LIFE CYCLE ASSESSMENT TO DI-2-ETHYLHEXYL PHTHALATE (DEHP), APPLICATIONS AND POTENTIAL ALTERNATIVES

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LIFE CYCLE ASSESSMENT TO DI-2-ETHYLHEXYL PHTHALATE (DEHP), APPLICATIOS AND POTENTIAL ALTERNATIVES

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Phthalate plasticizers are added to polyvinyl chloride (PVC) during manufacturing to increase resilience and softness, ease the processing, and optimize the lower temperature performance. Phthalates are widely applied in toys, construction materials, medical devices, food packaging, flooring and other product categories. After several decades of commercial use, recent investigations have prompted concern that phthalate exposure can cause human health issues. At the same time, a number of new plasticizers have been introduced as potentially greener alternatives to the most widely used phthalates (DEHP). We have employed process life cycle analysis (process LCA) to examine the life cycle impacts of bis(2-ethylhexyl)phthalate (DEHP) to those arising from the use of 1,2 cyclohexane dicarboxylic acid diisononyl ester (DINCH) and citrate esters. Our work has focused on the “cradle-to-gate” stage of the life cycle, comparing the raw material acquisition and manufacturing phases. Energy consumption is also an important concern for the environmental impacts. A complete LCA study to get a much “greener” plasticizer substitute is expected.

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ABBREVIATION AND ACRONYM

LCA - Life Cycle Assessment

LCIA - Life Cycle Impact Assessment

LCI - Life cycle inventory

ISO - International Organization for Standardization

ASTM - American Society for Testing and Materials

BEES - Building for Environmental and Economic Sustainability

TRACI - Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts

GHG - Green House Gas (CO_2)

CO_2e - Carbon Dioxide Equivalent

PVC - Polyvinyl Chloride

DEHP - Di-2-ethylhexyl phthalate [$C_6H_4(COO\text{-}C_8H_{17})_2$] [CAS number: 117-81-7]

DINP - Diisononyl phthalate [$C_6H_4[COO(CH_2)_6CH(CH_3)_2]_2$] [CAS number: 28553-12-0]

DIDP - Diisodecyl phthalate [$C_{28}H_{46}O_4$] [CAS number: 26761-40-0]

ATBC - Acetyl tributyl citrate [$C_{20}H_{34}O_8$]   [CAS number: 77-90-7]

TBC - Tributyl citrate

TOC - Trioctyl citrate

ATOC - Acetyl trioctyl citrate

THC - Trihexyl citrate

ATHC - Acetyl trihexyl citrate

TMC - Trimethyl citrate

DINCH - 1,2-Cyclohexane dicarboxylic acid diisononyl ester [$C_{26}H_{48}O_4$]   [CAS number: 166412-78-8]

DEHA - Bis(2-ethylhexyl) Adipate [$C_{22}H_{42}O_4$]   [CAS number: 103-23-1]

TOTM - Trioctyl Trimellitate

DBS - Dibutyl Sebacate

DOS - Dioctyl Sebacate

ASE - alkylsulphonic Phenyl Sster

VCT - Vinyl Composition Tile

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1.0 INTRODUCTION

1.1 PLASTICIZER

Plasticizers are a kind of substances added to plastics during manufacturing to increase their flexibility, softness, and feasibility for future process. The most primary polymeric host is Polyvinyl Chloride (PVC) products[1], and the most widely used plasticizers are phthalate (phthalate ester) families. Phthalates are almost equipped with all the outstanding properties for plasticizers, such as excellent compatibility with PVC resin[2]. In addition, diverse phthalates with different functions applied in extensive applications with good low temperature and high temperature behaviors. And the unbeatable advantage - low cost, makes them to be the favorite of the plastics industry. But after several decades' usage and investigation, people realize that phthalate can lead to health concerns to human bodies [3-7], which are covered by their merits in early days. This finding created quite a stir in both academic and industry since 21 century, because phthalates accounts for approximately 70% of the plasticizer consumption, up to 7.7 billion pounds[8].

In the 1920s, phthalates (or phthalate esters) were first introduced as plasticizers into plastics industry. The primary polymeric host is polyvinyl chloride (PVC) products, which are widely used all over the world for various applications.

People have started the extensive study of the mechanism behind phthalates' plasticization behaviors since 1960s. Normally the host resin is polar polymer, and in fact the mechanism is an interaction happening between the positively charged areas of the polymer chain and the polar centers of the phthalate plasticizers (the C=O functional group). Heat should be added to the polymer at the presence of plasticizer, reaching the polymer T_g (glass transition temperature), and then into the melt state. This process promotes the mix of polymer and plasticizer and the interactions happening. After cooling, the network between plasticizers and PVC chains remained, but it's physical connection, not chemical.

Generally, phthalates are organic liquid materials, clear and lower price comparing with other plasticizers. They quickly replaced the existing plasticizers, because of their great improvement to the polymer products as expected, such as decreasing the T_g (glass transition temperature) of the polymer, which resulting in increasing elongation and decreasing tensile strength, making the material more flexible, modifying rheological properties, increasing compatibility among additives, viscosity control, and so on[9]. As the development of the PVC industry and plasticizer family, phthalates occupied a dominant role in PVC production, the most commonly usages are toys, construction materials, medical devices, and food packaging, flooring and so on. Among them, DEHP is the most widely used phthalate plasticizer. But recent years studies indicate that there are some potential health and environmental concerns for phthalate family, it is conjectured because of the aromatic function part. Some clinical data and animal experimental results display endocrine disruption, effects to reproductive system, especially for male infants, and even carcinogen possibilities for some specific phthalates[10, 11]. Based on these, some regulations have been published to restrict specific phthalates usage in U.S. and E.U., especially for toys. Since 1999, DEHP, DBP, and BBP are restricted for all toys in E.U., DINP, DIDP, and DNOP are restricted only in children' toys those might be taken into mouth. Even though some phthalates can be applied in toys or toys not for mouth, the concentration of phthalates may not be greater than 0.1%wt of the plasticized part of the toy[12]. From February 10th, 2009, the similar law was applied in United States as well[13]. But phthalate family still plays an important role in many other fields, particularly in PVC manufacture. The big concern about the health issue is still in front of the government and public, but right now it cannot be replaced completely. Then finding out a non-hazardous and environmentally friendly plasticizer is an imperative responsibility for the plastic industry.

Currently, there are various alternative plasticizers depending on different end usages, and few of them can replace phthalates completely, but still have some candidates attracting our interest a lot. 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH) was firstly produced and sold by BASF as a plasticizer alternative in 2002 under the trade name of Hexamoll DINCH[14]. Up to now, it is one of the most widely used phthalate substitutes in the world. In 2007, the production capacity of DINCH was quadrupled from 25,000 to 100,000 metric tonnes each year[15]. Citrate ester (e.g. Acetyl tributyl citrate (ATBC)) is another interesting substitute because of its health safety, so widely used in food packaging[16]. The above two can replace phthalates in some application areas functionally, but more time is needed to explore whether they are green to the environment and healthy enough for human. The chemical structures of DEHP, ATBC, and DINCH are shown in Fig. 1-1.

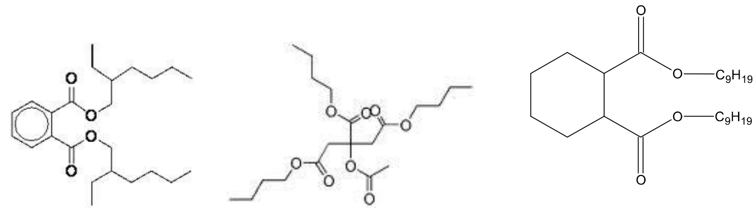


Figure 1-1. Chemical structures of DEHP (left), ATBC (middle) and DINCH (right).

1.2 LIFE CYCLE ASSESSMENT (LCA)

Several classes of techniques are used to help make the environmental decisions, which including environmental audit for existing facilities, and environmental impact analysis as a prediction for the planned product or facilities. Most of the times, not one but multiple techniques are applied to the complex network of an individual activity. Life Cycle Assessment (LCA) is one of them.

Life Cycle Assessment (LCA) is a tool used to establish the environmental impacts for the target product or system associating with all of its life stages (Fig. 1-2), which starting from the raw material extraction, through manufacturing, distribution, use phase, and final disposal. LCA is powerful to integrate the factors in both ecosystem and human society; it can provide a complete networking connection consisting of technique, market and economic assessments in the evaluation process. LCA also provides a prediction for the potential application within environmental management systems. LCA is standing on inventory only, then the inventory must be translated into impacts using one of several systems; we typically employ mid-point analysis, which is embedded within SimaPro software. Other systems for calculating impact are also possible.

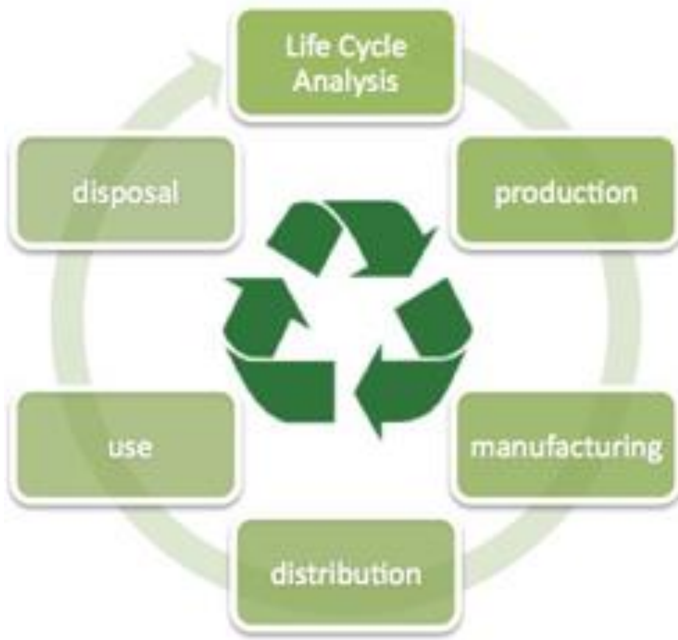


Figure 1-2. Life Cycle Assessment (LCA) components[17]

LCA is a developing scientific method, adopted more and more widely in environmental impacts assessment. It is a valuable approach, which could be used in diverse areas to improve environmental quality and sustainability, such as research and developing a process, guiding any evolution, comparison and selection among different options, and even identifying weakness in a supply chain. Based on its comprehensive database, LCA can provide a quantitative and qualitative assessment for target product or process over the entire lift cycle, helpful for decision-making. So far, it is mainly used for products. There are four basic steps to conduct LCA: goal and scope definition, inventory analysis, impact assessment, and interpretation. The raw material and energy usage inputs could be compiling in LCA to construct the inventory and output the environmental releases, the output environmental impacts data is the clue for decision making.

1.3 MOTIVATION

Phthalate esters have been used as plasticizer more than eighty years. Their good compatibility with PVC, high temperature and low temperature behaviors, and especial low cost, made them to be a best choice in PVC product manufacturing in last several decades, but people did not realized their hazardous impacts for natural environment. And also because the data collecting of leaching and the impacts for human health need a time range, safety protection and monitoring technic haven't been well developed until recent decade, the health concerns from phthalate families appearing The widely usage of phthalate esters, and the huge production per year, the by-products and degradation problems for phthalate cannot be ignored any more. This thesis focuses on one of the most widely used plasticizer - phthalate; it is the primary plasticizer for plastic products. Complementally, three other kinds of high production volume phthalates were introduced as well - DEHP, DINP and DBP. The main idea for this research is to investigate the impacts of DEHP manufacturing on raw material resources, water, energy flows, and electricity, this is a "Cradle-to-Gate" life cycle assessment, then following the product - vinyl flooring, which is one of DEHP's primary applications, as the usage phase assessment, completing a "Cradle-to-Grave" life cycle assessment, some parts of the transformation were included depending on the data availability. This study involves the green chemistry view, the novel concept "life cycle assessment", and combining with the real industry world as well.

Various alternatives have been introduced and investigated in the past decade, citrates, adipates, trimellitates, polymers, and so on[18-21]. But none of them can completely replace phthalates so far, which is not only because phthalates are involved in industrial manufacturing so widely, they almost have all the admirable properties required for a plasticizer, but also the low product cost, which can bring the manufacturers considerable economic profit. The health problems leading from phthalates have been proved, from sustainable development view, suitable replacements are the final destination.

2.0 BACKGROUND AND LITERATURE REVIEW

2.1 PVC PRODUCTS WITH PLASTICIZERS

2.1.1 Polyvinyl chloride

PVC use has grown significantly since the 1930s. Before that, the immature technique and processability, and lack of effective stabilizers held up its widely applications. When the technique was conquered, PVC yield grown steadily, and dominated several polymer markets. The historic data (Fig.2-1) shows that the PVC sales amount in U.S. increased year over year. By 2003, it reached about $7*10^6$ metric tonnes per year; the world's total sales amount was even more than $2.5*10^7$ metric tonners[22-24]. And it is still trending to accelerate.

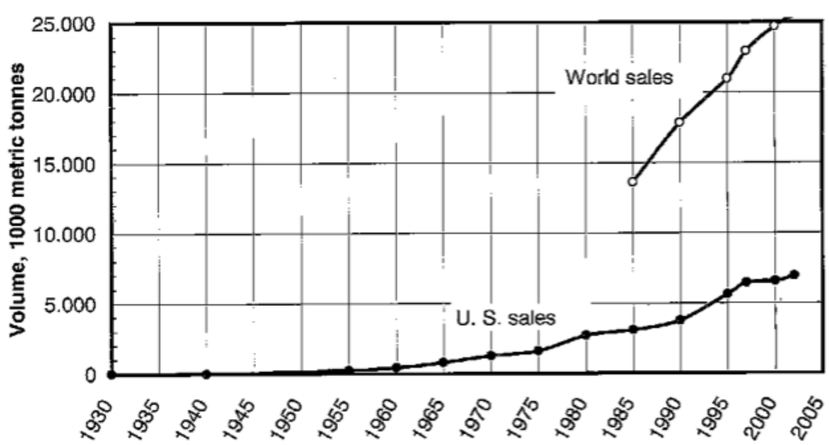


Figure 2-1. Growth of PVC in the Unites States and worldwide[22, 23]

In the last several decades, the production process was optimized and mature. And also as the intensive study of PVC's physical and chemical properties, it plays a more important role in diverse fields. Good weatherability, and flame-resistant features give vinyl a successfully commercial significance. It is widely utilized for windows, auto interiors, siding, and pool-lines. It is also used by auto industry for instrument panel and door panel coverings. Construction is the fastest growing part, with a projected annual average growth rate of 3.5% between 2002 and 2007. PVC dominates 69% of the plastic construction market[24]. Within the construction, the fastest growing PVC products are special applications, such as gutters, fencing and decking (growing at 8.1% per year), windows and doors (6.1%), vinyl siding (4.5%) and pipes and tubing (2.5%)[25].

In addition, the excellent combustion resistance also provides vinyl more than half of wire and cable plastics market. PVC is also an important part in flooring market, especially for kitchens and bathrooms, because of its water resistance property. In the thin film market, vinyl only accounts for a certain parts, but for those products, which require highly fire resistance, PVC is the perfect choice. Vinyl is also the main resource for electrical enclosures due to its excellent combustion resistance.

U.S. vinyl chloride production and prices are listed in Table 2-1. The production amount for vinyl chloride is increasing as time going. Though there were vast fluctuations for the prices, but in general, the tendency is rise. From middle 20th century to early 21st century, the price was tripled, but the production was almost increased more than 30 times.

Table 2-1. U.S. vinyl chloride annual production with prices[24, 26, 27]

Year	Production (1,000 t)	List price (c/kg)
1955	240	22
1960	470	26
1965	907	18
1970	1,833	11
1975	1,903	24
1980	2,933	49
1985	3,586	36.5
1990	4,678	43.3
1991	5,031	32.6
1992	5,374	30.3
1993	5,496	36.7
1994	6,020	46.5
1995	5,875	52.0
1996	6,552	44.6
1997	6,971	49.5
1998	7,031	34.3
1999	7,323	40.9
2000	7,023	56.4
2001	6,740	42.1
2002	6,995	44.3

Table 2-1 (continued)

2003	7,334	57.3
2004	7,609	67.9

2.1.2 PVC's various properties with applications

All the specific properties of plastics profit from their chemical composition and molecular structure. It is also the truth for PVC. PVC is partially crystalline with polar chlorine atoms. They are related to each other, and have a combined effect for PVC's features. In daily life, we can find out many kinds of plastic products made from various polymers, such as poly(vinyl chloride) (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS). Except PVC, the other three only have carbon and hydrogen elements. All of the four are general-purpose plastics, but PVC exhibits some different properties in performance and functions comparing with the other hydrocarbon compounds. The properties' comparison of these four is listed in Table 2-2.

