ASPECTS OF GREEN DESIGN IN THE POLYMER INDUSTRY

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This dissertation study addresses two important topics – development of a non-phosgene route for manufacture of isocyanates & a life cycle analysis comparison between polycarbonate and Tritan.

Isocyanates are currently manufactured by the phosgenation route which involves reaction of an amine with phosgene. This process requires handling of hazardous chemicals and is not considered environmentally benign due to issues related to disposal / recycle of the hydrochloric acid formed as a byproduct. McGhee et al [1] have previously worked on a non-phosgene route for manufacture isocyanates from primary amine, carbon dioxide, nitrogenous base and an electrophilic dehydrating agent. However, due to the generation of large amount of salt of the dehydrating agent and the base, and due to the absence of an appropriate recycling strategy this route could not be commercialized. To reduce the salt formed, a modification to this route is presented by eliminating the use of the nitrogenous base and carrying out the reaction in excess of carbon dioxide. The effect of different solvents, dehydrating agents, varying temperature and pressures on the conversion to isocyanate and a recycling strategy for the by-products formed has been studied. The energy requirement for this process is compared with the traditional route using ASPEN Plus. The results have been used to understand the potential roadblocks in the commercialization of the new process and the future direction of work to improve it.

The second part of the study is a life cycle analysis (LCA) comparison of polycarbonates with Tritan, which has been claimed to be an effective replacement for polycarbonates as it does not contain bisphenol-A, but still matches its physical and mechanical properties. However, the environmental impacts due the production of Tritan had not been studied yet. Hence, LCA study for polycarbonate and Tritan is performed on the basis of published literature. Effect due to different recycling strategies and different allocation techniques are studied on the overall environmental impact of these polymers. The study indicates that Tritan has lower impacts compared to polycarbonates in most of the impact categories studied. However, the extent to which Tritan performs better strongly depends on the functional unit considered.

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PREFACE

I would like to thank my thesis advisor, Dr. Eric Beckman for his guidance, encouragement and suggestions during the completion of my PhD dissertation study. I would especially thank him for sharing his passion for green chemistry and green design, and eventually inculcating the same in me. His willingness to listen to new ideas and experimentation with them has made these five years a great learning experience for me.

I am thankful to my thesis committee comprising of Dr. Robert Enick, Dr. Götz Veser and Dr. Terry Collins for their valuable suggestions and for being supportive of the direction of my research. I am particularly thankful to Dr. Enick for allowing me to sit through his course on Process Design where I learnt the most about Aspen Plus as a tool for process simulation. I extensively used this software in my research work and his tips and advice always came in handy. I would also thank him for giving me the access to his lab equipments for some of my experiments. I also want to express my appreciation the Chemical Engineering department staff comprising of Kim Wisniewski, Rob Toplak, Bob Maniet, Ron Bartlett, Adrian Starke, Allison Crick, Rita Leccia and Pat Park for their assistance and cooperation.

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Pittsburgh will always have a special place in my heart as it is here that I first met my fiancé Devika Kelkar. It was fun rediscovering Pittsburgh all over again along with her. I am thankful to her for her unconditional love and for being supportive and understanding over the past two years which were the most demanding years of my PhD life. I would also thank her, Vinit and Prachi for cheerfully proof-reading my papers and thesis though it had no relevance to their line of work.

Finally, I would like to dedicate my dissertation to my parents Vilas & Neeta Tople for their upbringing and for being responsible for fostering the value of education right through my childhood. Their constant motivation, words of advice and support for my decisions encouraged me to follow my dreams and have shaped me in the person I am today. I am glad that I was able to fulfill their wish and do my part in instilling a sense of pride in them by successfully completing my PhD.

