

**Process Intensification via Batch-to-Continuous Transition: Acquisition of Robust  
Reaction Kinetics for the Production of Dispersants**

by

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# **Process Intensification via Batch-to-Continuous Transition: Acquisition of Robust Reaction Kinetics for the Production of Dispersants**

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University of Pittsburgh, 2019

Transition from batch to continuous processing promises strong improvements via reduced energy demand, resource consumption, waste production, and physical footprint of the plant — so-called “process intensification”. This transition has been already demonstrated in the pharmaceutical industry but is largely lacking to-date for the—much larger scale—specialty chemicals industry. A critical step in this transition is the acquisition of robust and accurate reaction kinetics, which are typically poorly understood (if known at all) for conventional batch processes.

In this work, a detailed kinetic investigation of the kinetics for succinimide dispersants production via amination of polymeric anhydrides was conducted in a small laboratory-scale batch reactor using online IR spectroscopy as the analytical tool. The use of a small batch system enables the acquisition of large amounts of data through measurement of long concentration time traces, thus facilitating the acquisition of robust kinetics. MATLAB was used to fit the experimental data and deduce robust reaction kinetics. We found that the reaction kinetics could be described by a two-step mechanism, and that the kinetics of each reaction step could be determined separately in different temperature windows. In this way, we were able to obtain the first robust reaction kinetics for this reaction system. This work can be further applied to simulate the kinetics for a family of related lubricant chemistries by varying feed and operating conditions (temperature, feed ratio, etc.) and thus provides a strong support for the design of a continuous processing system.

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## Preface

I sincerely thank to my academic supervisor Dr. Götz Vesper and all my group members especially Edmund Sam-Gyandoh and Nasser Al Azri for their direct help and guidance on my study and research. I thank to Dr. Robert M Enick and Cliff Kowall for all their contribution to the project. I also thank to the committee of my thesis defense, Dr. Götz Vesper, Dr. Robert M Enick, and Dr. Lei Li, for their suggestions on my thesis. I thank to all the faculties and students who have helped me on my graduate study. I need to thank to our department and our university because of the good research and study environment. And I should thank to all financial supports of our group especially Lubrizol and RAPID without which we cannot finish the project smoothly. Finally, a special acknowledgement needs to be made to my fiancée, Congyue Wu, for all her supports during the time I prepared this thesis.

## **1.0 Introduction**

### **1.1 Process Intensification**

“Process intensification (PI) targets dramatic improvements in manufacturing and processing by rethinking existing operation schemes into ones that are both more precise and efficient.” [1] PI involves combining separate unit operations such as reaction and separations into a single piece of equipment with advanced reactor design [2], which provides the opportunities to run a more efficient, cleaner, and economical manufacturing process. PI technologies can significantly enhance the mixing on molecular level and thus improves mass and heat transfer, reaction kinetics, yields, etc. [1]

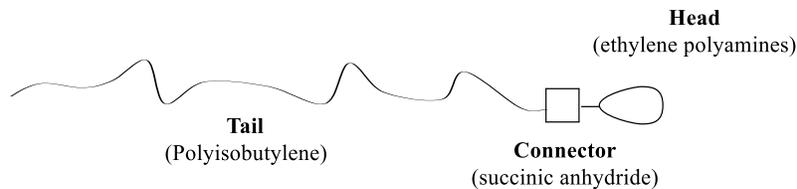
Transition from batch to continuous processing, as one of the most important application of process intensification, promises strong improvements via reduced energy demand, resource consumption, waste production, and physical footprint of the plant. This transition has been already well demonstrated in the pharmaceutical industry [3] and significant reduction of materials can be achieved with appropriate feedback control. [4, 5] However, due to various reasons including the historical popularity of batch operations, the well-established regulatory framework for quality control of products and the difficulties of continuous processing, [6] this transition is largely lacking to-date for the – much larger scale – specialty chemicals industry. A critical step in this transition is the acquisition of robust and accurate reaction kinetics, which are typically poorly understood (if known at all) for conventional batch processes. The ultimate objective of this work is to transform a large batch (about 50k gallons) reaction system to a much smaller continuous tubular (about 30 gallons) reaction system with the same or even higher production

efficiency. Appendix Figure 1 shows a visual comparison of both the reaction systems and a normal human. It is obvious that this transition dramatically reduces the footprint of the production system. Additionally, as another direct and significant benefit, this project will be able to reduce the cost in order of magnitude as well.

## **1.2 Dispersant Chemistry**

Since the 1950s, dispersants have been studied and used as oil additives, with fundamental motivation to improve engine oil performance by ensuring decrease in fuel consumption, pollution emission and soot aggregation. Dispersant also has the eminent ability to bind this soot (carbon rich particles) and hold them in suspension, forming a thickened sludge that prevents flow and premature engine wear. [7-9] Soot typically results from incomplete oxidation of fuel after ignition, over-fueling, improper functioning of a coke mechanism or a failed oxygen sensor with the environment of the car engine.

Figure 1 shows a typical molecular structure of the dispersant. Dispersant molecular contains ethylene polyamine as a polar “head” and a long non-polar polyisobutylene “tail”, while in between the “head” and “tail”, succinic anhydride works as the connector. The polar “head” of the dispersant can attach with the contaminants like soot, while the non-polar “tail” has a good solubility in the engine oil. This structure ensures the ability of dispersant to evenly disperse contaminants in engine oil and prevent the attachment of solid contaminants to the inside wall of engine so that the engine can be well protected. Appendix Figure 2 shows a typical composition of engine oil and dispersant is the main component of additives to engine oil.



**Figure 1 Dispersant structure**

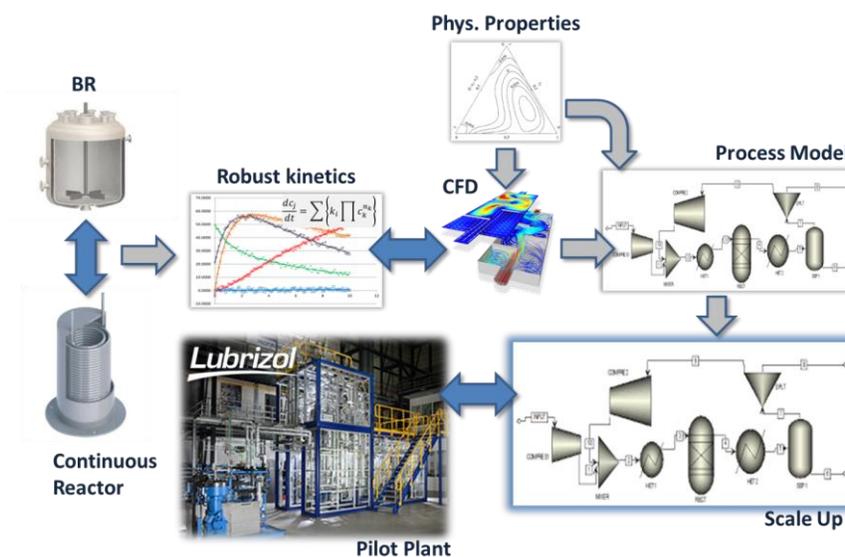
There are various forms of dispersants across industry, typically produced with various materials through batch and semi-batch processes for mostly economic purposes, with little to no knowledge of the kinetics of the reactions system(s). This work, however, focuses on the fundamental understanding of the kinetics of dispersants (succinimide products) produced from the reaction of polyisobutylene succinic anhydride (PIBSA) with various “light and heavy” amines. Reactions are conducted in organic solvents and a complete family of dispersants, aiming to accommodate different kinds of contaminants, are made by varying molecular weight of PIBSA, structure of polyamine, and stoichiometric ratio of the various reactants.