Table 2-2. Properties comparison of PVC, PE, PP and PS.

Name	Molecular Formula	Properties	Application
Poly(vinyl chloride) (PVC)	$(CH_2CHCl)_n$	Fire resistance, good insulation properties (but inferior to PP and PE), chemical/oil resistance, pool heat stability	Pipes, electric cables, flooring, clothing, medical devices, blood bags

Table 2-2 (continued)

Polyethylene (PE)	$(C_2H_2)_n$	Flammable, poor temperature capability, low strength/stiffness	Plastic bag, plastic film, geomembranes, food packaging, piping, container, etc.
Polypropylene (PP)	$(C_3H_6)_n$	Fatigue resistance, heat resistance	Packaging and labeling, textiles, automotive component, living hinge, etc.
Polystyrene (PS)	$(C_8H_8)_n$	Thermoplastic polymer, hard plastic	Foam packaging, building and insulation material, crafts and model building material,

Chemical durability is one of the basic requirements for general plastics used in daily life. PVC's own molecular structure gives its end products significant merits: fire resistance, durability, and chemical/oil resistance. Fire retarding properties is one of the most important properties that PVC can be utilized so widely in plastics markets, except the one reason mentioned above, chlorine content, it also has high ignition point, as high as 455°C, made it less risk to be ignited. In addition, the heat released in PVC burning is rather lower than other plastics materials[24], shown in Table 2-3[28], so it will not contribute that much to spread the fire to nearby environment. At this point, PVC is a safe choice for those products close to the daily life.

Table 2-3. Heats of combustion for various materials (kJ/kg)[28]

Chemical Name	Heat of Combustion (kJ/kg)
Polyethylene	46500
Polypropylene	46000
Gasoline	44000
Polystyrene	42000
ABS	36000
Polyamide	32000
Polycarbonate	31000
PMMA	26000
Polyurethane	25000
Rigid PVC	20000
Paper	18000
Wood	17000
PTFE (Teflon)	4500

In daily general usage, the resistance to oxidation in atmosphere is a challenge for a material's durability. In PVC's molecular structure, each chlorine atom is bound to the carbon chain regularly, almost no chance for oxidation happen, maintaining its performance in good conditions.

PVC is dissolvable in many solutions, such as aromatic hydrocarbons, ketones, and cyclic ethers, not in other organic or most of the inorganic chemicals. This characteristic gives PVC the competitive strength in exhaust gas ducts, sheets used for construction, tubes and hoses.

Not only the above advantage properties, but also some others made PVC such a worldwide plastic material. PVC's chemical stability also results in a great mechanical strength, matching the requirements for pipe material. PVC has good processability, it is suitable for complex shaped extrusion profiling, and calendaring of films and sheets, which results from its stable viscoelastic behavior. PVC has a great compatibility with various substances; diverse end products can be designed via adding plasticizers, additives, and modifiers to achieve required characteristics such flexibility, elasticity, and impact resistance.

In commercial market, low cost is an attractive factor of PVC as well.

2.1.3 Environmental issues, health and safety

In the early 1970s, the carcinogenicity of vinyl chloride monomer came into notice among workers in the polyvinyl chloride industry. Workers in polymerization section near Louisville, Kentucky (US) were diagnosed with liver angiosarcoma, a rare disease[29]. Since that time, the studies of PVC and its monomer associated with cancer were started widely in Australia, Italy, Germany, the UK, and so on, and finally it was accepted that VCM is a carcinogen[30].

As more and more PVC products are utilized, after purchasing and end use, the PVC disposal problems float out. The five major PVC waste ultimate disposals are: (1) municipal solid waste (MSW); (2) medical waste; (3) construction and demolition (C&D) debris; (4) discarded products collected for recycling; and (5) industrial solid waste generated during manufacturing. In Table 2-4, the annual total amount from the above five major sources is about 1.8 to 3.6 million tons[25]. And according to the PVC annual production data, the general trend of production is growing; it can be predicted that the final waste of PVC products will accelerate by years.

Table 2-4. Annual PVC Waste Production in the U.S. [25]

Waste Stream Total Quantity Generated	Description of PVC Portion of Waste Stream	VC Content of Waste Stream	
		Percent	Amount (tons)
Municipal Solid Waste (MSW) 229 million - 369 million tons	Packaging and other disposable vinyl products	0.62%	1,420,000 to 2,290,000
Medical Waste (Biomedical/Infectious) 3.4 million tons	Mostly medical tubing and bags with some vinyl gloves and supplies	5% to 15%	170,000 to 510,000
Construction & Demolition (C&D) Debris 136 million tons	Vinyl pipes only and vinyl pipes and siding (Does not account for other types of PVC C&D debris)	0.18% to 0.63%	245,000 to 856,000
Discarded Products Collected for Recycling Unknown amount	PVC-contaminated plastics from bottles, electronics, automobiles, scrap wood, cardboard, etc.	Varies	Unknown

Table 2-4 (continued)

Manufacturing Waste Unknown amount	Complete range of PVC products including manufactured homes and plastics fabrication	Varies	Unknown

Some other concerns are not from PVC itself directly, but from the additives added to the PVC products. Plasticizer is the most significant one. PVC is the primary polymeric host, and phthalate is the main plasticizer candidate. According to PVC's world spread applications, we can approximate the mount of plasticizer consumption - around 7.7 billion pounds per year, which will be the potentially environmental hazard. It is also the motive power of our research.

2.2 PHTHALATE FAMILY

Phthalates are a family of phthalic acid esters, and they are primarily used as plasticizers for various PVC products, and also used in personal care products for compatibilization. Fig. 2-2 is the general chemical structure of phthalates, basically the R and R' groups are typically alkyl chains. Based on different product properties and manufacturing requirements they can be the same or diverse functional groups. Phthalates are produced from petroleum. The most widely manufactured and used phthalates in industry field are Di(2-ethylhexyl) phthalate (DEHP), Diisononyl phthalate (DINP), Di-n-butyl phthalate (DBP), Butyl benzyl phthalate (BBP), etc.. Those most commonly used phthalates (with different R groups) are listed in Table 2-5.

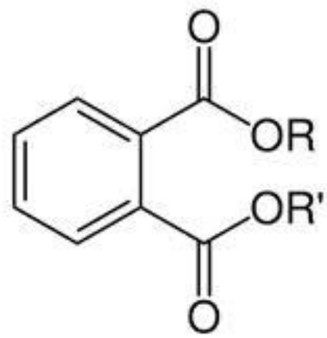


Figure 2-2. General chemical structure of phthalates (R and R' can be the same or different structures)

Table 2-5. Commonly used phthalates

Chemical Name	Abbreviation	Structural Formula
Di(2-ethylhexyl) phthalate	DEHP, DOP	$C_6H_4[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]_2$
Diisodecyl phthalate	DIDP	$C_6H_4[COO(CH_2)_7CH(CH_3)_2]_2$
Diisononyl phthalate	DINP	$C_6H_4[COO(CH_2)_6CH(CH_3)_2]_2$
Di-n-butyl phthalate	DBP	$C_6H_4[COO(CH_2)_3CH_3]_2$
Butyl benzyl phthalate	BBP	$CH_3(CH_2)_3OOCC_6H_4COOCH_2C_6H_5$
Butyl decyl phthalate	BDP	$CH_3(CH_2)_3OOCC_6H_4COO(CH_2)_9CH_3$
Di(n-octyl) phthalate	DNOP	$C_6H_4[COO(CH_2)_7CH_3]_2$
Dimethyl phthalate	DMP	$C_6H_4(COOCH_3)_2$
Diethyl phthalate	DEP	$C_6H_4(COOC_2H_5)_2$
Di-n-hexyl phthalate	DNHP	$C_6H_4[COO(CH_2)_5CH_3]_2$
Diisooctyl phthalate	DIOP	$C_6H_4[COO(CH_2)_5CH(CH_3)_2]_2$

Phthalates have abroad applications. They work as plasticizers in diverse fields and for various plastic products. Phthalates are so closed to human, and some commonly used daily life stuffs having phthalate ingredient are exhibited in Fig. 2-3, piping, medical devices, bloody bags, capsule casing, toys, food packaging, shower curtains, mats, and so on. Phthalates also can be used in cosmetics, for instance, shampoo and perfume. It works at the scent carrier, helping the cosmetic products keep the smell a longer time.

Some specific phthalates with high production amount are introduced more in the following paragraphs.

Figure 2-3. PVC products with phthalate plasticizers

2.2.1 Di-2-ethylhexyl phthalate (DEHP)

Di-2-ethylhexyl phthalate (also named as Bis(2-ethylhexyl) phthalate; dioctyl phthalate, DOP), is an organic phthalic diester with the formula $C_6H_4(C_8H_{17}COO)_2$, and the chemical structure is described in Fig. 2-4. It is a colorless viscous liquid, soluble in oil, but not in water. This compound, as one of the most widely used phthalates, is used as the international standard for plasticizer studies[31]. Other plasticizers are reported and compared with DEHP, showing the differences in characteristics and effectiveness. Some other physical and chemical properties of DEHP are listed in Table 2-6.

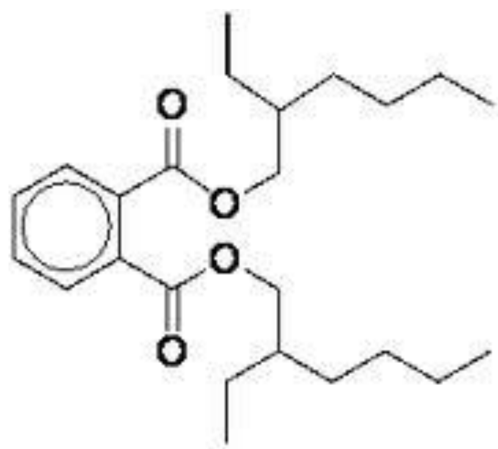


Figure 2-4. Chemical structure of DEHP

Table 2-6. Some physical and chemical properties of DEHP[32]

Particle	Value
Melting/Boiling Point	$-50^oC/230^oC$
Vapor Pressure	1.32 mm Hg at 200^oC ($1.4*10^{-6}$ mm Hg at 25^oC)
Biodegradation	Half-Life in water = 2 to 3 weeks

Table 2-6 (continued)

Specific Gravity	0.99 at 20^{o}C
Solubility	0.285 mg/L at 24^{o}C (slightly soluble in water)
Bioconcentration Factor	Log BCF = 2 to 4 in fish and in invertebrates, Log BCF = 2.93 in fatheads minnows, Expected to bioconcentrate in aquatic organisms

DEHP almost has all the desirable properties as a good plasticizer, such as great compatibility with polymer host, good high temperature and low temperature behaviors, etc. It is estimated that 90% of the DEHP is used as plasticizer for plastic products, especially for PVC[31]. The primary function for DEHP's present is to soften the rigid plastics. It has excellent compatibility and fusion qualities, applied in broad uses. Comparing with other plasticizers, DEHP needs less modification, but having great properties. It exhibits diverse properties, which are advantages for plasticizer behavior, such as great plasticizing efficiency, good gelation property, and adequate viscosity in PVC emulsions. In addition, as one of the most cost effective general purpose plasticizers, cheap price is another important reason in commercial industry.

DEHP has a broad daily use, and Table 2-7 is a summary of it applications, it presents the information of various usages of DEHP, including categories, amounts, and the usage amount data in Massachusetts if available. The information is collected in EU, and assumed to apply to the United States. Industrial/Commercial Uses and Medical Devices are the two major use categories for DEHP, accounting for 45% and 25% of the total usage respectively. Most of the applications are close to human's daily life, such as the shower curtain, wall covering, car coating, flooring, plastic bags, and so on. But because of the potential health concerns, DEHP is banned in children's toys in many countries, avoiding the direct ingestion by mouth. So far, DEHP is the choice for medical devices. No other materials can qualify all the vital performance qualities required by the regulations, but also with an affordable price. But DEHP did it. It saved thousands of patients in the medical application field. But all of those contributions are reconsidered when people realized the safety concerns from phthalate. No studies indicated the direct relevance between the medical issues and the phthalate exposure from daily use, but some works confirmed the harmness for particular area[33-35].

Table 2-7. Applications of DEHP[32]

Major Use Category	Applications	Used in Product in EU	Used in Mfg in MA (lb/yr)
Polymer Uses	Consumer Products		
Polymer Uses	Toys	(no longer permitted in US)	
	Sheet/Film (e.g. food contact)	15% of total use (for all sheet materials)	180,600 (otherwise used) 734,000 (incorporated into product)
	Vinyl Shower Curtain		
	Vinyl Wall Covering		
	Car Undercoating	1% of total use	
	Footwear	8% of total use	

Table 2-7 (continued)

	Upholstery		
	Medical Devices (approximately 25% of total US consumption of DEHP)		
	Plastic sheet materials (e.g. bags)	15% of total use (figure for all sheet materials, not just medical devices)	566,300 (typically 20-40% DEHP)
	Tubing		Minimal
	Industrial/Commercial Uses (approximately 45% of total US consumption of DEHP)		
Polymer Uses	Resilient flooring (also residential uses)	15% of total use	1,049,500
	Roofing		
	Aluminum Foil Coating/ laminating		
	Paper Coating		
	Extrudable PVC Molds/Profiles	1% of total use	649,000
	Electronic Component Parts		58,6000
	Wire/Cable Coating/Jacketing	15% of total use	21,200 (manufactured) 70,000 (incorporated into product)
Non- Polymer Uses	Lighting Ballasts & Electric Capacitors		

Table 2-7 (continued)

Non- Polymer Uses	Vacuum Pump Oil		
	Perfumes/Cosmetics		
	Pesticides		
	Printing Inks	<1% of total use	
	Paints & lacquers	<1% of total use	
	Adhesives & Coatings	2% of total use	
	Ceramics	<<1% of total use	13,500

Note: blank cell indicates no data available

DEHP is traded all over the world. It may involve a large number of articles. Data on export and import of relevant products were collected for the period 2005 to 2007 from Eurostat. The estimated amount of plasticized PVC products, the phthalate content, and the DEHP content are shown in Table 2-8[36]. The total amount of exported phthalate content is estimated to be 183,000 tonne/yr, which seems to be quite realistic considering that the amount for manufacturing of products in the EU is 900,000 tonne/yr. It is assumed that DEHP accounts for 20% of the total phthalates amount, then the import and export is estimated to be 40,000 tonne/yr and 37,000 tonne/yr respectively. For the imported products part, the estimated percentage of DEHP may be a little bit higher, but no available data indicating the real DEHP content of imported products.

Table 2-8. Estimated DEHP content of EU-extra traded articles[36]

Product group	Tonnage products t/yr		Tonnage phthalates t/yr		Tonnage DEHP t/yr	
	Import	Export	Import	Export	Import	Export
Hoses and profiles	49,335	80,319	8,000	15,000	1,600	3,000
Flooring and wall covering	78,677	244,355	13,000	32,000	2,600	6,400
Film/sheets and coated products	917,478	852,398	68,000	82,000	13,600	16,400
Coated fabric and other products from plastisol	407,365	739,136	11,000	7,000	2,200	1,400
Wires and cables	483,976	454,392	31,000	28,000	6,200	5,600
Moulded products and other	604,415	529,002	68,000	19,000	13,600	3,800
Total			199,000	183,000	40,000	37,000

Because of the data availability, some import/export articles may not be covered by this estimation, e.g. vehicles. But it is believed that the total tonnage within these ignored articles will not significantly change the totals, since the dominant applications are almost covered in this statistics. Fewer assessments were done in North America, so no enough information to provide us a complete understanding about the phthalate import and export balance. The data from EU is a good estimation for North America market. From the data we can see that, the import and export amounts of DEHP per year are extremely high, indicating that the annual world production amount of DEHP is even much higher than predicated, and the accelerated environmental impacts from DEHP manufacturing, process, and end use could not be ignored.

