only be used within the following ranges:

\begin{align*}
48 & \geq Re_b \geq 1305 & \quad 660 & \geq \rho_{\text{slurry}} \text{ (kg/m}^3\text{)} \geq 1155 & \quad 4.1 & \geq P \text{ (bar)} \geq 31.9 \\
0.2 & \geq We \geq 31.5 & \quad 9 & \geq \sigma_{\text{liquid}} \text{ (mN/m)} \geq 27 & \quad 323 & \geq T \text{ (K)} \geq 531 \\
0.05 & \geq E\text{o} \geq 143 & \quad 1.7 & \geq \rho_G \text{ (kg/m}^3\text{)} \geq 23.4 & \quad 0 & \geq C_s \text{ (vol. %)} \geq 15.2 \\
0.2 & \geq \mu_{\text{slurry}} \text{ (mPa} \cdot \text{s)} \geq 24 & \quad 0.05 & \geq U_G \text{ (m/s)} \geq 0.29
\end{align*}

The calculated arithmetic mean bubble size and variance are plotted in Figures 12-6 and 12-7 with an absolute average relative errors (AARE) of 9.49% and 5.87%, respectively.

As can be deduced, Equation (E-15), coupled with Equations (E-16) and (E-17) can be used to calculate the bubble size distribution inside the pilot-scale SBCR available in our laboratory at elevated pressures, temperatures and different gas velocities. Therefore, our novel approach overcomes the problems associated with the oversimplified method adopted when using the DGD technique data as reported by numerous investigators [144, 155, 306, 312, 348, 461, 623, 650].
Figure E-6: Comparison between experimental and predicted values of the mean bubble diameter

AARE: 9.49%
In addition, the predicted values of $f(d_{b,i})$ and $d_{b,i}$ using Equations (E-15), (E-16) and (E-17) were used to calculate the Sauter mean bubble diameter with Equation (E-21) using the experimental data obtained in this study and those obtained for different gas-liquid-solid systems under various operating conditions inside the same pilot-scale SBCR [8, 46, 81, 637, 649, 651].

$$d^{32} = \frac{\sum_i f(d_{b,i})d_{b,i}^3}{\sum_i f(d_{b,i})d_{b,i}^2}$$  \hspace{1cm} (E-21)

The calculated values using Equation (E-21) are plotted in Figure E-8; and as can be observed in this figure, the novel method is capable of predicting the Sauter mean bubble diameter with an absolute average relative error (AARE) of 8.87%. This is a significant improvement over
our initial correlation [651], Equation (E-22), which employed the equation by Fukuma et al. [622] to predict the intermediate bubble sizes. It should be noted that Equation (E-22) was able to predict the experimental data with an AARE of 37.4%, which was an improvement when compared with other commonly used correlations available in the literature [492, 635], as highlighted by Sehabiague et al. [651].

\[
d_{32} = 0.213e^{2.81c_s}F \quad \text{if } C_s < 5 \text{ vol. } \%
\]

\[
d_{32} = 0.0574e^{2.9c_s}F \quad \text{if } C_s \geq 5 \text{ vol. } \%
\]

\[
F = \frac{\mu_{\text{liquid}}^{0.08} \sigma_{\text{liquid}}^{1.22} \rho_G^{0.02} T^{1.66} U_G^{0.14} D_c}{\rho_{\text{liquid}}^{1.82} M_W^{0.12}} \left( \frac{D_c}{D_c + 1} \right)^{0.3} (1 - \epsilon_G)^{1.56} (\Gamma^{-0.2})
\]  

(E-22)

Figure E-8: Comparison between experimental and predicted values of the Sauter bubble diameter using Equation (E-21)
REFERENCES


L. Sehabiague, R. Lemoine, A. Behkish, Y. J. Heintz, M. Sanoja, R. Oukaci, and B. I. Morsi, "Modeling and optimization of a large-scale slurry bubble column reactor for