NOTATIONS

$	dollar
(g)	gas
atm	atmospheric
¢	cent
cm	centimeter
ΔH	Heat of reaction
g	gram
hr	hour
K	Equilibrium constant
k_1	Rate constant - forward reaction
k_{-1}	Rate constant - backward reaction
kg	kilogram
kW	kilowatt
kW.hr	1 kilowatt used for 1 one
lbs	pounds
m	meter
Mcf	millionm cubic feet
mg	milli gram

MMBtu	million British thermal unit
mmHg	milli meter of mercury
mmol	milli mole
pKa	negative log of dissociation constant to the tenth base
ppm	parts per million
psi	pound per square inch
psig	pound per square inch - guage
R	Gas Constant
Rfa	Response factor
T	Temperature
™	Trademark
wt%	weight percent

ABBREVIATIONS

ACID	Acidification
BASF	Badische Anilin und Soda Fabrik
BPA	Bisphenol-A
BPA-PC	Bisphenol-A based Polycarbonate
CAR	Carcinogen
CFC	Chlorofluorocarbons
CHDM	1,4-cyclohexanedimethanol
CyTEG	N-cyclohexyl - N’,N’,N”,N”- tetraethylguanidine
DCB	Dichlorobenzene
DMC	Dimethyl carbonate

DMK	Dimethyl ketene
DMT	Dimethyl terephthalate
DPC	Diphenyl carbonate
ECO	Ecotoxicity
EDC	Endocrine disrupting chemical
EPA	Environmental Protection Agency
EUTR	Eutrophication
FID	Flame Ionization Detector
FT-IR	Fourier Transform - Infra Red
GC	Gas Chromatography
GWP	Global Warming Potential
HDI	Hexamethylene diisocyanate
IPDI	Isophorone diisocyanate
ISO	International Organization for Standardization
LCA	Life cycle Analysis / Assessment
LCIA	Life cycle impact assessment
MDI	Methylene diisocyanate
MPC	Methyl phenyl carbonate
NCAR	Non-carcinogen
NDI	Naphthalene diisocyanate
NEt3	Triethylamine
NTP	National Toxicology Program
OZDP	Ozone depletion

PC	Polycarbonate
PET	Polyethylene terephthalate
PPE	Polypropylene ethylene
PVP	Polyvinyl pyridine
RESP	Respiratory Effect
SMOG	Smog
TDA	Toluene diamine
TDI	Toluene diisocyanate
TFA	Trifluoroacetic acid
TFAA	Trifluoroacetic anhydride
TMCD	2,2,4,4-tetra methyl-1,3-cyclobutanediol

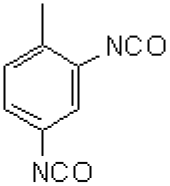
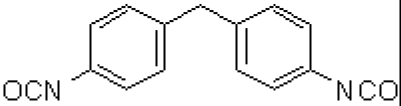
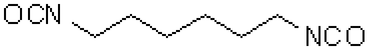
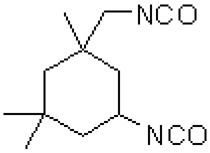
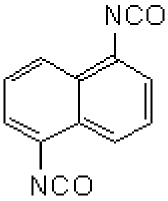
1.0 INTRODUCTION

Isocyanate is the functional group –N=C=O and any organic compound which contains this group may also be referred to in brief as an isocyanate. They are esters of isocyanic acid and the first member of this family of compounds was synthesized by Wurtz in 1848. Shortly thereafter, several prominent nineteenth century scientists, such as Hofmann and Curtius, systematically investigated the chemistry of isocyanates.

An isocyanate may have more than one isocyanate group and the ones with two isocyanate groups are known as a diisocyanate. Aliphatic and aromatic monoisocyanates are widely used as building blocks for more complicated molecules. Especially, numerous pharmaceutical and agricultural products are manufactured using isocyanates as intermediates. Diisocyanates are used the most industrially. Diisocyanates are used in the production of polyurethanes by reaction with polyols, which are alcohols containing multiple hydroxyl (-OH) groups.

The main use of isocyanates is prompted by their unique capability to undergo nucleophilic addition reactions with many substrates. Table 1 shows the widely used isocyanates and their applications. Some of the other applications include use in the manufacture of wear-resistant polymers in shoe soles or small wheels, pre-polymers for industrial use, glues for a range of applications, binding agents for molding sand in foundries, electrical insulating varnishes etc.

Table 1. Industrial isocyanates and their uses

Type	Structure	Use
Toluene diisocyanate (TDI)		A liquid, available as a mixture of 2,4 and 2,6 isomers, used to produce flexible foams for furniture & car seats.
Methylene diphenyl diisocyanate (MDI)		A solid, available in the form of a concentrated solution to produce rigid foams for solid car parts such as car bumper bars or for thermal insulation.
Hexamethylene diisocyanate (HDI)		A liquid, pre-polymers of which used in some paints and lacquers for car re-finishing
Isophorone diisocyanate (IPDI)		A liquid, used to make enamel coatings resistant to abrasion and degradation from ultraviolet light.
Naphthalene diisocyanate (NDI)		A solid used in the manufacture of some elastomers.
Methyl isocyanate	CH_3NCO	A gaseous intermediate in the production of certain pesticides.