Medical field applications are the ones with the highest health concerns. The primary uses in medical industry are listed in Table 2-9[37]. The content of DEHP in these medical products is 20-40% by weight. For IV tubing, this number can even up to 80 percent[24]. The DEHP can leach out of these devices and come into the atmosphere or solutions. During the treatment, it can even be ingested into human bodies. Actually, people are exposed to DEHP every day, normally in a lower level. But in certain medical procedures[38-40], DEHP leaching out from those medical devices, such as tubing or bags, solubilizes into the content, then directly goes into the patients. In this condition, people are exposed to a pretty high DEHP level. The leaching activities depend on many factors, for instance, the temperature, solution, storage time, DEHP concentration in the device, degree of PVC degradation and so on. But one thing is for sure, the longer time and more medical treatments the patients need, the higher the exposure to this chemical, especially for children with less immunity, they are facing more severe threat[40]. So the children or infants undergoing long-term bloody transfusion and hemodialysis are the main population for this risk.

Table 2-9. The primary uses of DEHP in medical field

IV tubing and IV bags	Umbilical artery catheters
Blood bags and infusion tubing	Enteral nutrition feeding bags
Nasogastric tubes	Ventilator tubing
Tubing used during hemodialysis	Tubing used in cardiopulmonary bypass procedures (CPB)

So for the equivalent softness effect, DINP requires a greater loading than DEHP. Some physical and chemical properties of DINP are listed in Table 2-10. The average empirical formula for DINP is $C_{26}H_{42}O_4$, and average molecular weight is 420.6. The high molecular weight improves the high temperature performance and resistance to extraction[41]. DINP is synthesized through an esterification process of PAN (phthalic anhydride) and C9 oxo alcohols (Isononyl alcohol), which happens in a closed system. The isononyl alcohol is composed of various branched C9 alcohol isomers. Two general routes for Isononyl alcohol synthesis: either the oligomerization of propylene/butene or the dimerization of butane, then following with esterification process. After that, the excess alcohol will be removed, and products will be neutralized. The standard procedures - water washing and filtering, will be applied as well. The reaction rate is accelerated through increasing the temperature and involving catalyst, typically in the range of 140-250 °C[31, 42].

Table 2-10. Physical and chemical properties of DINP

Property	Value
Empirical formula	$C_{26}H_{42}O_4$ (average)
Molecular weight	420.6 (average)
Melting point	-40 to -54°C
Boiling point	424°C
Density	0.975 at 20°C
Viscosity	ca. 100-150 mPa.s

Table 2-10 (continued)

Vapor pressure	6×10^{-5} Pa at 20°C
Solubility in water	0.6 µg/l 20°C

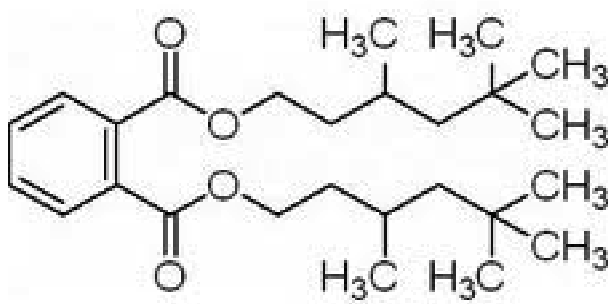


Figure 2-5. Chemical structure of DINP

DINP is a widely used plasticizer, 95% of it is used in plastic applications. For the non-plastic applications part, more than 50% of it is applied in polymer related fields, such as rubbers. The remaining portion is mainly shared in inks and pigments, adhesives, sealants, paints and lacquers and lubricants[31]. One application we need to mention is that, DINP can be used in food-packaging materials, contacting with food directly. But the maximum migration limit for the sum of diisononyl phthalates (DINP) and diisodecyl phthalates (DIDP) is 9 mg/kg food, which is the regulation set by European Union[31].

In Table 2-11, volumes of DINP in various applications and their respective service life are listed. For the indoor usage, “wires and cables” and “floor” are the two major applications, 14,510 t/yr and 10,658 t/yr respective. And as the construction materials, their estimated lifetime can last 20 - 30 years. “Wires and cables” accounts for the main portion of outdoor applications as well. In general, DINP applied in construction materials attribute the largest part in the total applications, and also their lifetime is relative longer than other applications.

Table 2-11. Volumes of DINP in different articles and their respective service life[43]

Application	DINP [t/a]	Technical service life [yr]
In-door application		
Wires & cables	14,510	30
Floor	10,658	20
Out-door application		
Roofing material	230	20
Roofing (coil coating)	1,150	10
Wires & cables	14,510	30
Coated fabric	4,850	10
Hoses & Profiles	1,380	10
Car under-coating	7,714	14
Shoe soles	8,313	5
Sealings	915	20
Paints & lacquers	915	7

It is confirmed by the EU that DINP is safe in current applications, it is only restricted in children's toys, which may be placed in the mouth. DINP was mistakenly referred to be an endocrine disruptor, because some experiments suggested that DINP might disrupt the function of the hormones estrogen and testosterone, resulting in a negative effect on the reproductive system. After a decade study of DINP using yeast cells and human cell models, indicating that DINP is not responsible for the negative effects in the endocrine systems, either in humans, or in other animals[44-47].

2.2.2 Diisodecyl phthalate (DIDP)

Diisodecyl phthalate (DINP) is another kind of commonly used phthalate plasticizer; it has a similar structure with DINP (Fig. 2-6), but contains 10-carbon chains as the major portion. The average formula of DINP is $C_{28}H_{46}O_4$, and the average molecular weight is 446.66. Some other relative properties are listed in Table 2-12.

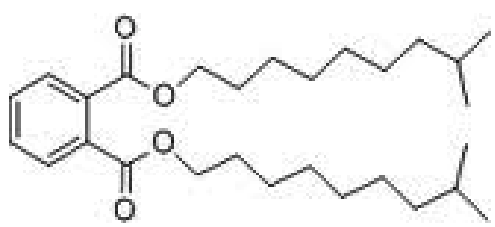


Figure 2-6. Chemical structure of DIDP

Table 2-12. Physical and chemical properties of DINP

Property	Value
Empirical formula	$C_{28}H_{46}O_4$ (average)
Molecular weight	446.66 (average)
Melting point	-53 to -39°C (av. -45°C)
Boiling point	> 400°C
Density	0.966 at 20°C
Viscosity	ca. 130 mPa.s
Vapor pressure	5.1x10-5 Pa at 25°C
Solubility in water	0.2 µg/l at 20°C

In Europe, in early 1990s, the average annual consumption of plasticisers was 970 000 tonnes, of which 894 000 tonnes were phthalates, accounting for 92% of the total amount[43]. In Fig. 2-7, it is the approximation of the relative importance of the consumption of the primary phthalates used in the EU in the 1990s, showing that DEHP accounted for more than half of the phthalate consumption, and DIDP, DINP and DBP took up to 21%, 11% and 2% respectively. Other phthalates occupied the rest 15%.

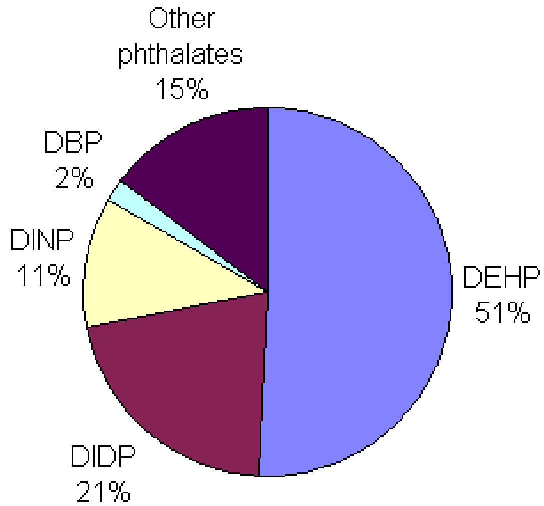


Figure 2-7. Approximation of the relative importance of the consumption of the primary phthalates used in the European Union in the 1990s[43]

The data of indoor and outdoor applications for DIDP is also collected as DINP, in Table 2-13. Construction material, such as the Wires & cables, flooring, is the main field for DIDP usage as well, similar to DINP. But the annual consumption amount is almost the doubleness of DINP. The lifetimes are various from 5-30 years, depending on the end use products. But in general, construction materials have relative longer service life.

Table 2-13. Volumes of DIDP in different articles and their respective service life[43]

Application	DIDP [t/a]	Technical service life [yr]
In-door application		
Wires & cables	27,400	30
Floor	20,055	20
Out-door application		

Table 2-13 (continued)

Roofing material	430	20
Roofing (coil coating)	2,150	10
Wires & cables	27,400	30
Coated fabric	9,060	10
Hoses & Profiles	2,590	10
Car under-coating	14,516	14
Shoe soles	15,843	5
Sealings	520	20
Paints & lacquers	1,040	7

2.2.3 Other phthalates

Phthalate is a big family, not only the above mentioned three phthalates (DEHP, DINP, and DIDP), but also having other members. Table 2-14 lists the commonly used phthalates with their full names, acronyms, and the popular applications. Depending on their different performance properties, they are applied in various application areas. Phthalates almost can cover all the plastic market.

Table 2-14. Some phthalates and their applications[43]

Acronym	Full name	Applications
DEHP	Di-Ethyl-Hexyl-Phthalate	Perfumes, flexible PVC products (shower curtains, garden hoses, food containers, plastic film, blood bags, and other medical equipment, etc.)
DIDP	Di-Isodecyl-Phthalate	Vinyl wall and floor coverings, gloves, wrapping food packaging
DINP	Di-Isononyl Phthalate	Toys, vinyl floor coverings, gloves, wrapping food packaging, drinking straws, garden hoses
DBP	Di-Butyl-Phthalate	PVC, perfumes, deodorants, hair sprays, nail polish, printer inks, insecticides
BBP	Butyl-Benzyl-Phthalate	Perfumes, hair sprays, adhesives and glues, automotive products, vinyl floor coverings
DOP	Di-Octyl-Phthalate	Flexible plastic-based products
DCHP	Di-Cyclo-Hexyl-Phthalate	Laboratory research
DMP	Di-Methyl-Phthalate	Deodorants
DEP	Di-Ethyl-Phthalate	Perfumes, deodorants, hair gels and mousses, shampoos, soaps, hair sprays, nail polish, body lotions

2.2.4 Health concerns

Phthalates are not chemically bonded to the plastics, but physically mixed, so as the end products age or break down, phthalates will leach out into the surrounding directly and accelerate. Phthalates emit in each step starting from manufacturing through transportation, further processing, end products, until final disposal. They can migrate to in atmosphere, soil and water, and inhaled by human beings as well.

Recent years studies didn’t indicate the direct relationship between phthalate family (especially the aromatic function part) and the health concerns, but some clinical data and animal experimental results display endocrine disruption, effects to reproductive system, especially for males, and even carcinogen possibilities for some specific phthalates[10, 11]. So in now days, most of the countries are monitoring the phthalate produce and usages, and relevant regulations are issued as well.

2.3 POTENTIAL PHTHALATE ALTERNATIVES

Some criteria are very important for choosing the alternatives of phthalate plasticizers: excellent compatibility, miscibility and stability with the plastic hosts; lower plasticizer volatility; good performance at expected temperature range; great plasticizer efficiency and lower cost; and environmental and health safe, etc.[32].

From the review of the previous studies for phthalates free alternatives[18, 19, 32, 48, 49], we can summarize some substitutes: citrate, Hexamoll DINCH, adipate, trimellitate, acetate, polyurethane. Following we will introduce citrate, Hexanoll DINCH, and adipate, the two front alternatives will be briefly going through the LCA.

2.3.1 Citrates

Citrate based plasticizers are used for PVC over years[50]. The raw material citric acid is a natural product, citrates might have less health and environmental concerns comparing with other plasticizer compounds, which are manufactured from petroleum products, this is an attractive reason that people hope citrates can be applied more broad as plasticizers, and even can replace those having health concerns. But the cost for citrates is relative higher than phthalates， the estimated cost for ATBC is $2.45/lb, which is only $0.70/lb for DEHP[32], which constraining the widely manufacturing of citrates in industry. Citrates are primarily for food packaging and medical applications[50]. It is a promising alternative to phthalate because of its biodegradability and less biochemical affects, which is an excellent factor for medical field applications, such as the PVC blood bags, controlled release pharmaceutical drugs, gums, and other usages which have the high probability to be ingested or inhaled into human bodies.

Some examples of commercially used citrates are listed in Table 2-15. Especially for ATBC, it is a Non-Toxic and FDA approved Plasticizer[51], widely used for PVC products. The chemical structure of ATBC is in Fig. 2-8, and some of the physical properties of ATBC are listed in Table 2-16. ATBC is a kind of transparent and odorless oily liquid. It is insoluble in water, but soluble in alcohols and other organic solvents. ATBC has many application fields, such as it can be used as the plasticizer for PVC in food packing, medical devices, and precise instrument packing; it can be used as plasticizer for sustained-release pharmaceutical tablets and latex adhesives; it also can be used in toys manufacturing, and so on[52].

Table 2-15. Commercially used citrates

Name	Abbreviation
Acetyl tributyl citrate	ATBC
Tributyl citrate	TBC
Trioctyl citrate	TOC
Acetyl trioctyl citrate	ATOC
Trihexyl citrate	THC
Acetyl trihexyl citrate	ATHC
Trimethyl citrate	TMC

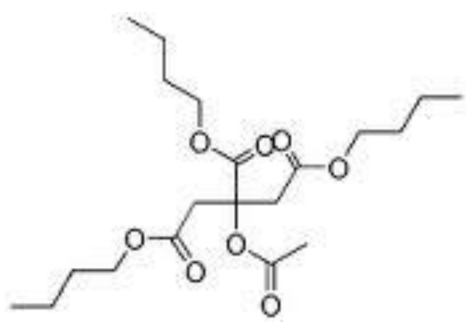


Figure 2-8. Chemical structure of ATBC

Table 2-16. Physical properties of ATBC

Chemical Name	Acetyl Tributyl Citrate
Trade name	ATBC
Molecular Formula	$C_{20}H_{34}O_8$
Molecular weight	402.5
Specific gravity (@ 27 °C)	1.050
Boiling point (@1.33 mbar)	173 °C
Viscosity (@20 °C)	34 cp

2.3.2 Hexamoll DINCH

1,2-Cyclohexane dicarboxylic acid di-isononyl ester (Hexamoll DINCH) was developed by one of the world's leading manufacturers of plasticizers (BASF), and started selling as a commercial product with the trade name Hexamoll DINCH in 2002. It is used as a plasticizer for plastic products, particularly for sensitive applications, which all have highly safety requirements, such as medical devices, toys, and food packaging materials. BASF claims that Hexamoll DINCH is "the most widely used phthalate substitute in the world"[53].

From the chemical structure, DINCH belongs to aliphatic ester; Fig. 2-9 is its structure sketch. DINCH has the average formula $C_{26}H_{48}O_4$, and average molecular weight 424.7. Some physical properties and product descriptions are list in Table 2-17. Although the molecular weights of DINCH and DEHP are comparable, the structural differences still lead to many different physical and chemical properties. DINCH is clear and colorless, and it can be applied not only to PVC, but also some other polar polymers. DINCH has high compatibility with almost all the commonly used monomeric plasticizers for PVC, only minor adjustments needed to process the PVC compounds, but has a lower interactive compatibility with PVC than DEHP[54]. DINCH has lower initial viscosity and better viscosity stability. Comparing with other phthalates, it has the advantages on low temperature performance.