### 1.3 Approach

This project is a close collaboration between the university and our industry partner. The overall approach of the transition from batch to continuous processing of dispersant chemistry can be illustrated by Figure 2.

As shown in the figure, first, robust kinetics of the reaction need to be obtained via lab-scale batch (BR) or continuous reactors. Detailed kinetics for the dispersant chemistry is poorly defined because they are usually not needed to operate the batch processing. However, these kinetic data are critical because they are the initial input of the following process modeling work as well as the design of the continuous reactor. By applying reaction kinetics and physical

properties of the materials to the process modeling software (CFD modeling was applied in this project), behaviors of the process in the system can be well understood. After that, ASPEN modeling can help with the reaction scale-up to provide sufficient parameters for the design of pilot-scale equipment. Finally, all the research results will be sent to the pilot plant for further tests and modifications.



**Figure 2 Approach**

This thesis demonstrates the basic but very important step of the approach – kinetic data acquisition. In this work, a detailed kinetic investigation of the kinetics for succinimide dispersants production via amination of polymeric anhydrides was conducted in a small laboratory-scale batch reactor using online IR spectroscopy as the analytical tool. The use of a small batch system enables the acquisition of large amounts of data through measurement of long concentration time traces, thus facilitating the acquisition of robust kinetics. MATLAB was used to fit the experimental data and deduce robust reaction kinetics.

## 2.0 Methodology

### 2.1 Reaction Mechanism

The reaction system follows a proposed two-step mechanism as shown above in Figure 3: the amination and dehydration steps. In the amination step, polyamine reacts with succinic anhydride ring of PIBSA via a ring opening process to form amide as the intermediate. Amination reactions, due to the formation of C-N bonds, are highly exothermic [10, 11] and usually react very fast. The dehydration step, which is basically a ring closing reaction and was reported as an endothermal reaction. [12, 13] This step undergoes a much slower reaction rate and needs a relatively high temperature. Amide transforms to succinimide, which is the final product, by the second step. The two-step mechanism was determined both with specialists in our industry partner and the IR trends obtained from experiments.

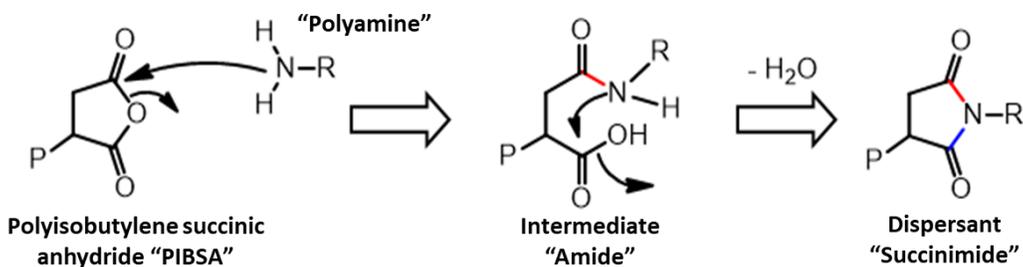


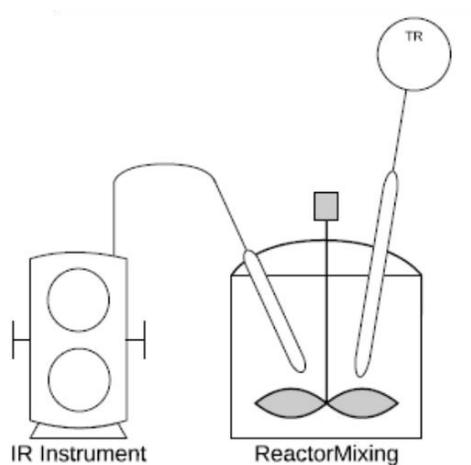
Figure 3 Reaction mechanism

At the beginning of this work, an industrial process was reproduced in lab to determine the process. Lab-scale batch reactor (BR) kinetic experiments quickly identified an unexpected feature of the reaction kinetics at higher temperatures. The reaction proceeds with rapid consumption of PIBSA (within 30 seconds) and conversion to the final imide with little build-up of intermediate

amide observed at temperature ranging from 100°C to 150°C, rendering determination of full and full reaction kinetics for the two-step reaction unreliable rather challenging. In order to circumvent this problem, the initial amination step was successfully decoupled from the dehydration step at temperatures below -10°C. No trace of succinimide product was observed at this low temperature which confirmed that the dehydration step was completely frozen.

## 2.2 Experimental Set-Up

As the second reaction step can be completely prevented at very low temperatures, kinetics of each reaction step was determined separately in different temperature windows.



**Figure 4 Experimental set-up**

To obtain robust kinetics, a small lab-scale batch system was built as illustrated in Figure 4. The batch reactor was equipped with a thermometer, an impeller and a heating jacket. Different reactors connected to a heating circulator (temperature: 100°C to 150°C) or a chiller (temperature: -10°C to -22°C) were applied to gain kinetics of the two reaction steps separately.

(As shown in Appendix Figure 3) Specially, an extra baffle was added to the low-temp reactor to increase the mixing efficiency because the materials are having a very high viscosity even at a relatively low concentration.

For the IR instrument, Mettler Toledo ReactIR 15 with AgX 6mm × 1.5 fiber (Silver Halide) as probe interface and DiComp(Diamond) for Probe tip was used to monitor the reaction process and acquire IR signals. The matched software iC IR 7.0 was used to treat and trace the IR data.

Numerical analysis was done using MATLAB from MathWorks. Non-Linear least square regression (based on known MATLAB inbuilt function “lsqnonlin”) and reaction models (based on inbuilt MATLAB ode45 and ode15s functions) was developed by the research group and used.