The global market for diisocyanates in the year 2000 was 4.4 million tonnes, of which 61.3% was methylene diphenyl diisocyanate (MDI), 34.1% was toluene diisocyanate (TDI), 3.4% was the total for hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), and 1.2% was the total for various other isocyanates. The demand and hence the global production was predicted to grow at the rate of 4-5 % per year. Such quantities of isocyanate are industrially manufactured via the phosgenation of a primary amine which replaces the amine group with an isocyanate group in a two step process [2].

The phosgenation of amines to produce isocyanate was first reported by Hentschel in 1884 [3]. It requires the addition of amines to excess amount of phosgene in an inert solvent. In principle, the process is simple as the highly reactive phosgene molecule reacts very rapidly with amine group to produce the carbamoyl chloride group and hydrogen chloride gas, which is easily removed from the relatively non-volatile product. If the reaction is carried out under pressure, liquid phosgene can be used as a diluent because a slurry of carbamoyl chloride and amine hydrogen chloride is formed in the initial reaction. Also, good stirring is necessary to prevent by-product formation. In order to control mixing and the reaction temperature, inert solvents are used. The slurry is subsequently heated to dissociate the carbamoyl chloride and to convert the amine hydrochloride into the isocyanate. Heating above 50 °C usually is sufficient to dissociate the carbamoyl chlorides and the phosgenation of the amine hydrochlorides occurs above 100 °C at a reasonable rate [4]. The reactions occurring are shown in the equations 1.1, 1.2.

$$\mathrm{RNH_2 + COCl_2 \longrightarrow RNHCOCl + HCl} \tag{1.1}$$

$$\mathrm{RNHCOCl \longrightarrow RNCO + HCl} \tag{1.2}$$

Higher temperature and increased pressure increases the rate of reaction of the slower reacting amine hydrochloride. Also, the polarity of the solvent has an influence on the rate of reaction. Polar solvents, such as anisole and chlorobenzene provide faster reaction rates compared to non-polar solvents (toluene, xylene, etc).

The main reaction is faster compared to the two exothermic side reactions that occur as shown in equation 1.3 & 1.5 [2]. The first leads to an amine hydrochloride precipitate that is highly insoluble in the reaction medium. This precipitate reacts slowly and endothermically with phosgene to produce the desired isocyanate and three molecules of hydrogen chloride as shown in equation 1.4. As the base strength of the amine increases more of the insoluble amine hydrochloride is generated. The resulting amine hydrochlorides are less soluble in the typical phosgenation solvents.

$$RNH_2 + HCl \longrightarrow RNH_3Cl \qquad (1.3)$$

$$RNH_3Cl + COCl_2 \longrightarrow RNCO + 3\,HCl \qquad (1.4)$$

$$RNCO + RNH_2 \longrightarrow R\text{-}NHCONH\text{-}R \qquad (1.5)$$

The reaction 1.5, producing urea is undesirable because of the resulting lower yield since the formation of one urea group effectively leads to the loss of two molecules of isocyanate. In case of aromatic amines, the urea by-products undergo phosgenation to give carbodiimides, which undergo further reaction with phosgene and / or the generated isocyanate. Disubstituted ureas, obtained as by-products in the phosgenation of aliphatic amines react with phosgene to give allophanoyl chlorides, which can be thermally converted into isocyanates [5].

In order to prevent side reactions, such as the reaction of the isocyanate with unreacted amine to form disubstituted ureas, an excess of phosgene (20 – 50 %) is necessary and the concentration of the amine in the reaction solvent should not exceed 20%. Various proprietary processes exist in which the temperature and pressure vary widely. In principle, low pressure processes allow more of the slow reacting amine hydrochloride to form, while high pressure and high temperature processes prevent this. However, the higher pressure processes need to overcome the carbamoyl chloride equilibrium.