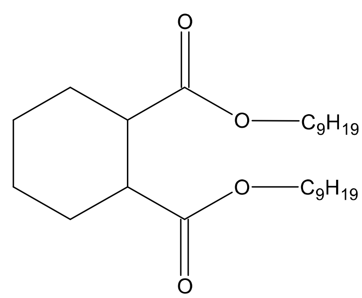


Figure 2-9. Chemical structure of Hexamoll DINCH

Table 2-17. Physical properties and product specifications of Hexamoll DINCH

Physical properties		
Formula		$C_{26}H_{48}O_4$
Molecular weight		424.7
Specific gravity@ 25°/25°C		0.947
Boiling range @ 7 mbar		240 -250 °C
Dynamic viscosity	@5°C	135 cP
	@20°C	52 cP

Table 2-17 (continued)

Dynamic viscosity	@40°C	19 cP
Flash point (COC)		224 °C
Odor		Mild characteristic
Product Specifications		
Ester content, by weight (% minimum)		99.5
Acid Number, mg KOH/gm (maximum)		0.07
Water, by weight (% maximum)		0.1
Color, Pt-Co units (APHA, max)		40
Phthalate content (% maximum)		0.010
As, Ba, Cr, Hg, Pb, Sb, Se, Sn (ppm max.) Cd (ppm max.)		0.6

There are two commercial paths for Hexamoll DINCH manufacturing: one is catalytic hydrogenation of diisononyl phthalate (DINP)[20, 54], through which six hydrogen atoms are added to the aromatic ring of DINP, the rest part is not affected; the other route is the Diels-Alder reaction of a maleic acid ester with 1,3-butadiene, then following with hydrogenation. DINCH is mainly manufactured for tubing, catheters, breathing masks, bags, gloves, and so on[49]. In 2002, the production of DINCH was 25,000 tons, it was expanded to 100,000 tons in 2007[55].

2.3.3 Adipates

Adipates are esters of adipic acid, and the general structure of adipates is schemed in Fig. 2-10, where R is a linear alcohol chain. There are several forms of adipates with different compositions and uses, such as potassium adipate and sodium adipate used as the food additives. Adipate plasticizers are primarily used to improve low temperature behaviors of the products. They can either be used alone as the major plasticizer, or combined with other phthalates together. The classic example of adipates used as plastic plasticizer is Bis(2-ethylhexyl) adipate (DEHA). Fig. 2-11 is the chemical structure of DEHA. Table 2-18 lists some physical properties of DEHA. DEHA is a clear liquid at room temperature. It is primary used in in hydraulic fluids, aircraft lubricants, and plastic food wrap.

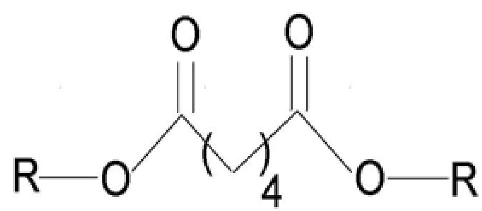


Figure 2-10. General structure of adipates (Where R = linear alcohol chain)

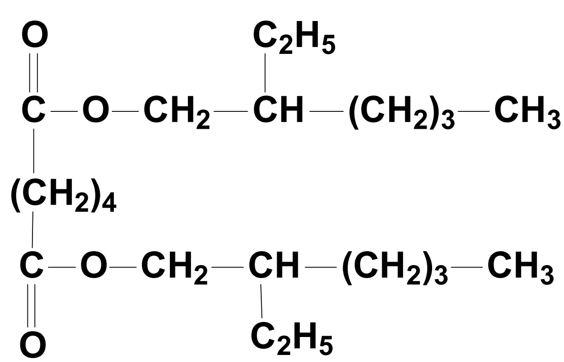


Figure 2-11. Chemical structure of DEHA

Table 2-18. Physical properties of DEHA[19]

Formula	$C_{22}H_{42}O_4$
Molecular weight	370.64
Melting point	-67.8 °C
Boiling point	417 °C
Vapor pressure (@ 20 °C)	1.1E-4 Pa
Density	0.922 g/ml
Henry's Law Constant (atmosphere)	1.3E-4 m^3/mol
Autoignition temperature	377 °C

DEHA was considered to be a possible human carcinogen, or cancer causing substance. Some studies showing the carcinogenicity of DEHA on mice, but still can not confirm the compound could lead cancer in humans[33]. Because of this, DEHA was removed from the toxic chemicals list by the United States Environmental Protection Agency's (EPA)[56]. Approximately 10,000 to 50,000 tonnes DEHA are manufactured each year in closed systems. The major exposure path to the general population is via consumer products. It is estimated that the migration rate of DEHA from food wraps is around117 ug/kg/d[19].

Previous studies indicates that DEHA has low acute mammalian toxicity in rats, and no mortality in rodents exposed via inhalation[19]. And in animal studies, DEHA is not irritating to skin or eyes[19]. A one-generation reproductive toxicity test shows that there were no effects on reproduction in rats although the body weight gains of first generation pups was reduced at a high dose level[19]. DEHA also has no apparent toxicity effects to aquatic organisms. It is reported that at the solubility limit of DEHP (0.0032 mg/L), no aquatic toxic effects were observed. The non-toxic concentration limitation is estimated to be 0.035 mg/L[19]. DEHA is a low bioaccumulation potential compound, and is readily to degrade via abiotic (hydrolysis) and biotic processes.

2.3.4 Other potential alternative plasticizers

Except the above three alternatives, there are also some other substitute options based on different applications and the property requirements. Trimellitates are the optional alternatives in automobile interiors, and other fields where high temperature durability is required. In addition, Trimellitates have extremely low volatility, good water resistance, and less migration tendency. One example in Trimellitates family is Trioctyl Trimellitate (TOTM). The typical end usages for trimellitates are blood bags, PVC tubes, catheters and so on[57]. Sebacates are the alternatives mainly used as a plasticizer in production of plastics, namely cellulose acetate butyrate, cellulose acetate propionate, polystyrene, many synthetic rubbers, and so on. Sebacates have excellent low temperature performances. Dibutyl Sebacate (DBS) and Dioctyl Sebacate (DOS) are the important members in sebacate families. Epoxy based monomeric plasticizers are another kind of substitutes[58]. They can be used in almost all the PVC formulations. They could improve the heat aging stability when mixed with other plasticizers. There are several commercial epoxide products. Considering the source availability, cost-performance, and efficiency, Epoxidized Soy bean Oils (ESO) is the predominantly used epoxy plasticizer. But there are some uncertain factors for using epoxides. One of them is that epoxides can photo-oxidized in certain conditions, decreasing the compatibility with the host. Therefore, the applications of epoxides plasticizers for PVC products are in a narrow field.

Not only the above mentioned plasticizers, but also some others, such as Phosphates, Benzoates, sulfonic acid esters and so on[57], they have the ability to replace phthalates in the specific application areas. But right now, no one can completely replace phthalate family, which has such comprehensively desirable properties required for a plasticizer.

2.4 ECO-EFFICIENCY DISCUSSION

An eco-efficiency discussion including four non-phthalate plasticizers comparing with DEHP (DEHTP in Fig. 3-7) was done by BASF. They are all popularly and widely used plasticizers for PVC applications. The four non-phthalate plasticizers are: Hexamoll® DINCH (diisononyl-cyclohexane dicarboxylate), acetyltributyl citrate (ATBC), acetylated castor oil derivative, and alkylsulphonic phenyl ester (ASE)[48], the latter two are not the targets in this thesis.

In Fig. 2-12 we can see that, among all the five plasticizers, Hexamoll® DINCH is the most eco-efficient one, even better than DEHP. The cost of DEHP is a slight lower than DINCH, but DINCH has the lowest overall environmental impact advantage, which is one of the most attractive merits for the society. ATBC is in the intermediate eco-efficiency level. ASE has comparable costs to ATBC, but the eco-efficiency is relative lower comparing with the other four plasticizers, which is due to its high material consumption, energy usages and emissions during manufacturing. Acetylated castor oil derivative has the lowest eco-efficiency of those five, with fair environmental performance but a much higher cost.

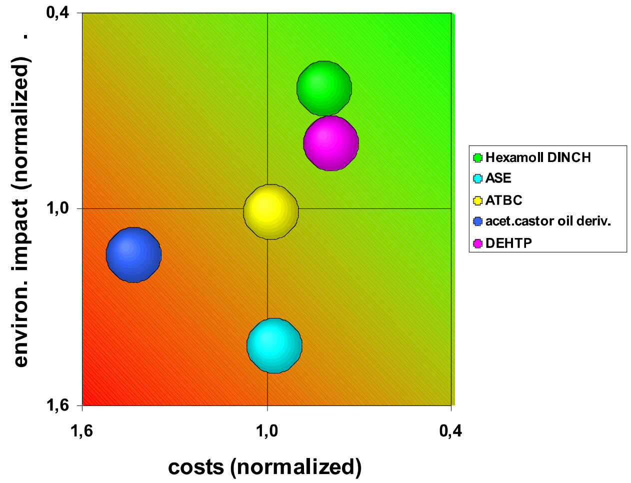


Figure 2-12. Eco-efficiency of non-phthalate plasticizers for PVC applications - results for base case: production and use of 1000 toy PVC balls[48]

The detailed cost estimation and normalized cost factor for DEHP and some other plasticizers are listed in Table 2-19[32, 59]. We can see that combining the cost and efficiency consideration, DEHP is still in the dominant position in plasticizer market. DEHA is almost equivalent to DEHP, and the normalized cost of DINP is a little bit higher than the previous two, but rather closes. The value for DINCH is acceptable, but for TOTM is significant high.

Table 2-19. Plasticizer Cost Estimation[32, 59]

Plasticizer	Cost Estimate ($/lb)	Substitution Factor (SF)	Normalized Cost (raw cost x SF)
DEHP	$0.70	1	$0.70
DEHA	$0.73	0.94	$0.70
DINP	$0.74	1.06	$0.77

Table 2-19 (continued)

DINCH	$0.91	unknown	$0.91
TOTM	$0.95	1.17	$1.11
ATBC	$2.45	1	$2.45

Data from Industry Sources, March 2006

2.5 LCA DVELOPMENT

LCA can show us a broad look for the relative environmental concerns. It has four main stages (Fig. 2-13). The initial step is to clarify the goal and scope definition, illustrating the boundary of the study, and ensuring the collected data is relevant to this study. In general, there are several boundaries definitions for LCA depending on the scope (Fig. 2-14). "Cradle-to-grave" LCA is from the extraction of raw materials through manufacturing, transportation, and use phase, finally end up to disposal.. The "cradle-to-gate" LCA just stops at the use phase, discarding the following disposal step. The "gate-to-gate" boundary only focuses on the manufacture part. And the "gate-to-grave" boundary starts from the use phase ending with disposal. Which boundary to choose depends on the goal of the study and data availability. The next step is to collect and quantify the data, which is called Life Cycle Inventory Analysis (LCIA), including the relevant energy and raw material inputs and the releases to the surroundings associated with the product or system. In the last two decades, the methodologies for LCIA was constructed and developed. The mature ISO standards for the LCI analysis and calculation are the instruction to follow: ISO 14040 is the principles and framework of LCA; ISO 14041 responds for the goal and scope definition and inventory analysis[31]. The third step is to evaluate the potentially environmental impacts associated the identified inputs and releases data. During the process, the software called SimaPro will be used to obtain the impacts results. And the last stage is interpreting the results to make a more reasonable decision. From the results, we can determine in which phase of the product or service life, would cause the greatest hazard to the environment. Then the corresponding activities will be identified and applied to minimize the impacts.

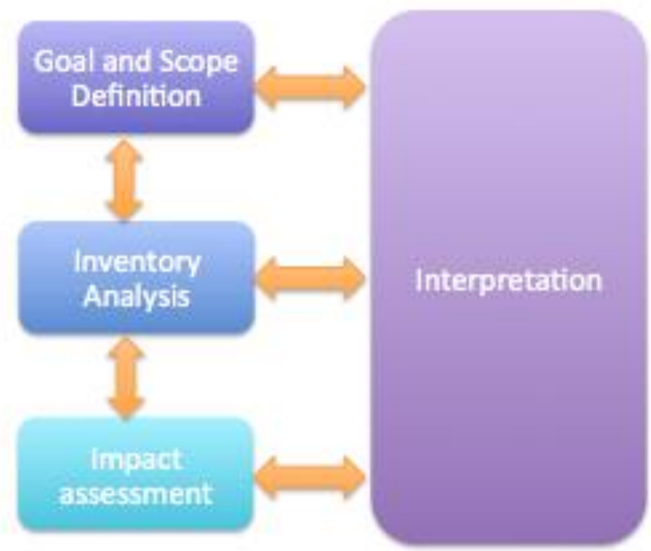


Figure 2-13. LCA strategies

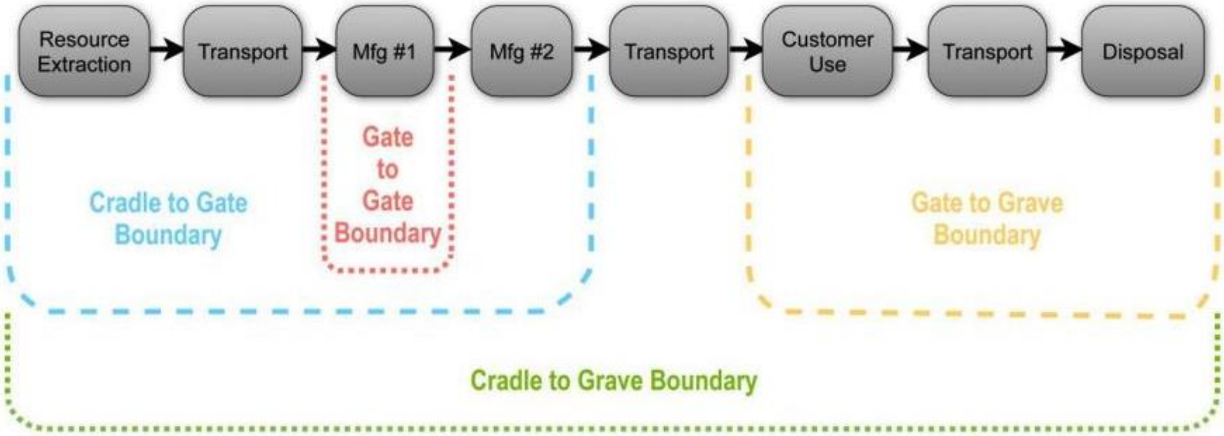


Figure 2-14. Common boundaries for life cycle assessment[60]

3.0 LCA TO DEHP AND TWO ALTERNATIVES (ATBC AND DINCH)

3.1 LCA TO DI-2-ETHYLHEXYL PHTHALATE (DEHP)

3.1.1 System descriptions

3.1.1.1 Goal of the study

The "cradle-to-gate" life cycle inventory and eco-profile of DEHP were represented. And the main sources of environmental impacts in DEHP production routes were identified as well. The investigation of potential alternatives is another important supplement for this study.

3.1.1.2 Scope Definition

There are two analysis systems in this study. The one in this chapter is “cradle-to-gate” boundary (Scope 2) focuses on DEHP manufacturing routes (Fig. 3-1) It gets starting from the raw chemicals acquisition, through adding the energy flows into the manufacturing process to complete the LCIA. Transportation data is not available for the raw materials from local to manufacturer. In general, the plant sites are located in the reasonable distance to the raw material resources, this is considered even before plant construction. So the impact for this part is not included in our study. This second system will be introduced in next chapter.

The geographical scope of this study is North America. The environmental impact for phthalate esters is a global problem, people in every country are facing PVC products every day, all of us are exposed in the atmosphere with phthalate, the concentrations may be various, but they definitely exist. Assessment should be done based on the data availability, EU and North America did much effort on collecting the data, so this report is mainly focus on North America, and some estimation is also partial from EU data as complement.