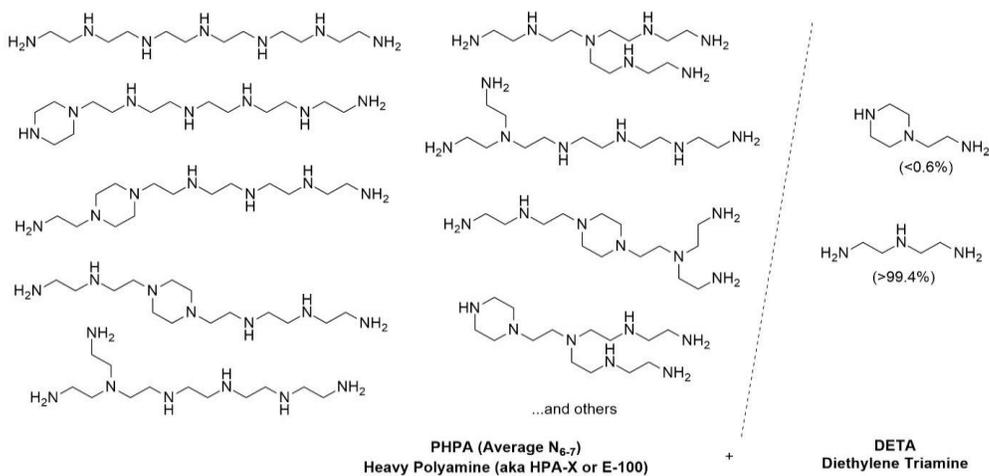
### **2.3 Materials**

1000 and 2000 molecular weight (MW) polyisobutylene succinic anhydride (PIBSA), mineral oil (colorless liquid, C20 to C30 hydrocarbons from oil refining), and heavy polyamines (PHPA and DBDA) were obtained from industrial partner and used as received. Diethylenetriamine (DETA 99%), hexylamine, dibutyl amine, octadecyl amine and dioctadecyl amine were obtained from Sigma Aldrich and used as received (structure of the last 4 amines can be found in Appendix Figure 6). Stoddard solvent (a mixture of aliphatic and alicyclic C7 to C12 hydrocarbons) was obtained from Fisher Scientific and used as received.

PIBSA with different molecular weights have the same succinic anhydride head but with different length of polyisobutylene (PIB) tails

For the high-temp experiments, mineral oil was used as solvent with the same dilution as the recipe from our industrial partner. While for low temperature experiments, Stoddard solvent was used to reduce the viscosity of the materials. A higher dilution was applied to low-temp experiments to further reduce the viscosity as well. Both solvent effect and dilution effect were tested and determined that the change of solvent and dilution would not affect the kinetics. (Appendix Figure 4 & 5)

DBDA, the industrial feed, is a mixture of 85 w% PHPA and 15w% DETA (Figure 5). DETA is a pure compound while PHPA is still a mixture of polyamines. In order to better define the kinetics, the reaction between PIBSA and DBDA was deconvoluted into two separate reactions for the acquisition of kinetic data: PIBSA+PHPA and PIBSA+DETA.



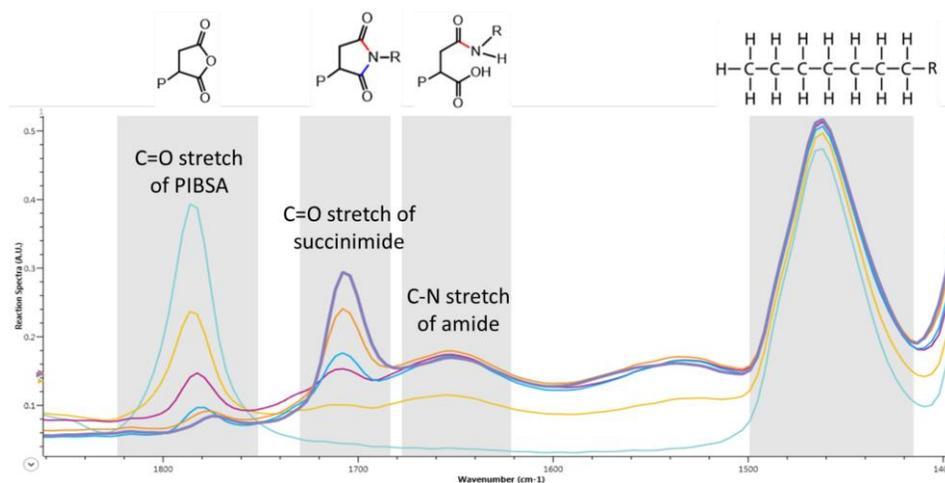
**Figure 5 DBDA composition**

As PIBSA and polyamines are all mixtures, it is impractical to determine the real molar amounts of the molecules. Instead, the analytical tool can give an “equivalent” amount of the main groups in the materials (i.e. CO group in PIBSA and N in amine). So, the “equiv” was used as the unit of amount for all concentration curves and kinetics fitting and CO and N equivalent amount

were used to represent PIBSA and polyamine amount in the system. The feed of PIBSA and polyamines were determined by N:CO equivalent amount ratio as well.

## 2.4 IR Analysis

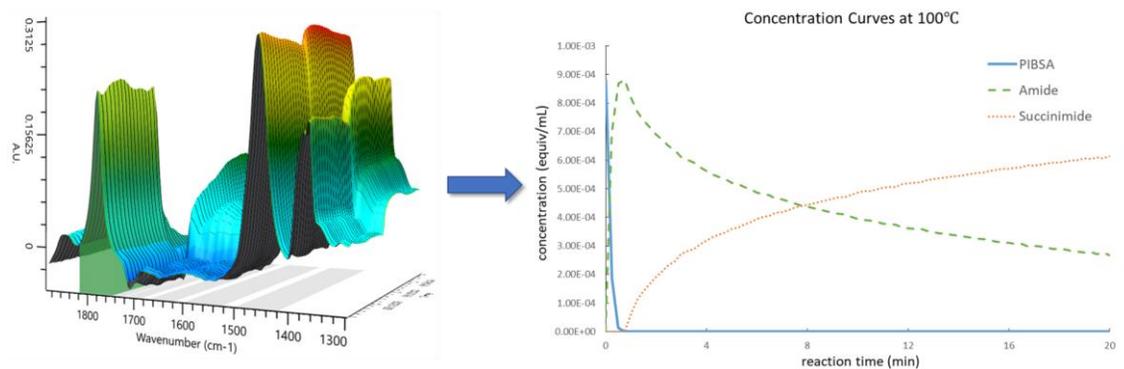
To use IR instrument as an analytical tool, the spectrum of the reaction process was first analyzed. Based on the fundamental knowledge of IR spectrum, the peak changing trend and the analyzing tools in the iC IR 7.0 software, significant IR peaks was assigned to represent bond stretches of different components in the process.



**Figure 6 IR spectrum**

As shown in Figure 6, Peak at  $1786\text{cm}^{-1}$  was assigned to be the C=O bond stretch in PIBSA. Peak at  $1708\text{cm}^{-1}$  was assigned to be the C=O bond stretch in succinimide. Peak at  $1650\text{cm}^{-1}$  was assigned to be the C-N bond stretch in amide. Peak at  $1462\text{cm}^{-1}$  was assigned to be the C-H bond stretches in the PIB tail of PIBSA. This peak almost doesn't change and was just used for reference.