The typical liquid-phase phosgenation process consists either of a (semi-)continuously operated cascade of agitated vessels or a continuously operated series of reaction towers. These are at atmospheric or slightly elevated pressures and temperatures between 20 and 180 °C with the use of an inert solvent [6]. The reaction proceeds efficiently, without the need to apply any catalyst, if a large excess of phosgene (50–200%), high dilution and an intense and rapid mixing of the reactants is maintained in the process.

After the reaction stage, hydrogen chloride and excess phosgene is boiled off and separated by fractionation or by absorption of phosgene in a solvent. The phosgene is recycled back and the anhydrous hydrogen chloride is used as a raw material in other processes. Recently, the hydrogen chloride is being used back in the process by splitting it into hydrogen and chlorine and using the chlorine to make phosgene [7]. This is done in order to make the process more efficient, avoid the issues related to disposal of anhydrous hydrogen chloride and reduce the cost of making isocyanates by recycling a useful raw material i.e. chlorine back into the process.

Anhydrous hydrogen chloride is fed to the inlet on the anode-side of an electrochemical cell, wherein the electrochemical cell comprises of a cation-transporting membrane, an anode disposed in contact with one side of the membrane and cathode disposed in contact with other side of the membrane. A voltage is applied to the electrochemical cell so that the anhydrous hydrogen chloride is transported to the anode and is oxidized at the anode to produce chlorine gas and protons. The chlorine is released from an anode side outlet of the cell.

$$2\ HCl\ (g) \xrightarrow[\text{Energy}]{\text{Electrical}} 2H^+ + Cl_2(g) + 2e^- \tag{1.6}$$

The protons get transported through the membrane to be reduced at the cathode of the cell. The cathode side is fed with oxygen to make the system thermodynamically favorable, producing water at the cathode of the cell. This is done because the splitting of hydrogen chloride in presence of oxygen to water and chloride ions involves a smaller free-energy change than the free energy change for conversion of hydrogen chloride to hydrogen and chloride ions. The overall reaction in the electrochemical cell is shown in equation 1.8

$$1/2\ O_2(g) + 2e^- + 2H^+ \xrightarrow[\text{Energy}]{\text{Electrical}} H_2O(g) \tag{1.7}$$

$$2\ HCl\ (g) + 1/2\ O_2(g) \xrightarrow[\text{Energy}]{\text{Electrical}} H_2O(l) + Cl_2(g) \tag{1.8}$$

The chlorine recovered is used to produce phosgene by a simple gas phase reaction of carbon monoxide with the chlorine through a fixed bed of carbon catalyst. The phosgene produced is immediately absorbed in a solvent and used back in the main process. The most commonly used solvents are monochlorobenzene, o-dichlorobenzene and toluene.

The current process gives satisfactory conversions and hence is commercially viable. However, it has the disadvantage that it is not considered environmentally benign and involves handling of hazardous chemicals like hydrochloric acid, chlorine and phosgene. The use of chlorine in the manufacture of phosgene results in high energy consumption (2800 – 3100 kW.hr per ton of Cl_2)

in the life cycle of the process. Also, for every mole of isocyanate formed, two moles of hydrochloric acid are formed [8]. Due to environmental regulations, the acid formed cannot be discarded and hence needs to be recycled. The present recycling strategy via electrochemical splitting is an extremely energy intensive process. A typical electrolytic cell used for this purpose consumes 1400-1500 kW.hr per ton of Cl_2 formed [9].

The significant use of chlorine in the isocyanate industry in the form of phosgene and chlorinated aromatic solvents can be demonstrated by the “Chlorine tree” shown in Figure 1 [10].