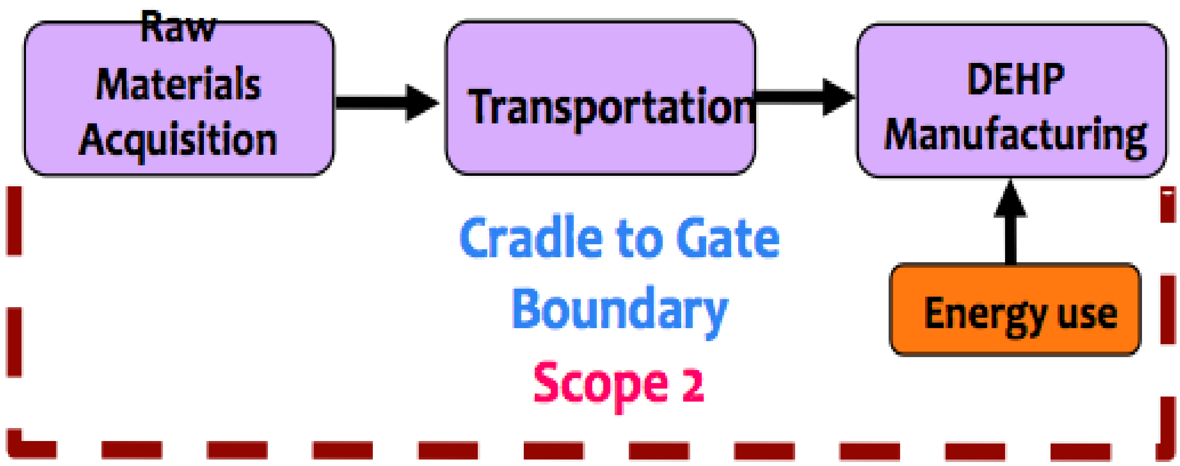


Figure 3-1. **Scope definition for DEHP manufacturing: "Cradle-to-Gate" boundary for DEHP**

3.1.1.3 Methods

TRACI

TRACI ("Tool for the Reduction and Assessment of Chemical and other Environmental Impacts") is a powerful LCA software developed by the United States Environmental Protection Agency (EPA). It is based on regional conditions of North America, including environmental factors for various materials and energy flows. TRACI is primarily a midpoint approach. It can be used to construct more accurately model American Life Cycle Assessment (LCA) studies, performs impact assessment starting from inventory data, facilitating the characterization of environmental factors that have potential effects. It can support consistency in environmental decision-making. TRACI mainly focuses on the impacts associated with the raw material usage and chemical releases from the manufacturing processes. The users are allowed to add the materials and energy needed, and getting the long-term environmental impacts as results, such as global warming, acidification, eutrophication, carcinogenic, non-carcinogenic, smog, ozone depletion, ecotoxicity, respiratory effect, and so on[61]. TRACI is used for DEHP manufacturing (raw material & energy flows) in this thesis.

Fig. 3-2 sketches the frame of TRACI[61], TRACI stores the inventory data, stressors classification, and characterization for the impact categories. Inventory data is collected on specific process within various life cycle stages. Either products or processes can be conducted via this program. Then incorporating with normalization and valuation steps, the result could be a good indicator for decision-making.

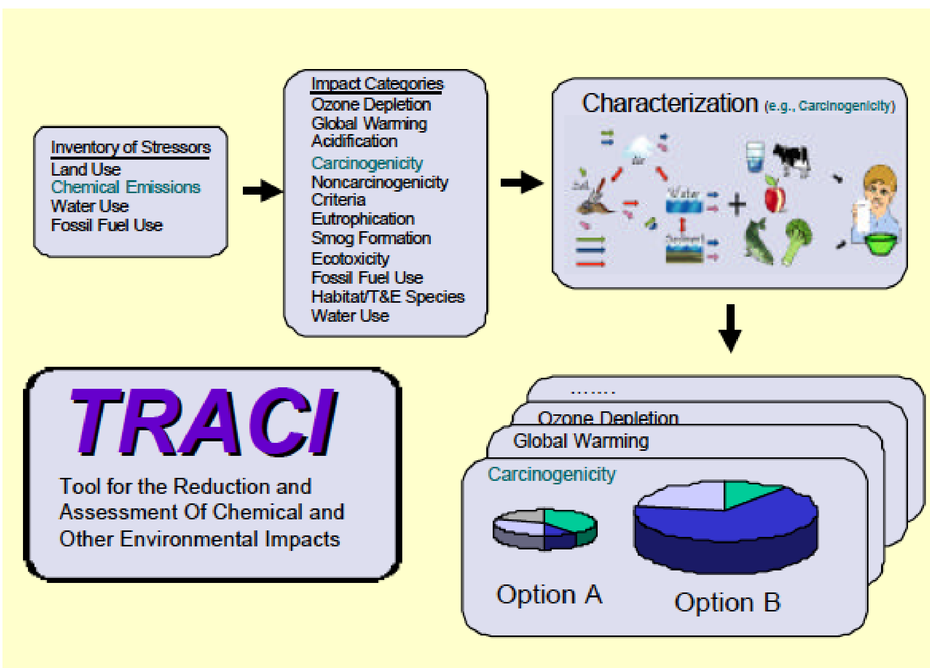


Figure 3-2. TRACI frame[61]

SimaPro is the most widely used LCA software. It offers the standardisation for LCA assessment, and provides reliable results for alternatives comparison. Various methods are built in SimaPro, so as TRACI and BEES (which is used in next chapter). SimaPro could provide comprehensive models from a lifetime perspective. SimaPro has various applications, such as carbon footprint calculation, product design and eco-design, environmental product declarations (EPD), environmental impact of products or services, Environmental reporting (GRI), Determining of key performance indicators[62]. All the methods in SimaPro are constructed based on diverse databases for different graphic locations. The geographical scope of this study is North America. Among all the methods included in SimaPro, TRACI and BEES are widely and mainly used in North America. So not only its powerful function, but also the geographical scope, made us this choice.

3.1.1.4 Functional Unit

After defining the goal and scope of the system, the system function could be determined. Only on the basis of similar system function, various products or services could be compared. Functional unit is defined based on the system function, and it is common to all scenarios. It is a representative of the system function, and serves as a basis for scenario comparison. It is a quantified and additive value, and normally in the inventory, inputs and outputs are calculated per Functional Unit.

- The functional unit for DEHP manufacturing is:

"To produce one kilogram of high volume commodity DEHP"

3.1.2 LCIA for DEHP manufacturing - raw materials & energy flows

Similar processes are used for DEHP manufacturing widely in North America and Europe. Fig. 3-3 is the Scheme for DEHP production procedures and the major applications. Esterification of phthalic anhydride with 2-ethyl-hexanol is the first reaction procedure, which includes two successive steps: formation of monoester by alcoholysis of phthalic acid, and then conversion of the monoester to the di-ester. The first step occurs rapidly and completely; the second step is a reversible reaction, and catalysts involved. Typically during the reaction, water is removed by distillation to shift the equilibrium towards the target products; different temperature ranges (140°C-250°C) are applied depending on the catalysts sorts. The second step is much slower than the first one. Catalyst, reactant alcohol and procedures chosen may results in purity variations. Alcohol excess is required for this reaction. All the excess raw materials will be recovered and recycled for the continuous process. The product DEHP will be purified and stored for the supply chain[63].

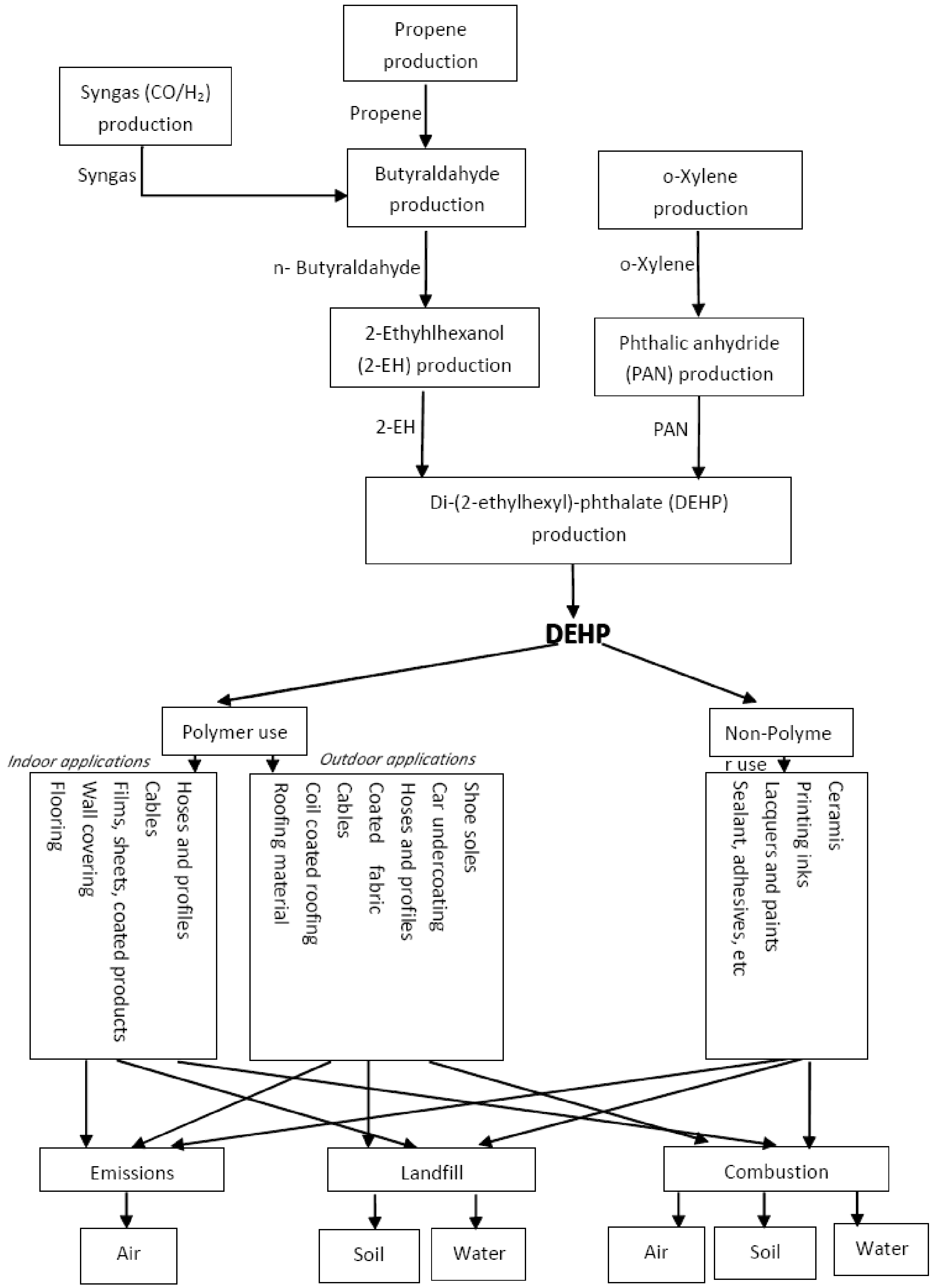


Figure 3-3. Schematic Flow Diagram for the Manufacturing and Applications of DEHP[63]

Two parts generate the DEHP manufacturing: raw materials acquisition and energy flows, so the LCIA for the produce route is also based on these two parts. In general, the raw chemicals' consumptions during processing follow the chemical reaction equations for DEHP manufacturing. But the real consuming capacity of each material is different from the theoretic amount after considering the thermo and catalytic promotion. In this study, due to insufficient industrial data available, and to simply the condition, we assume the LCIA for all the raw chemicals' consumptions is only based on the chemical reaction equations for DEHP manufacturing. The raw chemicals' amounts used in Table 3-1 are for 1 kmole (390kg) of DEHP manufacturing, which is also the input data for SimaPro. The corresponding environmental impacts data from TRACI and some calculations are listed in Appendix A, and Fig. 3-4 is the impacts results. The three major environmental impacts for DEHP manufacturing from raw materials are global warming, ecotoxicity, and acidification.

Table 3-1. Raw materials ratio for 390kg of DEHP manufacturing (based on the reaction ratio)

Amount	Unit	Product	Unit
8	kg	Hydrogen, liquid, at plant/RER U	Ecoinvent unit processes
112	kg	Carbon monoxide, CO, at plant/RER U	Ecoinvent unit processes
168	kg	Propylene, at plant/RER U	Ecoinvent unit processes
148	kg	Phthalic anhydride, at plant/RER U	Ecoinvent unit processes

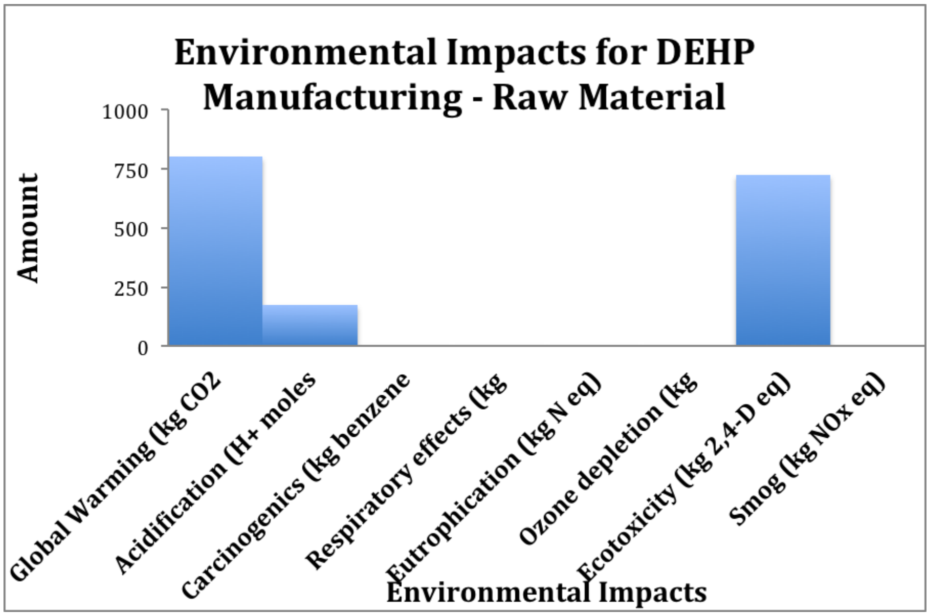


Figure 3-4. Environmental impacts for DEHP manufacturing

Energy flow is the other important component for DEHP manufacturing. The primary fuels and feedstock to produce 1 kg of phthalate ester are outlined in Table 3-2, data obtained from ECPI (2001). The data output from TRACI are listed in Appendix B, from which we can obtain the Environmental impacts for energy flows of 1 kg DEHP production in Fig. 3-5, this is the absolute value result. In this figure, “energy content of delivered fuel” refers to the energy used during manufacturing; “energy use in transport” refers to the energy used during all the transportation processes; feedstock energy refers to the energy embedded in feedstock, and “fuel production and delivery energy” refers to the original energy used to produce and delivery fuel. This result indicates that “Feedstock Energy” and “Energy Content of Delivered Fuel” are the two major sources for the environmental impacts. “Fuel Production and Delivery Energy” and “Energy Use in Transport” contribute much less than those two. The two dominant environmental impacts from energy flows are global warming potential and acidification. The absolute values for others impacts are tiny comparing with the dominant two, but we can obtain the details for each category from the normalized result, which is shown in Fig. 3-6.