The assigned IR peaks can be traced by the continuous in-situ IR instrument. Based on Beer-Lambert's Law, the peak area is proportional to concentration. Thus, the concentration vs time plots can be obtained by converting the IR peak changing trends. (As shown in Figure 7)



**Figure 7 IR trends**

### 3.0 Results

#### 3.1 Kinetics of the reaction

As shown in Figure 3, the reaction undergoes two steps. From the kinetics view, based on chemistry knowledge, the first step (amination) is irreversible and involves both PIBSA and amine as reactants, while the second step (dehydration) is a reversible reaction and amide becomes succinimide and water in this step. The rate law should be expressed as the following equations:

$$r_1 = k_1[PIBSA]^\alpha[amine]^\beta$$

$$r_2 = k_{2f}[amide]^\gamma - k_{2r}[succinimide]^\lambda[H_2O]^\omega$$

In these equations,  $r_1$  and  $r_2$  represent the rate of the two steps separately;  $k_1$  is the rate constant of the amination step;  $k_{2f}$  and  $k_{2r}$  separately represent the rate constant of the forward and reverse reactions in the dehydration step.  $[component]$  represent the concentration of the main functional group in each component and the unit is equiv/mL.  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\lambda$ ,  $\omega$  are all reaction orders of each component.

Considering the situation in batch system, when operating the dehydration step, the temperature range is 100°C to 150°C and the head space of batch is open to atmosphere. The water produced in this step is actually removed to the head space and hence will not participate in the reverse reaction. So the revised second step rate law should just be:

$$r_2 = k_2[amide]^\gamma$$

In kinetic fitting of this work,  $k_i$  was expressed as:

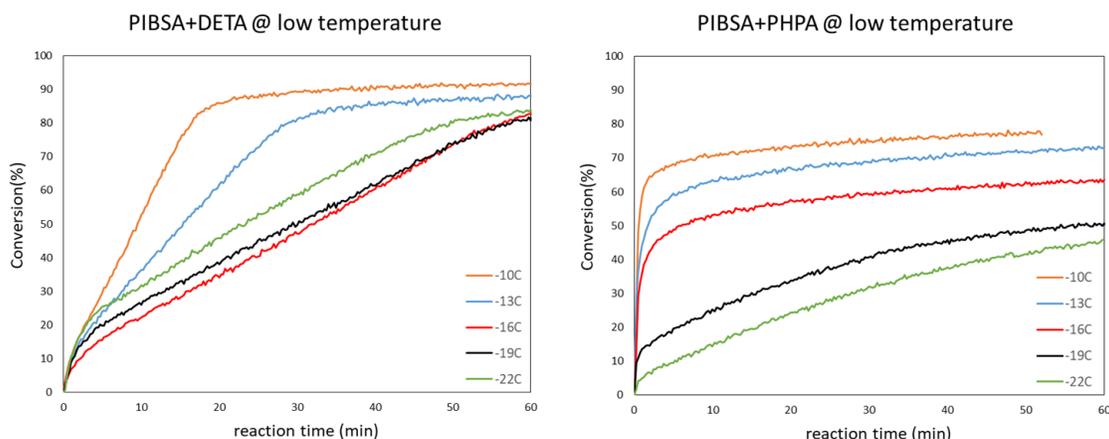
$$k_i = k_{0,i} \exp\left(-\frac{Ea}{RT}\right)$$

The input of the kinetic fitting were concentration and temperature profiles and the kinetic parameters from data fitting are preexponential factor ( $k_{0,i}$ ), activation energy (Ea) and reaction order ( $\alpha, \beta, \gamma$ ).

### 3.1.1 Amination Step

As discussed above, the rate expression for the first step is:

$$r_1 = k_1[PIBSA]^\alpha[amine]^\beta$$



**Figure 8 Conversions of PIBSA in first step**

However, experimental results (Figure 8) for the amination reaction with DETA and PHPA are totally different. Reaction of PIBSA and DETA shows an obvious zero-order kinetics. While PIBSA and PHPA reactions shows a much faster and non-zero-order kinetics. For both of them, PIBSA curves always reach plateau after a while and cannot be fully consumed.

In order to get the first kinetics, a zero-order fitting was applied to PIBSA and DETA reaction and a “Q” factor was introduced to the PIBSA and PHPA kinetics fitting.

**Table 1 Kinetics of Amination Reaction**

Reaction system	Rate Law	$k_{0,1}$ (pre-factor)	$E_a$ [kJ/mol]	$Q$ [equiv/mL]
PIBSA+PHPA	$r_1 = k_1[\text{PIBSA-Q}][\text{PHPA}]^{1.5}$	$\sim 1.29 \times 10^{29}$ [mL <sup>1.5</sup> /(equiv <sup>1.5</sup> •min)]	$\sim 120$	$Q = -1.13\text{E-}05 \times T + 0.00306$
PIBSA+DETA	$r_1 = k_1$	$\sim 1.29 \times 10^{19}$ [equiv/(mL•min)]	$\sim 119$	

Table 1 shows the kinetics fitting results of the first step (amination reaction). Although the two different reactions show a totally different kinetics, the activation energies of them are surprisingly very close. This indicates that the ring opening process of the anhydride head of PIBSA is independent on the type/structure of amine. As a further thinking, this amination reaction may undergo a succinic ring opening process first and then the addition of amine. Ring opening process should be the rate limiting step of this amination reaction.

### 3.1.2 Dehydration Step

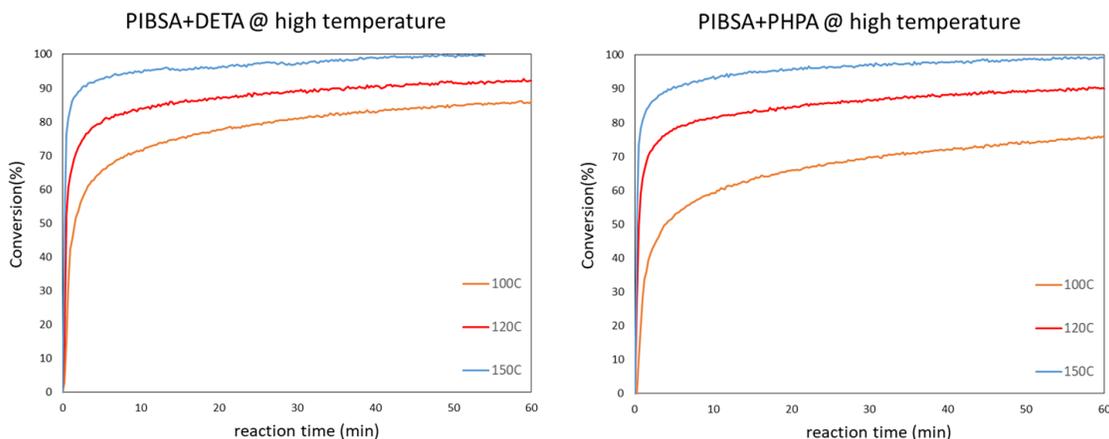
Kinetics fitting for the second step is much more straightforward. As PIBSA was consumed almost instantly (within 30s) at high-temp window, the dehydration reaction was considered to be the only reaction happened at high temperature. Followed by the rate law:

$$r_2 = k_2[\text{amide}]^y$$

Kinetic data were obtained from kinetics fitting and is shown in Table 2.