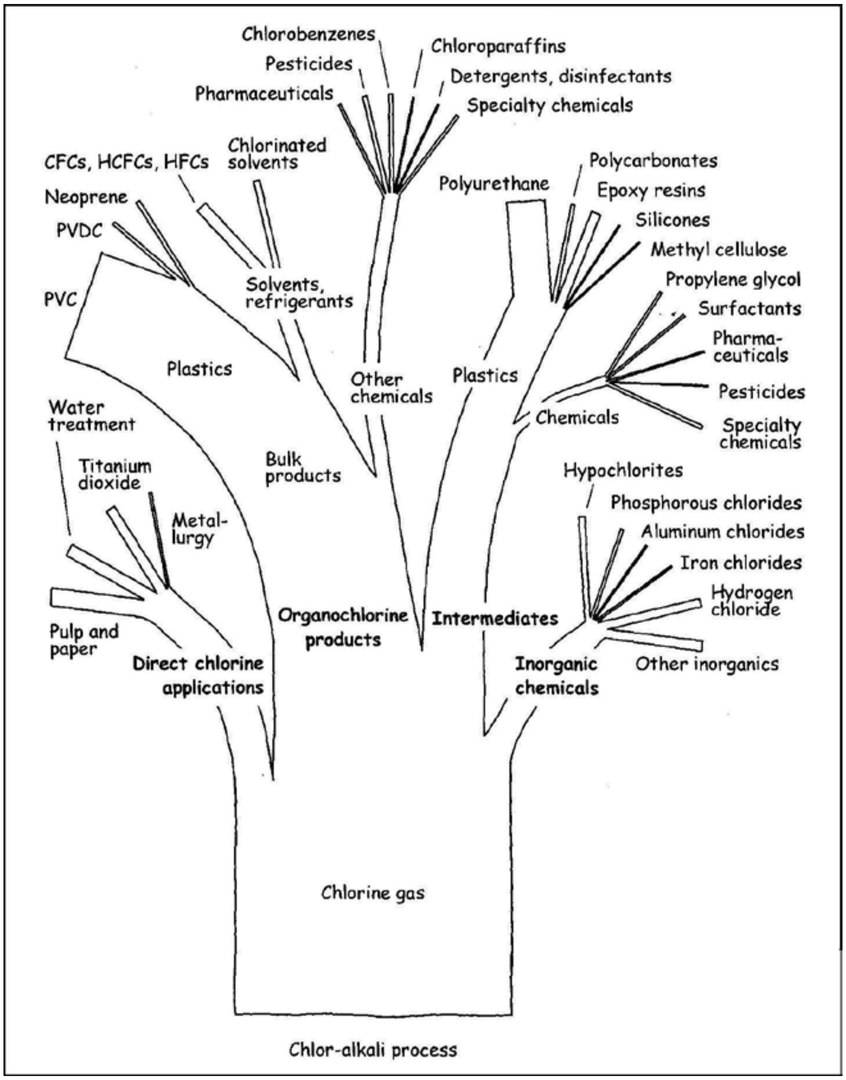


Figure 1. Chlorine tree representing the use of chlorine in various industries [10].

Size of each branch of the tree represents the extent to which chlorine is used in a particular industry. The branch for polyurethanes which is the main application industry for isocyanates is the second biggest in the figure with the biggest contribution by the poly-vinyl chloride (PVC) industry.

In accordance with the strategies put forth by environmental activists and academicians to gradually move away from the use of chlorine, it is required to find an alternate process to manufacture isocyanates that does not involve the use of chlorine in form of phosgene and chlorinated aromatic solvents. Also, it is important to address the safety concerns associated with the use of harmful chemicals like phosgene, chlorine and hydrogen chloride and the high energy consumption costs associated with hydrogen chloride recycle. With this objective, it is aim of this research study to develop a “green” non-phosgene route for manufacture of isocyanates which is safe, economical, commercially viable and can produce isocyanates in high yields under mild reaction conditions and short reaction times.

The 12 principles of “Green Chemistry” as listed in Table 2 have been the guidelines for developing benign alternate processes to replace the phosgenation route for manufacture of isocyanates. Green chemistry is defined as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances [11]. It was introduced in the early 1990s along with the increased public concerns about human health and environment impacts of chemical substances. Before the 1960s, it was common to think that the “mere decrease of concentration of a substance in a particular medium would be sufficient to mitigate its ultimate impact” [12]. Therefore, mere dilution was considered to be the solution to pollution.