Table 3-2. Gross primary fuels and feedstock to produce 1kg of phthalate ester (Modified from ECPI, 2001[31])

Fuel Type	Fuel production and delivery energy (in MJ)	Energy content of delivered fuel (in MJ)	Energy use in transport (in MJ)	Feedstock energy (in MJ)	Total energy (in MJ)
Coal	0.63	0.42	0.0005	0	1.06
Oil	0.84	7.97	0.20	24.11	33.11
Gas	2.81	10.73	0.05	22.60	36.19
Hydro	0.06	0.18	0.001	-	0.24
Nuclear	0.90	0.42	0.0002	-	1.32
Lignite	0.34	0.08	0.0002	-	0.42
Wood	0	-	0	0.0001	0.0001
Sulphur	0	0.0002	0.0001	0.022	0.02
Biomass	0.002	0.001	0.0001	0.0001	0.003
Hydrogen	0.0001	0.05	0.0001	-	0.05
Recovered energy	-	-1.64	-	-	-1.64
Unspecified	0.004	1.86	0.0001	-0.73	1.13

Table 3-2 (continued)

Peat	0.0002	0.0001	0.0001	-	0.0003
Total	5.57	20.07	0.25	46.00	71.90

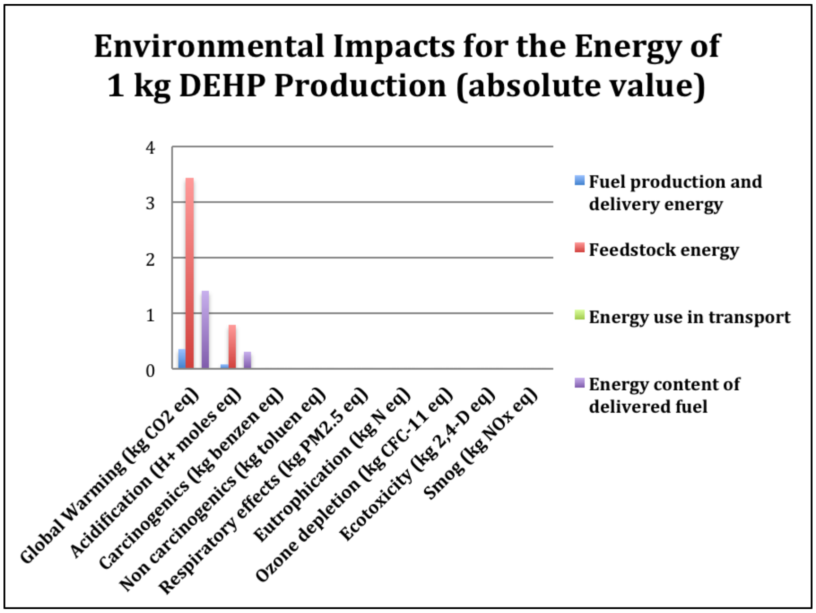


Figure 3-5. Environmental impacts for energy flows of 1 kg DEHP production (absolute value)

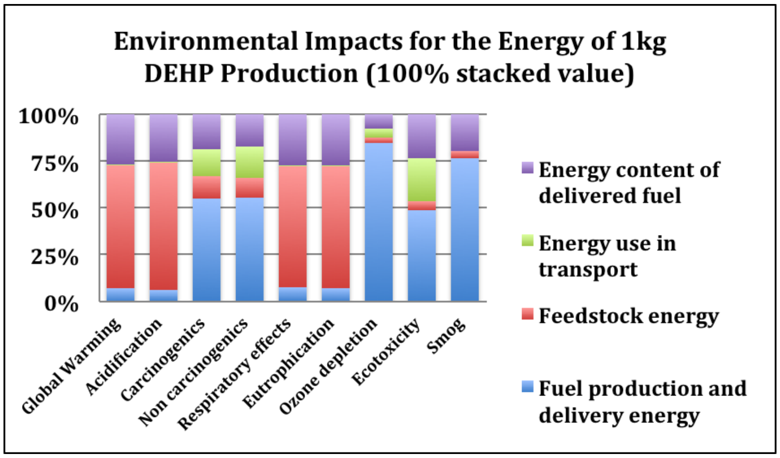


Figure 3-6. Environmental impacts for energy flows of 1 kg DEHP production (100% stacked value)

Fig. 3-7 shows the integrated environmental impacts for energy flows and raw materials of DEHP manufacturing (the raw data and calculation process are in Appendix C), indicating that the raw chemical materials contribute more environmental impacts during DEHP manufacturing than energy usages. The inputs for SimaPro for raw chemicals are for the ideal condition, 100% materials consumption, but in real industrial manufacturing, there will be a certain amount of materials are wasted, we assume the average conversion is 90%, the error bar indicates the tendency of real environmental impacts for raw materials (blue color), which even further larger than the energy flows' impacts.

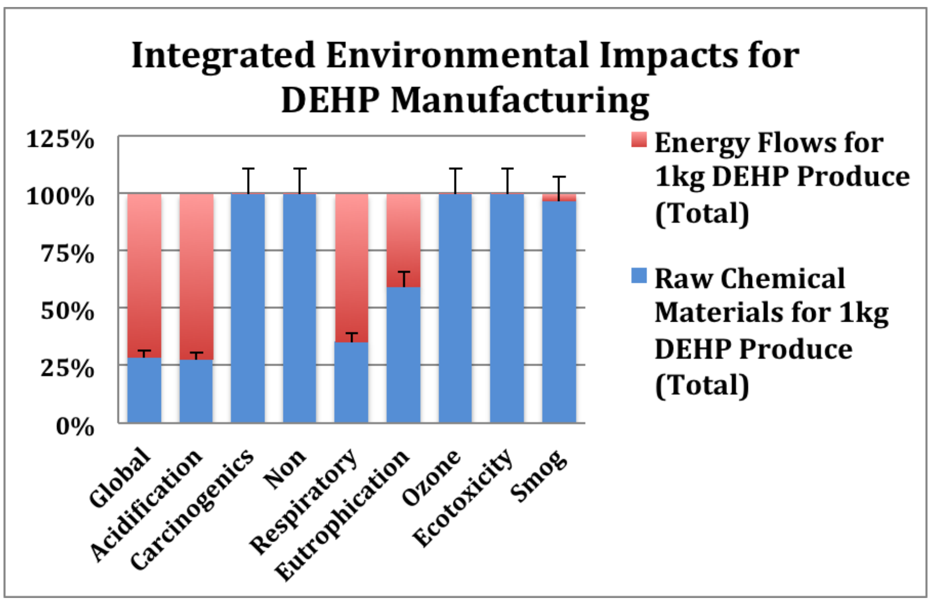


Figure 3-7. Integrated environmental impacts categories for DEHP manufacturing: raw materials & energy flows

3.1.3 DEHP release

Plasticizers are used widely indoors and outdoors. So far we are not clear that the environmental emissions of DEHP in each lifetime stage will maintain in DEHP form or decompose into other chemicals, but DEHP form is the source of those above health concerns, the emission data in DEHP form is collected in Fig. 3-8, showing the releases of DEHP from "cradle-to-gate" steps (from manufacturing to end use) in the EU in 2007[64]. The main DEHP releases resources are from use phase, both indoor and outdoor. And they primarily deposit into soil or waste water. The original data is in Appendix D.

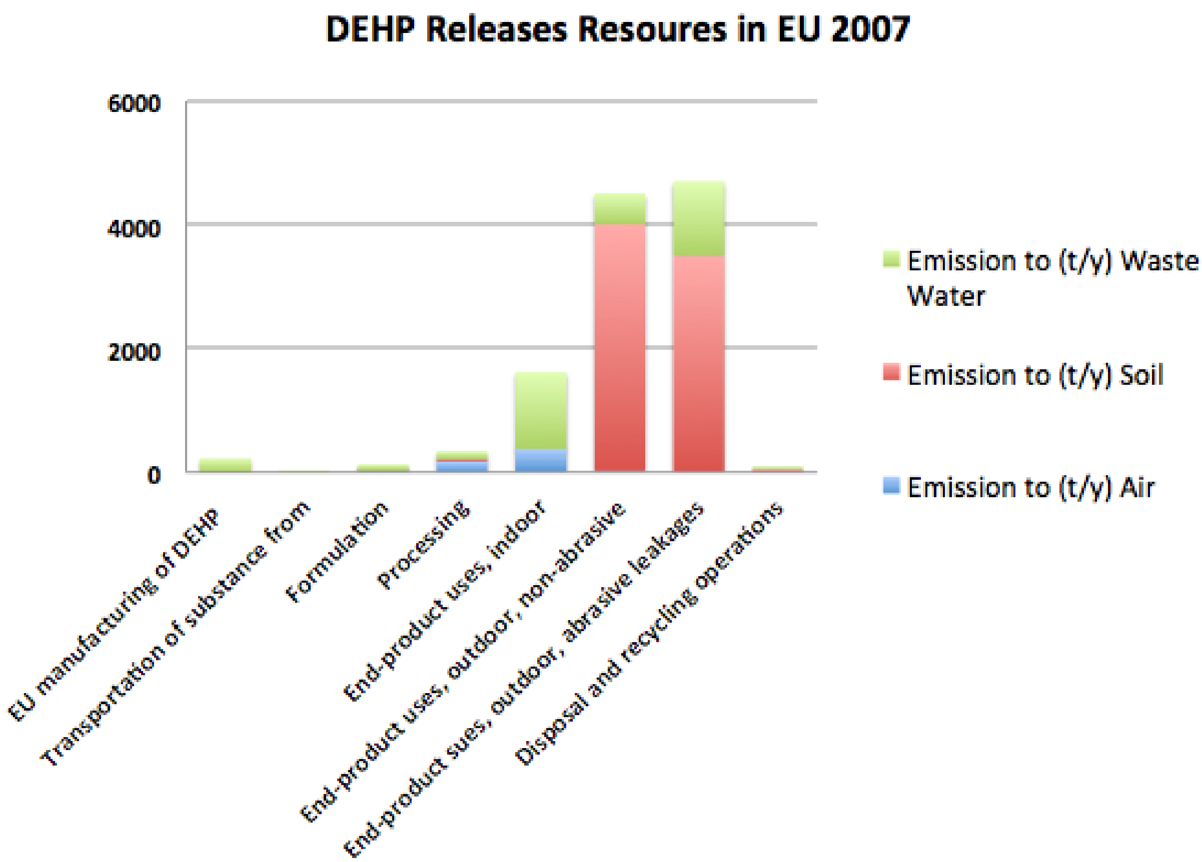


Figure 3-8. DEHP releases resources in EU 2007[63]

3.2 TOXICITY AND ECONOMIC ANALYSIS TO TWO PROMISING ALTERNATIVES: DINCH AND ATBC

DINCH and ATBC are two promising alternatives of DEHP. DINCH is one of the most widely used phthalate substitutes in the world, and recommended for use in medical products, toys, and food packaging applications etc. DINCH is only produced by BASF, it is a hydrogenated ester, and the chemical formula is $C_{26}H_{48}O_4$. DINCH is manufactured from hydrogenated DINP in the presence of a catalyst[24], aromatic functional group disappeared, but the alcohol component is maintained, Fig. 3-9 is the conversion process of DINP to DINCH. This is a suitable conversion. DINCH has the similar plasticizing properties as DINP. Further more, mixtures of diisononyl esters of 1,2-cyclohexanedicarboxylic acid, wherein which the branching degree of isononyl radicals increased from 1.2 to 2.0, are especially appropriate for replacing DEHP in PVC applications[65].

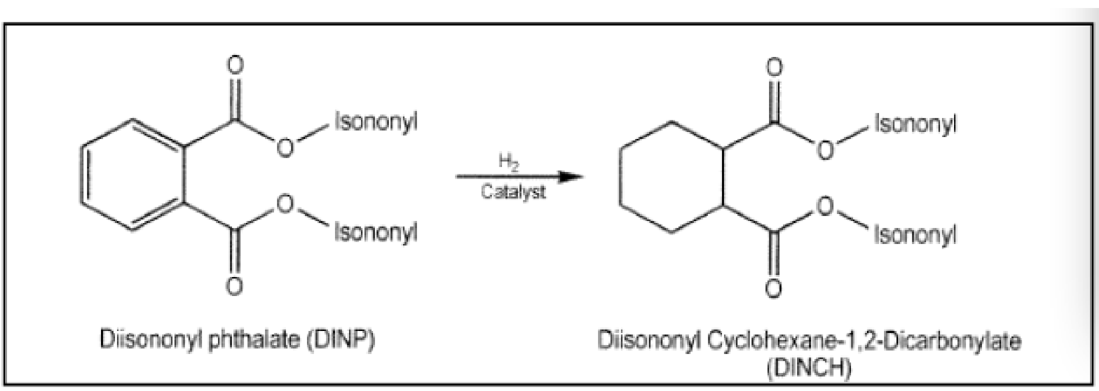


Figure 3-9. Conversion of DINP to DINCH.

ATBC is produced from natural raw materials, which is the reason why it is believed to be a safe substitute. The reactions get start from Citric Acid and n-Butanol at the presence of catalyst (H_2SO_4)[66], then Acetic Anhydride involved to synthesis ATBC. ATBC is recommended for food and medical applications. But the drawback for ATBC is that it is much more expensive than other commonly used plasticizers, shown in previous Table 2-19, almost three and a half times of DEHP. So it cannot be widely used for the industry now. But if the result indicates that it is environmental friendly, a low cost manufacturing method can be developed in future work.

The environmental impacts analysis for ATBC and DINCH from SimaPro cannot be done right now, because we do not have the inventory data for all the raw chemicals needed and the enough information about the energy flows for their synthesis, but a comparison among them with DEHP in toxicity, cost and efficiency was done (in Table 3-3). From the results shown below, ATBC and DINCH are definitely much more safe than DEHP in animal experiments. They two have much higher NOAEL (shown as the lowest effect amount in male or female rat) amounts than DEHP, which is the lowest effect amount in male or female rats; and they also do not have obvious effects for reproductive system. But from economic view, ATBC has the same efficiency factor as DEHP, and DINCH is a little bit lower. But combining with the cost indication, the price of DINCH is one and a half of DEHP, and ATBC is even 350% of DEHP. In another word, both DINCH and ATBC need much more cost to achieve the same efficiency as DEHP. So for the future work, if the production cost can be decreased sharply, ATBC and DINCH could replace DEHP in some specific applications very soon, but a complete LCA still need to be done for those two to confirm they are environmental friendly or not, this process needs more industrial data to support.

Table 3-3. Comparison among DEHP, ATBC and DINCH[21, 59]

Category		Plasticizers		
		DEHP	ATBC	DINCH
Toxicity	NOAEL mg/kg bw	4.8	100	107
	Reproductive Toxicity	Yes	No	No
	Critical Endpoint	Reproduction	Decreased bw	Kidney*
Cost	Price Indication	100% (Bulk Phthalates)	350% (Citrates)	150%
Plasticizer Efficiency for the Same Weight	Efficiency Factor	100%	100%	90%
Weight Equivalent	Weight Equivalent	1	1	1.11

NOAEL is shown as the lowest effect amount in male or female rat

Bw: body weight

*Kidney effects in male rats due to alpha-2-u macroglobulin, a mechanism not relevant to man.

3.3 ASSUMPTIONS AND LIMITATIONS

The chemical reactions for DEHP manufacturing in plant, due to no conversion rate data for each reaction available, we have to assume that in ideal condition, all the raw chemicals are 100% consumed following the chemical reaction ratios to finish the calculation. Although which is impossible in real industry reactions, but if we can get access to the industry data obtaining the conversion rate, based on some calculations, the amounts can be amended.

The amounts for all the original chemicals used for TRACI inputs, are based on the reactants ratio for ideal conditions. In real industrial reactions, because of the chemical equilibrium theories, some reactants should be more than needed to improve the productivity, and catalysts are applied as well. Again, because of the data not available, these factors are not included in this assessment.

When TRACI is applied to do the assessment, the environmental impact results are based on the overall raw material flow charts fed to the environment eventually (water, soil or atmosphere). Here DEHP is only an intermediate product, which will be introduced into further applications, which leading to some errors for the environmental impacts, but still acceptable.

4.0 LCA TO ONE OF DEHP’S APPLICATIONS - VINYL FLOORING

4.1 INTRODUCTION

Vinyl Flooring is one of the most important applications for DEHP. The annual consuming amount is around 33,000 tons in EU in 2007[59]. Less data for the usage amount in U.S., but from the worldwide usage condition, we can assume that it as least has the comparative amount with EU.

Vinyl composition tile (VCT) is the typical representative of vinyl flooring. In this study, we referenced EU VCT data to approach a relatively complete LCA for vinyl flooring, but we only consider the environmental impact of Green House Gas (GHG) as the evaluation criterion for the whole "Cradle-to-Grave" process, because of less data available. This "Cradle-to-Grave" analysis starts from the raw material acquisition and manufacturing GHG emission, combining with process energy and non-energy emissions, through transportation emission, end up with combustion and landfill disposals.

Vinyl flooring materials are diverse with different grades and quality. VCT construction is various from vinyl sheet. It contains a high proportion of inorganic filler, such as limestone, to increase its dimensional stability and reduce its elasticity. Some classic PVC tile samples with DEHP are shown in Fig. 4-1. Typically there are four primary layers for vinyl tile (Fig 4-2): the top layer is urethane wear which is used to resist scratches and scuffs, keeping the appearance of the tile; a second layer of clear film is added to protect against the damages such like gouging, rips and tears; next layer is a printed design layer carrying the realistic colors and patterns, to extend the tiles market diversity; the backing layer is also the structural sustaining layer maintaining the strength and durability of the tile, which is mainly made from vinyl composition[67].

Figure 4-1. Typical DEHP/PVC tile samples

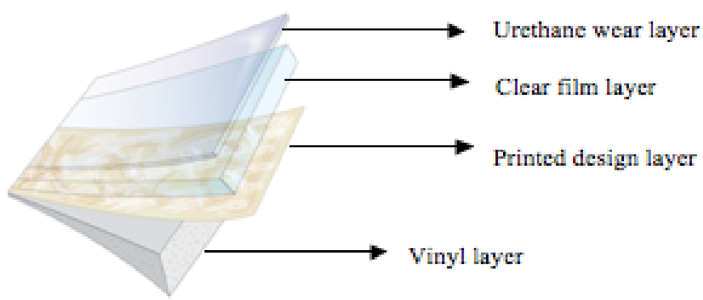


Figure 4-2. Vinyl flooring tile construction[63]

The general composition of the VCT flooring with DEHP plasticizer is listed in Table 4-1. From the table we can see that Limestone component accounts for nearly 80wt% of the whole flooring material, PVC and DEHP are 12wt% and 5wt% respectively. But considering the huge consumption amount of VCT per year, the totally annual usage of DEHP for vinyl flooring can lead a significant environmental issue.