**Table 2 Kinetics of Dehydration Reaction**

Reaction system	Rate Law	$k_{0,1}$ [mL/(equiv•min)]	$E_a$ [kJ/mol]
PIBSA+PHPA	$r_2 = k_2[\text{Amide}]^2$	$\sim 7.89 \times 10^{13}$	$\sim 86$
PIBSA+DETA	$r_2 = k_2[\text{Amide}]^2$	$\sim 1.59 \times 10^{15}$	$\sim 100$



**Figure 9 Yields of sccinimide in second step**

Figure 9 shows the conversion change for the dehydration step. PIBSA+DETA reaction and PIBSA+PHPA reaction are showing a pretty similar kinetics. Kinetics fitting shows that the two reactions follow the same reaction order but have different activation energies. It is very reasonable to have the same reaction order as they are undergoing the same type of reaction. As for the activation energy, no like the amination step, dehydration step is a ring closing process and the ring closing process is affected by the neighboring structure of the ring. As amine has multiple reacting sites (i.e. nitrogen groups) in one molecule, based on the feed ratio of PIBSA and amine, one amine molecule should react with multiple PIBSA molecules (2 or 3). DETA has a much shorter molecular chain than PHPA and thus after amination reaction, PIBSA molecules attached to DETA molecule are much closer than those attached to PHPA molecules. In dehydration step, when the ring closing happens, other PIBSA molecules attached to the same amine molecule may introduce steric hindrance to prevent the ring from closing. As PIBSA molecules attached to DETA molecule are much closer, PIBSA+DETA dehydration step will have more hindrance and hence need a higher activation energy comparing to PIBSA+PHPA dehydration step.

## 3.2 Prediction of the reaction

With the kinetics obtained from numerical fitting tools, reactions under different conditions were successfully predicted. This proves the kinetic data obtained in this work are robust with “predictive” capability

### 3.2.1 Mixed Amine

As mentioned in Section 2.3, industrial production utilizes DBDA, which is a mixture of 85w% PHPA and 15w% DETA, as the amine feed. In concentration profiles and kinetics fitting, equivalent amount was used as the unit of amount (explained in Section 3.1). So the composition of DBDA then becomes 82equiv% PHPA and 18equiv% DETA. To predict DBDA reaction process, the rate expression of DBDA is:

$$r_{DBDA\ prediction} = 0.82 * r_{PHPA} + 0.18 * r_{DETA}$$

Predictions were compared with experimental results as shown in Figure 10.

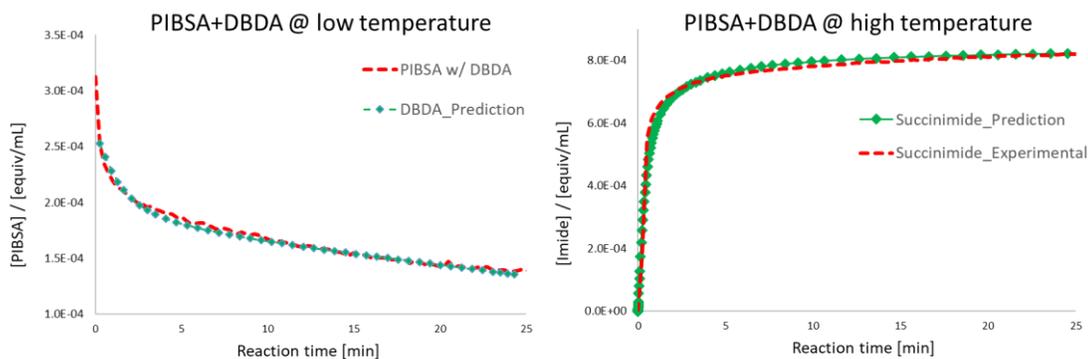


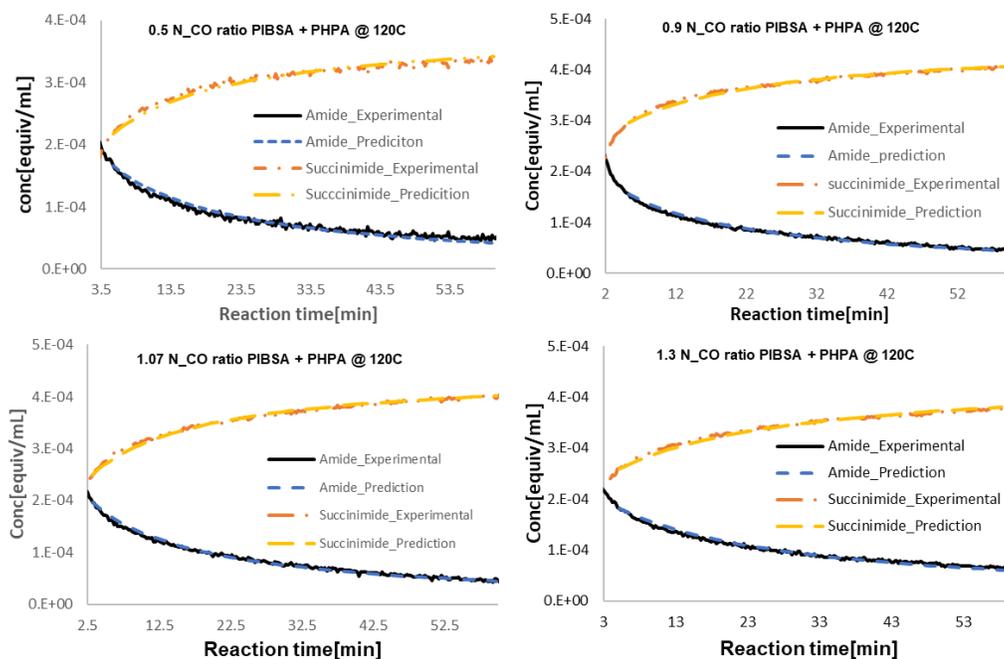
Figure 10 Comparison of predicted kinetics and experimental results

From the results, good agreements of prediction and experimental data were observed in both low-temp and high-temp conditions. On the one hand, these good agreements prove the predictive ability of the kinetics. On the other hand, the agreements were achieved by using linear superposition of separate kinetics indicates that reactions of PIBSA and polyamines are separate and independent. These results suggest that for a complex system with a mix of independent reactions, kinetics of the system can be obtained by separately measure the kinetics of each individual reaction.

### **3.2.2 Various Feed Ratio**

To change the properties and performances of dispersants, industrial companies change the feed ratio of PIBSA and amine to produce the products.

Kinetics discussed in the previous sections are all with a N/CO ratio at 1.07 as the PIBSA and amine feed ratio. Here, reactions with different N/CO feed ratios were predicted and the predictions were compared with the experimental results (Figure 11).



**Figure 11 Comparison of predicted kinetics and experimental results**

Kinetic expression determined at  $N/CO=1.07$  accurately predicted the reactions with different  $N/CO$  ratios (range: 0.5 to 1.3). These good agreements again prove the “predictive” ability of the kinetics discussed in previous sections. Furthermore, these results suggest that different feed ratios can be fully predicted with the kinetics from just one feed ratio and thus provide an efficient support for reactor design and future investigation.

### 3.3 Steric Hindrance

In low temperature results, residual of PIBSA was observed in all reactions. A reasonable hypothesis that the steric hindrance between PIBSA and amine was preventing the further reaction was proposed. The hypothesis was investigated from both PIBSA and amine sides.

### 3.3.1 PIBSA Effect

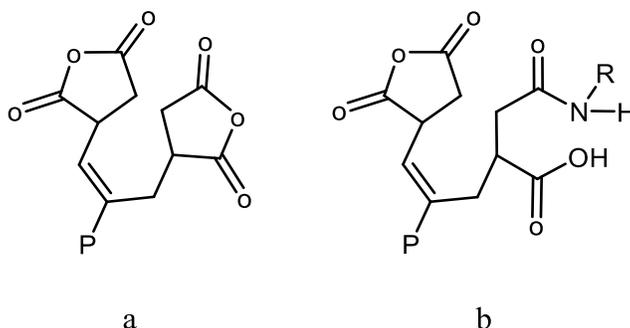


Figure 12 Di-succan structure

PIBSA used in this work is a mixture of a group of polyisobutylene succinic anhydrides with similar structures. Although most of the molecules can be expressed as one PIB tail with one anhydride head, 20-30% of the molecules are having two anhydride heads, which are called “di-succan”. For the PIBSA with di-succan structure (Figure 12a), when it reacts with amine and forms the amide (Figure 12b), it is possible that the existence of the amide structure or the amine chain hinders the reaction of the other anhydride head. Experiments of PIBSA and simple amines were done to test the hypothesis and the results are shown in Figure 13.

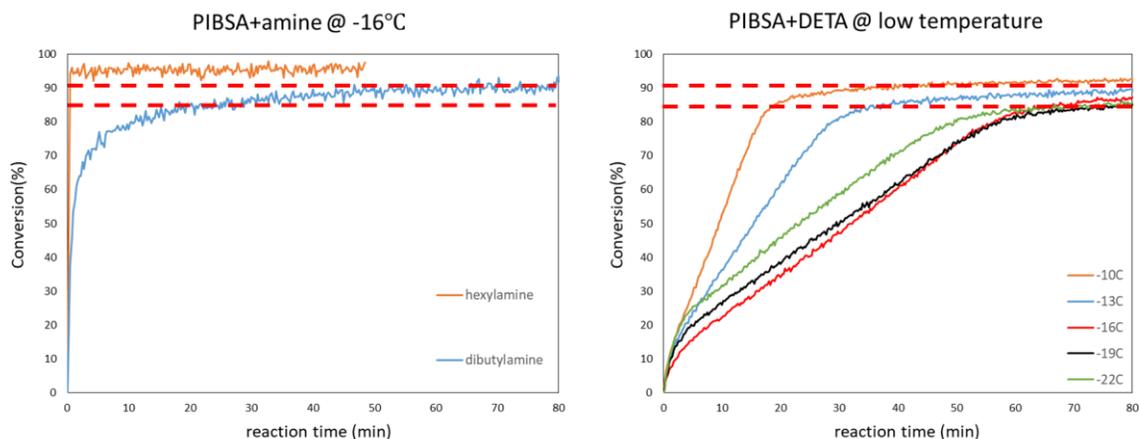
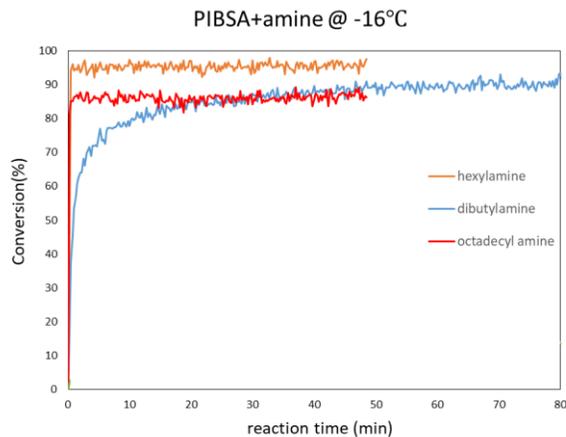


Figure 13 Comparison of predicted conversion region and experimental results

To test the hypothesis, hexylamine and dibutyl amine were used as the simple amine to eliminate the possible amine effect. As there are 20% to 30% of PIBSA with di-succan in the system, if the reaction of one anhydride head hinders the other anhydride head, the overall conversion of PIBSA should be in between 85% to 90%. Conversion of the reaction with dibutyl amine locates right in this region while that of the reaction with hexylamine has a higher conversion but still not 100% (Figure 13). A possible reason for this difference could be that as hexyl amine is very small, when it reacts with PIBSA, the amide formed with hexylamine is not bulky enough to fully hinder the other head. Considering that conversions of all reactions with DETA are in the 85% to 90% range as well, these results strongly support that the steric hindrance caused by di-succan structure could be the main reason for the residual of PIBSA in the system.

### **3.3.2 Amine Effect**

Besides the di-succan PIBSA effect, properties of different amines could also be the reason for the steric hindrance. Comparing with PHPA and DETA results, PHPA results are having more PIBSA residuals. PHPA is bulkier than DETA as well as having more secondary nitrogen groups. Either or both of these properties could cause the difference between PHPA and DETA results. The hypothesis here is that only primary amine react with PIBSA at low temperature or the bulkiness of the amine causes the steric hindrance.



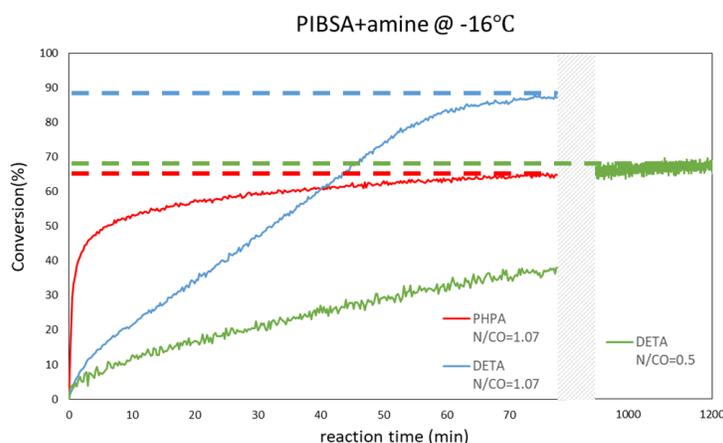
**Figure 14 Conversion of PIBSA different amine feeds**

First of all, to better understand amine effect, reactions with simple primary amine (hexylamine), simple secondary amine (dibutyl amine), bulky primary amine (octadecyl amine) and bulky secondary amine (di-octadecyl amine) were done and compared. As shown in Figure 14, both primary amines react very fast. The fact that bulky primary amine has a lower conversion (85%) than simple primary amine (95%) strengthens the statement made in section 3.3.1. As for secondary amine, simple secondary amine still has a pretty fast kinetics and very high conversion while the bulky secondary amine has a very poor solubility in the system so there were no valid results. These results suggest that amines always have a pretty good reactivity with anhydride, but the bulkiness of amine may hinder the reaction. Even for primary amines with very fast kinetics, the bulkiness can decrease the conversion. It is reasonable to infer that bulky secondary amines will have larger hinderance on the reaction. A new hypothesis that bulky secondary amine is the reason for the steric hindrance was then proposed.