Table 4-1. DEHP/PVC VCT flooring composition[32]

Wt. %	Material	Origin/Precursor Materials
12%	PVC	Ethylene dichloride, vinyl chloride
5%	Plasticizer DEHP	Phthalic anhydride, 2-ethylhexyl alcohol
80%	Limestone	Mineral
2%	Vinyl acetate	Ethylene, acetic acid
1%	Other ingredients	Stabilizers, etc.

4.2 BENEFIT OF SOFTENED VINYL FLOORING

PVC flooring has excellent durability; generally it can last for up to 20 years. Plasticizers can guarantee the flexibility of the end products during the designed lifetime. And also the degradation and discoloring from exposure to ultra violet light are resisted.

Softened PVC flooring gives the manufacturers more possibility for designing. It is easier to build up complex patterns, and multiple designs could be achieved to diverse the styles, which resulting in more modern and eye-catching flooring materials. Commonly, the softened vinyl flooring has a smoother, colorful and shiny surface, which can cut down the need for cleaning and polish maintenance. And combining with its low price and long lifetime advantages, vinyl flooring is the good choice for schools, offices, and other public constructions with large floor areas.

The smooth and tough surface layer of the softened vinyl flooring can also prevent dust and dirt from building up and microbes breeding, and reduce disease and infections, which is a merit function for sensitive condition applications, such as hospitals and clinics, where requiring high hygienic quality.

4.3 SYSTEM DESCRIPTIONS

4.3.1 Goal of the study

Choose vinyl flooring as the use phase, extend this "cradle-to-gate" approach of DEHP to build a "cradle-to-grave" profile.

4.3.2 Scope definition

Continuous from the previous chapter, the second system of this study is "cradle-to-grave" boundary (Scope 3) to do the LCIA for vinyl flooring (Fig. 4-3), which starting from raw material extraction, through transportation, manufacturing, use phase, and finally disposal. By now, we don't have enough input data, but the output data are in CO_2eq format, convenient for comparison. The geographical scope of this system is North America as well. But based on data availability, portion of the data is collected from EU, and estimated to have the equal effect to North America.

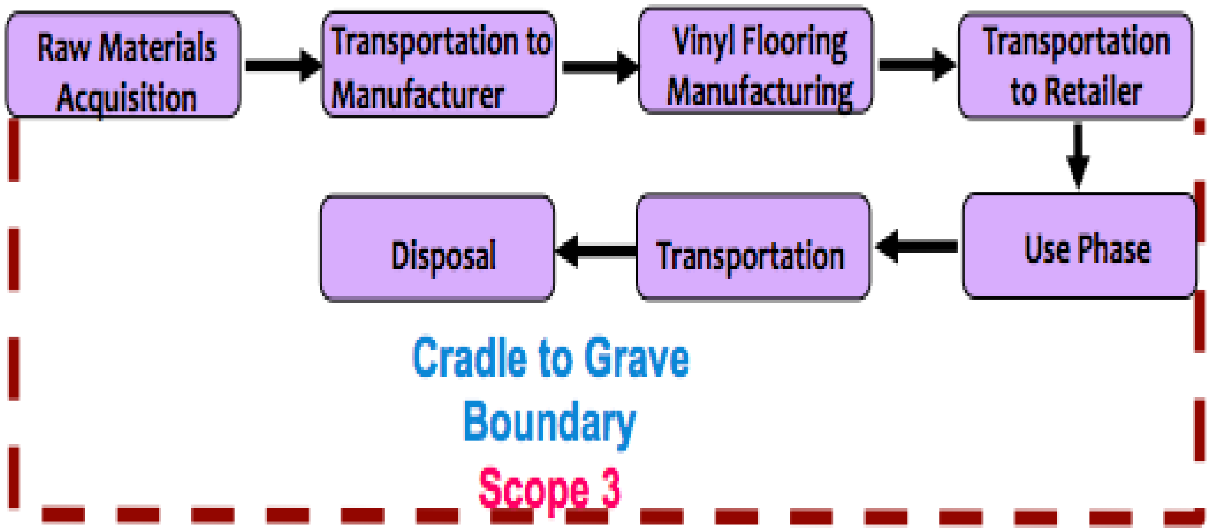


Figure 4-3. Scope definition for vinyl flooring manufacturing: "cradle-to-grave" boundary for vinyl flooring

4.3.3 Method

BEES

BEES ("Building for Economic and Environmental Sustainability") is developed by the Building and Fire Research Laboratory of the National Institute of Standards and Technology (NIST), it is an approach for measuring the life-cycle environmental and economic performance of a building for the entire lift-cycle stages. It has a database of 280 building products with various categories, and is adding more as time going. However, the shortcut for BEES method is that it is a generic method, the outcome is not for a specific product, but for the entire class. It is primarily used for North America as well. In this study, vinyl flooring is one of the construction materials, and all LCA data about vinyl flooring came from BEES model.

4.3.4 Functional unit

- The functional unit for the plasticizer application - vinyl flooring is:

"To produce one short ton of vinyl flooring"

4.4 ENVIRONMENTAL IMPACTS OF VINYL FLOORING

The environmental impacts result for Vinyl Flooring came from BEES, this is a "cradle-to-grave" LCA. Fig. 4-4 is the normalized environmental impacts results for vinyl flooring, the blue color refers to the raw materials, the red refers to manufacturing, and green refers to transportation. The other two stages "end of life" and "use phase" contribute tiny for the total impacts. The blue color (raw material) is the dominant part in each of the category. So the raw materials are the major resources of environmental impacts!

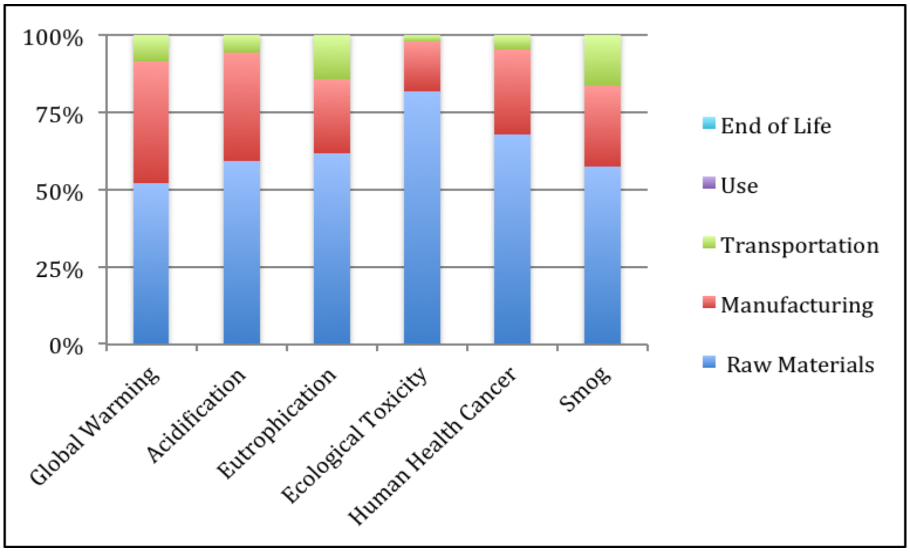


Figure 4-4. Normalized environmental impacts result for vinyl flooring

4.5 ASSUMPTIONS AND LIMITATIONS

The raw material mix for vinyl flooring is assumed to be 100% virgin inputs. In real industry, only very little amount of vinyl flooring, which has lower quality level requirements, and is manufactured from recycled inputs, we don't have any data about this part so this part is ignored in this study.

Life cycle datasets for infrastructure are not included in this study, i.e. energy and CO_2 emissions associated with producing the capital equipment used to make the products are ignored.

The life cycle data EPA used to develop the emission factors for vinyl flooring were collected from various data sources. A literature search did not identify a complete, publicly available U.S. specific dataset. So some estimates are representative of European processes to complete the estimation of US condition.

5.0 CONCLUSION

5.1 DISCUSSION AND CONCLUSIONS

We compared the environmental impacts of raw chemical materials and energy flows for DEHP manufacturing. The results (Fig. 3-6) indicate that the raw chemical materials contribute more environmental affect during DEHP manufacturing than energy usages. In the energy supply chain, “Feedstock Energy” and “Energy content of delivered fuel” are the two major sources for the environmental impacts. If we intend to decrease the environmental impacts for the product, the better way is to optimize the one or ones accounting for the larger part among all the impacts. Here, the chemicals' amounts are based on the reaction ratio, which contribute more than energy for the environmental impacts. Through optimizing the supply chain, developing the technique to increase the material usage efficiency (less material over usage), we believe a curtain amount of impacts still can be decreased. In addition, considering the health concerns to human, investigating the potential alternatives, and improving their technological process is another way to lower the impacts.

Because of the data availability, LCAs to ATBC and DINCH cannot be accomplished right now. But considering the health concerns and substitution factor, they are still good potential alternatives. DINCH has the similar chemical structure to DEHP. We can estimate that, the environmental impacts for DINCH are approximately equal to the impacts of DEHP plus an extra amount. So comparing with DEHP, DINCH has the increased embedded impacts, and decreased use phase impacts.

Vinyl flooring is chosen as the use phase to construct a complete "cradle-to-grave" LCA model. In Fig. 4-4, after normalizing all environmental categories, we can see that "Raw Material" contributes more environmental impacts in the entire life-cycle stages of vinyl flooring. Optimizing the material acquisition supply chain and improving the energy efficiency are the two aspects to decrease the environmental impacts.

5.2 IMPROVEMENT ANALYSIS

The case studies about DEHP and its alternatives in this report do not involve statistic data analysis, but follow the criteria in chemical reaction process. The inputs for SimaPro were based on the reaction ratios and the data from governmental and industrial investigations for the entire industry, so the traditional sensitivity OAT analysis was not suitable for this case study. The better idea for the improvement of this assessment is to increase the precision of the data. Some analysis is based on the data estimation, because of no data available. Especially for the application study, only limited data available, so to improve the analysis, more complete, more accurate, and more efficiency, cooperation with the industry should be considered.

5.3 COMPARE WITH OTHER LCAS

To our knowledge, most of the LCAs or Eco-Profiles for Plasticizers or Vinyl Flooring are focused on the use phase only; do not include the raw material acquisition, transportation, energy usages, and disposals. Therefore, we conducted an extensive review of the previous studies and the relative toxicological databases on phthalates and their substitute compounds. This study, as complete as we can, starts from the raw materials acquisition for DEHP to impel the LCA, after manufactured as a useful intermediate, choosing one of the most important applications - vinyl flooring to continue the LCA for use phase and disposal. Even finally these two parts were not integrated together because of less data for the other compositions of vinyl flooring, but this idea and model, can be used for further phthalates and their other applications' LCAs as long as we have enough data.

5.4 FUTURE WORK

Further work can focus on the potential alternatives. As we know, the hazard to the environment and threat for human health from chemicals, it needs a long time to accumulate, then appearing as a common issue to public attracting people’s attention. And the data collection also needs enough time periods to obtain effective data. The studies for the alternatives have started since people realized the hazard of phthalate family, but still not long enough to collect all the data needed for a complete life cycle analysis, which needs the information from various fields, raw materials, energy, transportation, emissions, landfill, health safety study, and so on. When enough data available, construct a LCA model comparing with DEHP, which will lead us a promising way to improve the technology and decrease the environmental impacts.

APPENDIX A

LCIA AND ENVIRONMENTAL IMPACTS FOR ALL THE RAW CHEMICALS FOR DEHP MANUFACTURING

The LCIA for all the raw chemicals is based on the real chemical reactions for DEHP production. Due to insufficient industrial data available, we have to assume that all the raw chemicals are consumed following the chemical reaction ratios to finish the calculation. The raw chemicals amount used in Table A-1 are for 1kmole (390kg) of DEHP manufacturing. Table A-2 is the corresponding environmental impacts data from TRACI, and Fig. A-1 is the result showing the major environmental impacts associated with DEHP manufacturing from raw materials.

Table A-1. Raw materials ratio for 390 kg of DEHP manufacturing (based on the reaction ratio)

Amount	Unit	Product	Unit
8	kg	Hydrogen, liquid, at plant/RER U	Ecoinvent unit processes
112	kg	Carbon monoxide, CO, at plant/RER U	Ecoinvent unit processes
168	kg	Propylene, at plant/RER U	Ecoinvent unit processes

Table A-1 (continued)

148	kg	Phthalic anhydride, at plant/RER U	Ecoinvent unit processes

Table A-2. Environmental impact for 390 kg DEHP manufacturing (data from SimaPro)

Impact category	Unit	Hydrogen, liquid, at plant/RER U	Carbon monoxide, CO, at plant/RER U	Propylene, at plant/RER U	Phthalic anhydride, at plant/RER U	Total
Global Warming	kg CO_2 eq	13.061	175.497	237.685	376.145	802.388
Acidification	H+moles eq	1.537	53.623	35.079	84.863	175.101
Carcinogenics	kg benzene eq	0.00364	0.368	0.0559	0.506	0.933
Respiratory effects	kg PM2.5 eq	0.00648	0.3076	0.144	0.442	0.900
Eutrophication	kg N eq	0.00180	0.147	0.0339	0.117	0.300
Ozone depletion	kg CFC-11 eq	2.634E-08	4.048E-05	1.384E-08	1.110E-05	5.16E-05

Table A-2 (continued)

Ecotoxicity	kg 2,4-D eq	3.474	374.682	50.403	296.365	724.925
Smog	kg NOx eq	0.0175	0.372	0.377	0.684	1.450

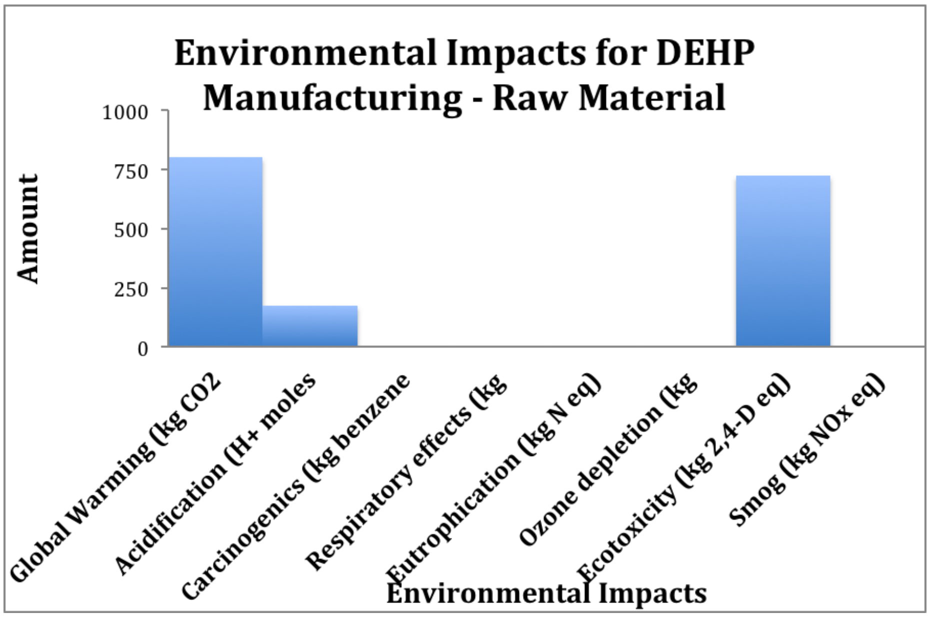


Figure A- 1. Environmental impacts for DEHP manufacturing - raw materials.

APPENDIX B

LCIA AND ENVIRONMENTAL IMPACTS FOR THE ENERGY USAGE OF DEHP MANUFACTURING

Following is the LCIA data for energy flows of 1kg DEHP from TRACI. Fig. B-1 indicates that “Feedstock Energy” and “Energy Content of Delivered Fuel” are the two major sources for the environmental impacts. “Fuel Production and Delivery Energy ” and “Energy Use in Transport” contribute much less than those two. The two dominant environmental impacts from energy flows are global warming potential and acidification. The absolute values for others impacts are tiny comparing with the dominant two, but we can obtain the details for each category from the normalized result, which is shown in Fig. B-2.