Now moving back to the much more complex system. PHPA is a mixture of polyamines, and it contains about 28% to 43% primary amine groups (base on the structures provided by our industry partner). DETA is a pure component and the content of primary amine groups in DETA

is 67%. In the reaction, primary amines react instantly and is much faster than secondary amines. Therefore, PHPA and DETA will instantly transform into bulky amines after the addition by react with two molecules of PIBSA on both primary amine sides. These bulky amines then are not supposed to react with PIBSA any more.

The feed ratio of the reaction is calculated based on N:CO ratio at 1.07. In reaction, one N group reacts with one anhydride ring which contains two CO groups (i.e. N:CO=1:2 for a unit reaction). Theoretically, with the current feed ratio, the hypothesis suggests that only 56% to 86% PIBSA can be consumed by PHPA while all PIBSA should be consumed by DETA. Considering the PIBSA di-succan effect (85% to 90% max conversion), PHPA and DETA should be able to consume 47% to 77% and 85% to 90% of PIBSA respectively. Experimental results (Figure 15) show very good agreements with the hypothesis. For PHPA reaction, the conversion is about 65% while for DETA reaction, the conversion is about 88%. Both of the conversions locate right in the predicted region.



**Figure 15 Conversion of PIBSA different amine feeds**

An extra test was done by using DETA, which is a pure compound, with 0.5 N:CO ratio. In this case, the hypothesis suggests that the primary amine in DETA should react 67% PIBSA

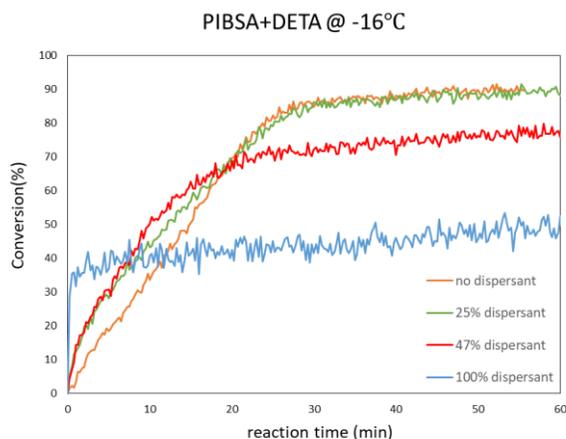
and leave 33% PIBSA staying with secondary amines. Experimental results agree with the prediction very well and this strongly support the hypothesis that only bulky primary amines can react with PIBSA while bulky secondary amines cannot.

### 3.4 “Zero-Order” Kinetics

A very surprising observation in this work should be the weird “zero-order” kinetics of PIBSA+DETA reaction. Usually, a zero-order reaction happens in metal surface catalytic reaction [14] or in a reaction system where one of the reactants is in bulk with no concentration dependence, like enzyme-catalyzed reactions. [15] However, PIBSA+DETA reaction is in neither of those conditions. Although the investigation of this phenomenon is still in progress, the current hypothesis is that the production of amide has an effect on the reaction.

It is known that DETA is almost immiscible in Stoddard Solvent. When DETA is injected to the system, it may exist as droplets. The reaction then only happens at the drop surface of DETA. The reaction rate will decrease along with the shrinking of DETA. Amide, as the intermediate component of the entire dispersant chemistry, has a very similar structure as a dispersant (i.e. a polar head with a long non-polar tail) and it could help to disperse DETA to the system. With the reaction goes further, more amide will be produced and a better dispersion of DETA can be achieved. During the reaction, shrinking of DETA droplets and dispersing of DETA molecules happen at the same time so that the decrease of reaction rate and the accelerating effect of amide could be cancelled out and this leads to an unchanged observed reaction rate (i.e. zero-order kinetics).

Effects of dispersant were tested by adding different amount of dispersant solution to the reaction system. Results are shown in Figure 16. Adding more amount of dispersant solution to the system obviously accelerate the reaction but at the same time, more PIBSA residual was observed as well. Clearly dispersant can hugely influence the reaction but a detailed mechanism behind this effect is still under investigation.



**Figure 16 Conversion of PIBSA and DETA reactions with different amount of dispersant**

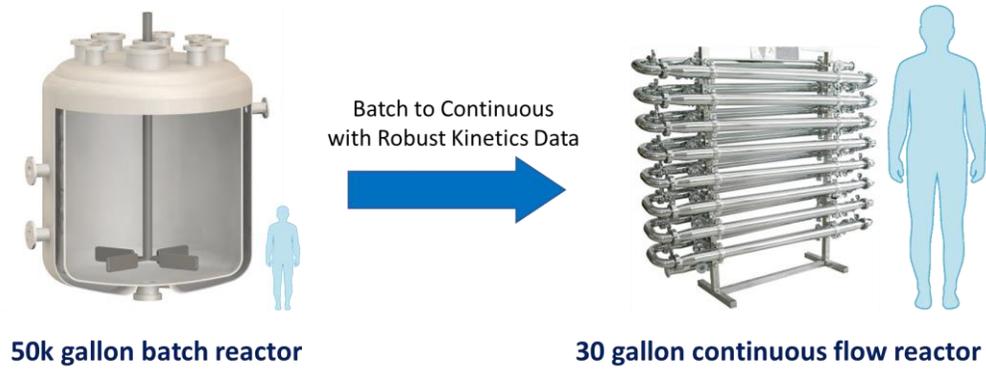
## 4.0 Conclusion

In conclusion, this work, for the first time, detailly investigated the reaction process of dispersant chemistry. The first robust kinetics of the reaction were determined separately in different temperature windows. Kinetics determined from different sets of experiments can be used to accurately predict dispersant production in different conditions. Furthermore, investigations on the steric hindrance effect and zero-order kinetics of DETA reaction were done. Although there are no final conclusions yet, research on these topics is on a good track.