Table B-1. Gross primary fuels and feedstock to produce 1kg of phthalate ester (Modified from ECPI, 2001[31])

Fuel Type	Fuel production and delivery energy (in MJ)	Energy content of delivered fuel (in MJ)	Energy use in transport (in MJ)	Feedstock energy (in MJ)	Total energy (in MJ)
Coal	0.63	0.42	0.0005	0	1.06
Oil	0.84	7.97	0.20	24.11	33.11
Gas	2.81	10.73	0.05	22.60	36.19

Table B-2 (continued)

Hydro	0.06	0.18	0.001	-	0.24
Nuclear	0.90	0.42	0.0002	-	1.32
Lignite	0.34	0.08	0.0002	-	0.42
Wood	0	-	0	0.0001	0.0001
Sulphur	0	0.0002	0.0001	0.022	0.02
Biomass	0.002	0.001	0.0001	0.0001	0.003
Hydrogen	0.0001	0.05	0.0001	-	0.05
Recovered energy	-	-1.64	-	-	-1.64
Unspecified	0.004	1.86	0.0001	-0.73	1.13
Peat	0.0002	0.0001	0.0001	-	0.0003
Total	5.57	20.07	0.25	46.00	71.90

Table B-2. Environmental impacts for the energy of 1kg phthalate ester production

Impact category	Unit	Fuel production and delivery energy	Feedstock energy	Energy use in transport	Energy content of delivered fuel
Global Warming	kg CO_2 eq	0.353	3.426	0.0193	1.398
Acidification	H+ moles eq	0.0734	0.793	0.00558	0.300
Carcinogenics	kg benzen eq	3.404E-08	7.47776E-09	8.980E-09	1.158E-08
Non carcinogenics	kg toluen eq	0.000452	8.383E-05	0.000136	0.000141
Respiratory effects	kg PM2.5 eq	0.000316	0.002743	1.402E-05	0.00115
Eutrophication	kg N eq	3.660E-05	0.000344	1.758E-06	0.000144
Ozone depletion	kg CFC-11 eq	1.572E-12	5.132E-14	8.878E-14	1.415E-13
Ecotoxicity	kg 2,4-D eq	0.000101	1.069E-05	4.762E-05	4.870E-05
Smog	kg NOx eq	9.441E-05	4.580E-06	1.041E-07	2.397E-05

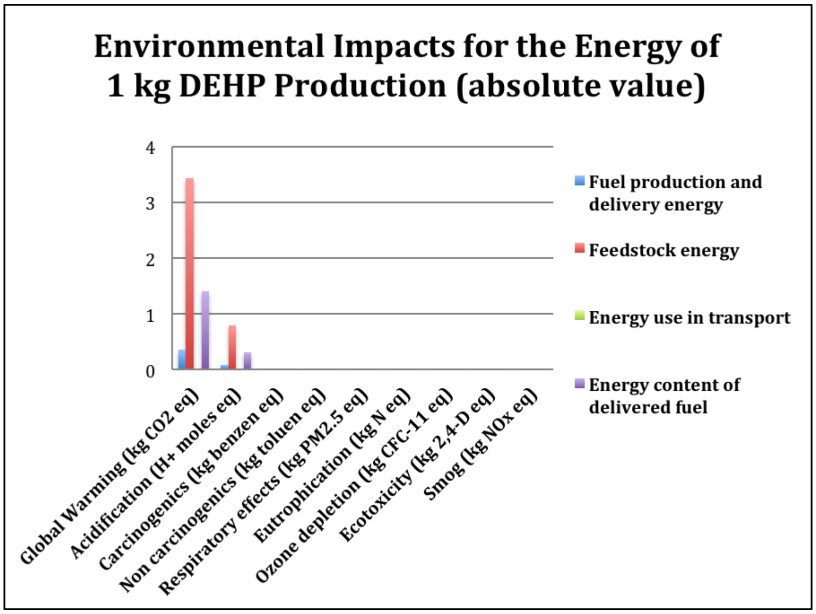


Figure B- 1. Environmental impacts for energy flows of 1 kg DEHP production (absolute value)

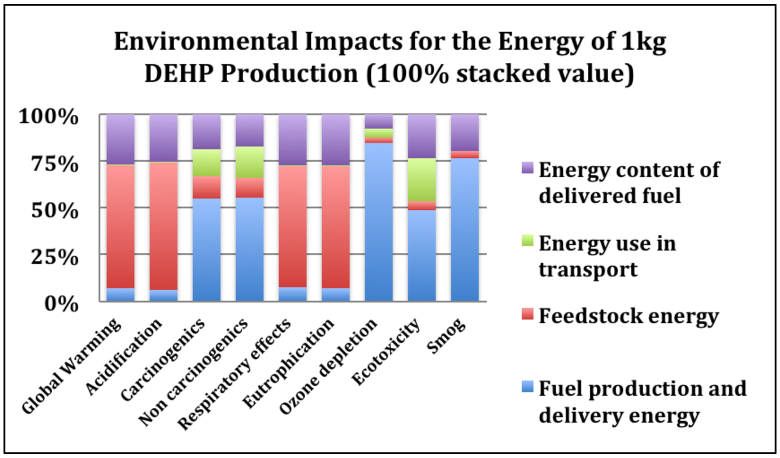


Figure B- 2. Environmental impacts for energy flows of 1 kg DEHP production (100% stocked value)

APPENDIX C

INTEGRATED ENVIRONMENTAL IMPACTS FOR DEHP MANUFACTURING

Combining the environmental impacts data from Appendix A and B (the data in A divided by 390 getting the results for 1kg DEHP), results showing in Table C-1, and the corresponding bar chart in Fig. C-1. The results indicate that for DEHP manufacturing, raw materials contribute more environmental impacts than the energy usages.

Table C-1. Integrated Environmental Impacts for DEHP Manufacturing

Impact category	Unit	Environmental Impacts	
		Raw Chemical Materials for 1 kg DEHP Production (Total)	Energy Flows for 1 kg DEHP Production (Total)
Global Warming	kg CO_2 eq	2.057405	5.195416
Acidification	H+ moles eq	0.448977	1.172328
Carcinogenics	kg benzene eq	0.002392	6.2079E-08
Non carcinogenics	kg toluen eq	17.75025	0.000813
Respiratory effects	kg PM2.5 eq	0.002308	0.004224
Eutrophication	kg N eq	0.000769	0.000526

Table C-1 (continued)

Ozone depletion	kg CFC-11 eq	1.32308E-07	1.85388E-12
Ecotoxicity	kg 2,4-D eq	1.858782	0.000208
Smog	kg NOx eq	0.003718	0.000123

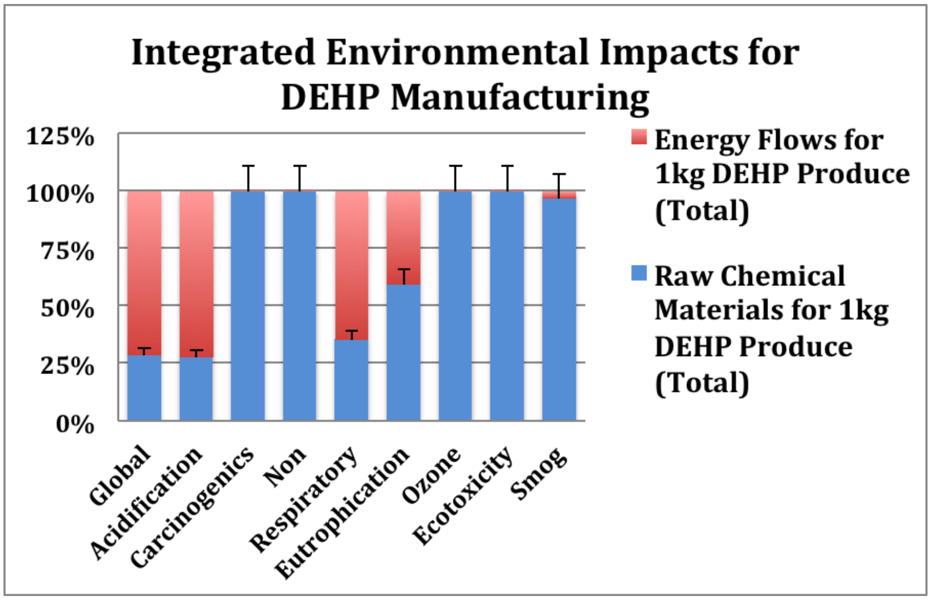


Figure C- 1. Integrated environmental impacts categories for DEHP manufacturing: raw materials & energy flows

APPENDIX D

DEHP HANDLING AND RELEASING IN EU 2007

Table D-1. Tonnage handled and releases of DEHP from manufacturing, formulation, processing, end-products use and disposal in the EU in 2007[64]

Activity	Tonnage handled t/yr	Emission to (t/yr)		
		Air	Soil	Waste Water
EU manufacturing of DEHP	341,000	1	4	220
Transportation of substance from manufacturin*	345,479	0	0	29
Formulation	61,000	30	1	97
Processing	283,000	174	41	125
End-product uses, indoor	223,000	380	0	1,240

Table D-1 (continued)

End-product uses, outdoor, non-abrasive leakages	33,000	30	3,980	500
End-product sues, outdoor, abrasive leakages	33,000	5	3,500	1,200
Disposal and recycling operations	275,133	9	48	10
Total releases (round)		600	7,600	3,400

The tonnage handled is the sum of EU production and import

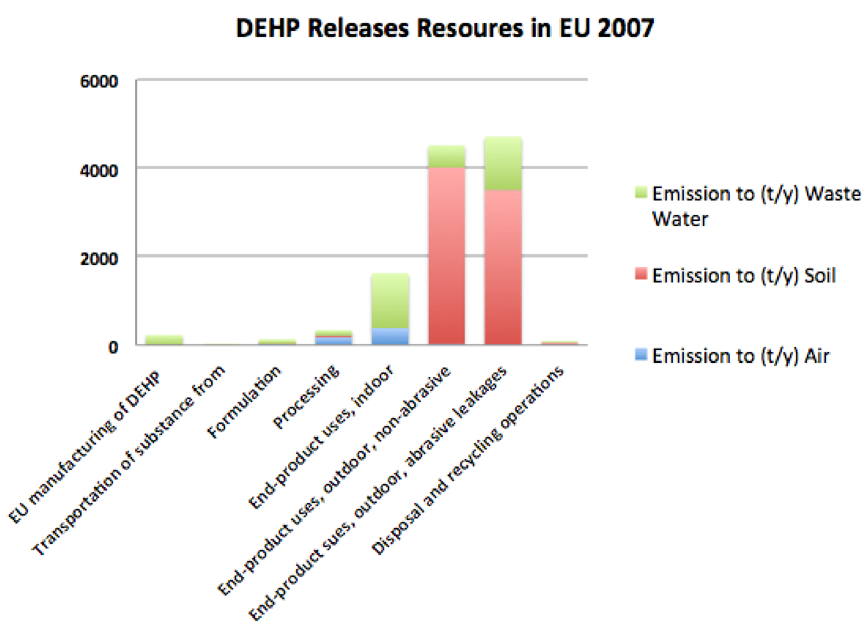


Figure D- 1. DEHP releases resources in EU 2007[63]

APPENDIX E

AIR EMISSIONS DATA FOR DEHP MANUFACTURING

Table E-1. Gross air emissions data in mg from the production of 1 kg of high volume commodity phthalate esters[31]

Emission	From fuel production (in mg)	From fuel use (in mg)	From transport (in mg)	From process operations (in mg)	From biomass use (in mg)	Total use (in mg)
Dust	500	174	6	32	-	712
CO	1173	604	25	13138	-	14939
CO_2	421699	1162500	9716	242743	-357	1836300
SO_x	1886	2833	184	288	-	5191
NO_x	3055	2713	137	153		6058
H_2O	2	3.1E-01	1	1.0E-01	3	3
Hydrocarbons	748	243	20	1036	-	2317
Methane (CH_4)	3902	546	1	170	-	4618

Table E-1 (continued)

H_2S	1	-	-	2	-	3
HCl	37	1	-	1	-	38
Cl_2	2.7E-06	-	-	1.2E-01	-	1.0E-01
HF	1	2.5E-02	-	1.8E-02	-	1
Lead (Pb)	7.0E-02	6.4E-03	4.5E-04	6.3E-03	-	8.3E-02
Metals (unspecified)	64	2	3.3E-01	2.7E-02	-	66
F_2	3.3E-05	-	-	6.2E-03	-	6.2E-03
Mercaptans	9.8E-09	6.2E-03	-	3.1E-02	-	3.7E-02
Organo Chlorine	8.0E-08	-	-	7.6E-03	-	7.6E-03
Aromatic hydrocarbons	4	-	2.3E-03	22	-	27
Polycyclic hydrocarbons	7.2E-03	-	8.3E-06	6.2E-03	-	1.3E-02
Other organics (unspecified)	45	-	-	85	-	130
CFC/HCFC	1.3E-02	-	-	4.0E-01	-	4.2E-01
Aldehydes (unspecified)	2.6E-02	-	-	3.0E-01	-	5.6E-01
HCN	1.5E-03	-	-	6.2E-03	-	7.7E-03

Table E-1 (continued)

H_2SO_4	-	-	-	6.2E-03	-	6.2E-03
Hydrogen (H_2)	-	-	-	34	-	34
Mercury (H_2)	2.3E-03	-	1.9E-05	9.7E-02	-	9.9E-02
Ammonia (NH_3)	1.2E-01	-	-	4.3E-01	-	5.5E-01
CS_2	-	-	-	8.9E-02	-	8.9E-02
DCE	-	-	-	3.4E-08	-	3.4E-08
VCM	-	-	-	1.9E-08	-	1.9E-08
Alcohols (unspecified)	-	-	-	10	-	10
Organic acids (unspecified)				184	-	184
Phthalate ester (unspecified)		-	-	7.1E-03	-	7.1E-03
Phthalic anhydride		-	-	6	-	6

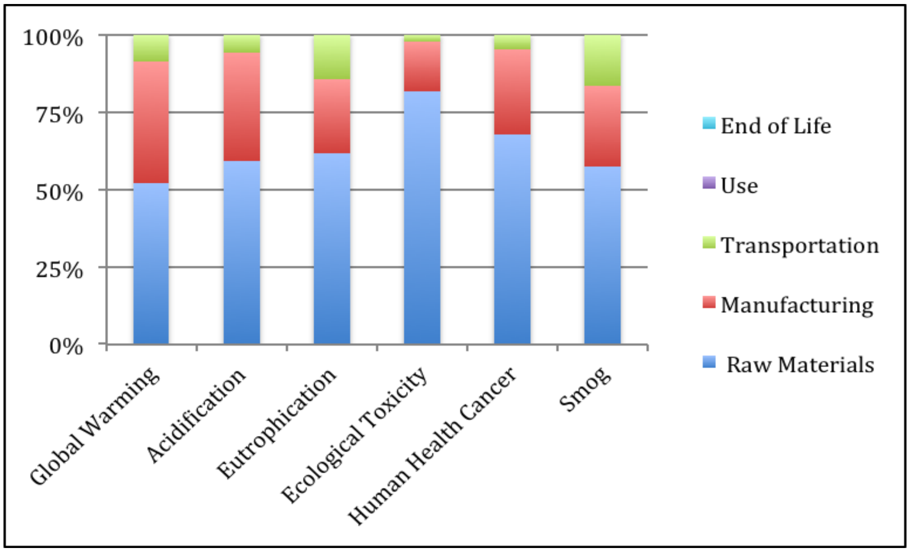
APPENDIX F

ENVIRONMENTAL IMPACTS ANALYSIS FOR VINYL FLOORING

The environmental impacts data for vinyl flooring from BEES. This is a complete LCA, from "cradle-to-grave", including the entire stages.

Table F- 1. Environmental impacts data for vinyl flooring

Category	Global Warming	Acidification	Eutrophication	Ecological Toxicity	Human Health Cancer	Smog
Raw Materials	595.7259	343.8862	0.1479	5.0505	0.6839	3.316
Manufacturing	447.576	204.2902	0.0568	1.0086	0.2803	1.5073
Transportation	97.251	34.0735	0.0346	0.1287	0.0451	0.9375
Use	0	0	0	0.0004	0	0.006
End of Life	0	0	0	0	0	0
Sum	1140.5529	582.2499	0.2393	6.1882	1.0093	5.7668



Figure

Figure F- 1. Normalized environmental impacts result for vinyl flooring

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