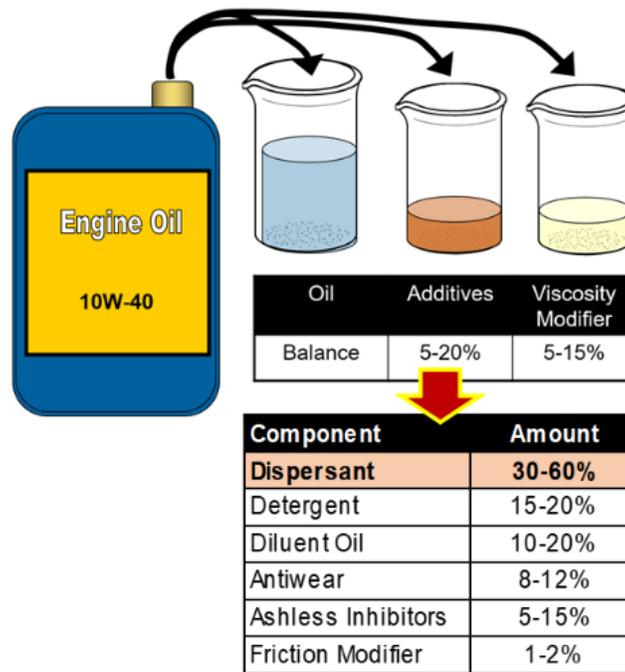
For the outlooks of this work, more research needs to be done on steric hindrance effect and zero-order kinetics. Thinking of bond rotation energies and molecules structures of PIBSA, amine and amide should be a good direction for steric hindrance research. To have a better understanding of the zero-order kinetics, shrinking core model may bring some inspirations.

In addition, as zero-order kinetics may not be the “real” kinetics for DETA reaction, more kinetic simulations need to be done in different conditions, especially varying the DETA condition to have a better estimation of the kinetics.

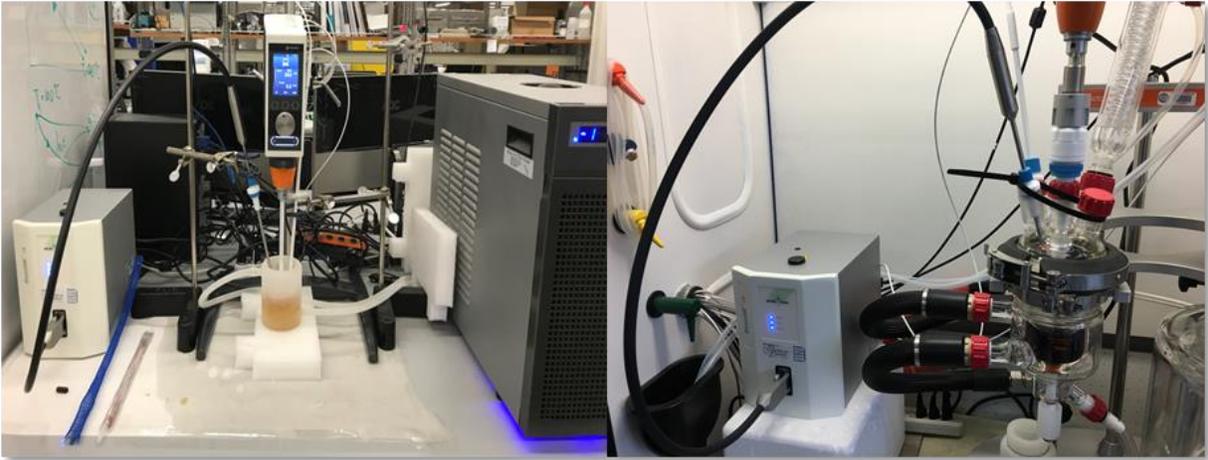
## Appendix



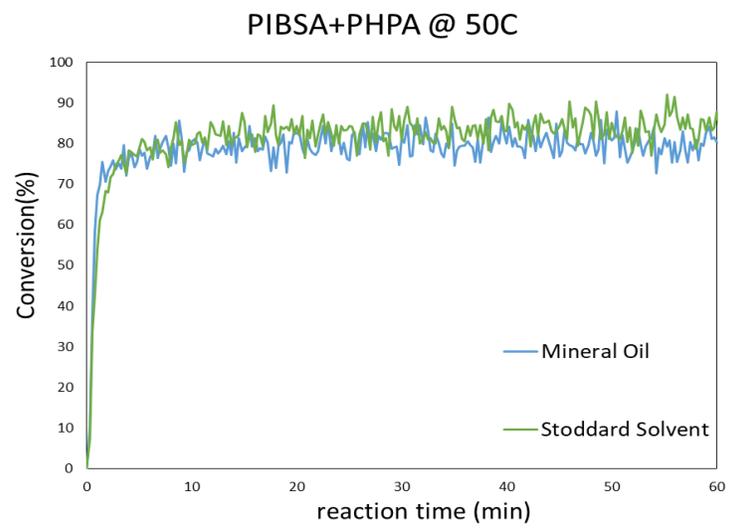
Appendix Figure 1 Transition from batch to continuous processing



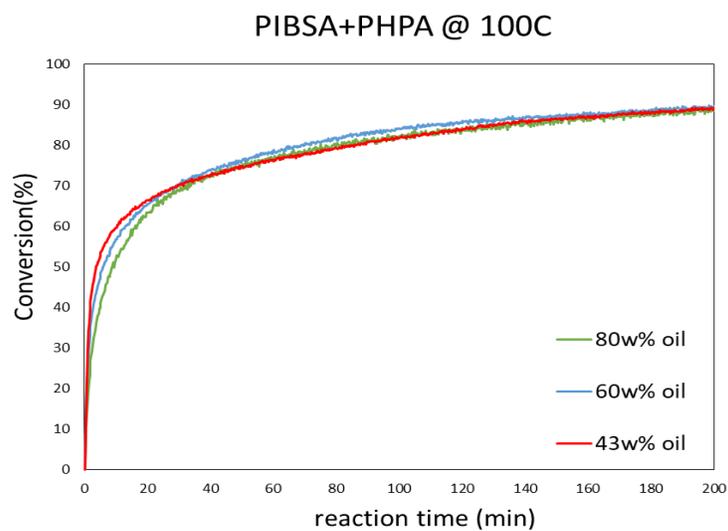
Appendix Figure 2 Engine oil composition



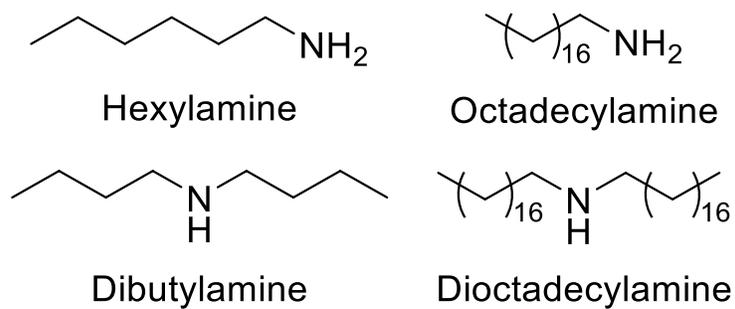
**Appendix Figure 3 Experimental set-up**



**Appendix Figure 4 Solvent effect test results**



**Appendix Figure 5 Dilution test results**



**Appendix Figure 6 Simple amine structures**

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