Table 2. Twelve principles of green chemistry [11]

1	It is better to prevent waste than to treat or clean up waste after it is formed.
2	Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3	Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4	Products should be designed to preserve efficacy of function while reducing toxicity.
5	The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
6	Energy requirements should be recognized for their environmental & economic impacts and be minimized. Synthetic methods should be conducted at ambient temp. & pressure.
7	A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8	Unnecessary derivatization (blocking group, protection/deprotection and temporary modification of physical/chemical processes) should be avoided whenever possible.
9	Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10	Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11	Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.
12	Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

The book “Silent Spring” in 1962 by Rachael Carson which detailed the adverse effects of pesticides, especially dichlorodiphenyltrichloroethane (DDT) on the eggs of various birds and a series of environmental disasters caused by toxic chemicals awakened the public to the environmental impact of toxic substances. In response, government passed various environmental laws to regulate the release of toxic substances. At this stage, regulation was considered to be the solution to pollution. The Pollution Prevention Act passed by US congress in 1990 marked the shift of public attitude toward pollution from treatment and abatement through command and control to the prevention of the formation of waste at the source. At present, it is believed that “prevention is the solution to pollution”. Ever since its first appearance, green chemistry is widely accepted as an effective strategy to develop inherently safer and environmentally benign processes. Hence, preventing the use of phosgene has been the focus of study for alternative processes for manufacture of isocyanates.

2.0 LITERATURE REVIEW AND BACKGROUND

Isocyanates in general can be prepared in many ways. Some of the well-known laboratory scale methods are on the basis of Curtius [13], Hofmann [14] and Lossen [15] rearrangement via nitrene intermediates. However, these are not at all suitable for large-scale operation. It is almost exclusively the reaction of phosgene with primary amines which is established commercially. The world's leading isocyanate producers for polyurethane applications; BASF, Bayer, Dow, Enichem, Huntsman ICI, Lyondell Chemical Technology and Mitsui use the typical phosgenation route described in Section 1.0.

This review has been formulated with the focus on summarizing the most promising alternative reaction pathways to isocyanates that have been explored in the past. Wegener et al. also provides a comprehensive overview of the new trends and research in the isocyanate industry [16].

2.1 DEVELOPMENTS IN PHOSGENE MANUFACTURE

When speaking about the production of aromatic diisocyanates and catalysis, one has to comment briefly on recent developments concerning the catalytic manufacture of phosgene on an industrial scale. The classical pathway in the production of isocyanates involves phosgene as the carbonylating reagent. Phosgene is obtained commercially by passing carbon monoxide and chlorine over activated carbon [17]. The reaction is strongly exothermic and is usually carried out in a multitubular reactor of carbon or stainless steel in which the tubes are filled with the granulated catalyst. The temperature of the activated carbon bed is up to approximately 400 °C in the very lowest region of the tubes, but it then falls rapidly along the tubes to product temperatures of 40 - 150 °C. The activated carbon catalyst can have a service life of up to several years. Carbon monoxide is added in stoichiometric excess to keep the free chlorine content of the phosgene as low as possible, since chlorine can lead to the formation of undesirable products such as carbon tetrachloride during further processing.

Developments in the catalytic production of phosgene focus on searching for catalysts that work under moderate temperatures and avoid by-product formation resulting in higher selectivity. It is shown that phosgene can be manufactured by reacting chlorine and carbon monoxide using a metal halide catalyst selected from group III metals. Preferred catalysts are $AlCl_3$, $GaCl_2$ (or $GaCl_3$), or chlorides prepared from metal alloy components. The reaction can be continuous or discontinuous and carried out preferably at 0 - 100 °C and 2 - 15 bars, and is preferably a single-stage process in a multi tubular reactor in which the catalyst activity is continuously maintained by sublimation [18].

Another process for producing phosgene involves contacting carbon monoxide and chlorine at 300 °C with a special carbon contact. The catalyst has a micropore / macropore ratio ≤ 3.5, a high degree of oxidative stability and a minimum surface area of $> 10 m^2/g$. The use of carbon having an active metal content of ≥ 1000 ppm in this process can reduce the amount of carbon tetrachloride produced as a by-product [19]. Low carbon tetrachloride contents can also be obtained by contacting carbon monoxide and chlorine at ≤ 300 °C with a silicon carbide catalyst having a surface area of ≥ $10m^2/g$. The catalyst is manufactured by contacting silicon monoxide with finely divided carbon [20].

Different starting materials can be used by first reacting perchloroethylene with hydrogen chloride and oxygen (e.g. air) in the presence of an oxychlorination catalyst (e.g. copper chloride). It is then followed by separating the resulting hexachloroethane from the aqueous mixture and reacting it with carbon monoxide in the presence of a second catalyst (e.g. activated carbon) to produce perchloroethylene and phosgene in high yield and selectivity [21].

Another easier, safer and less expensive approach is the direct electrochemical production of phosgene starting from the isocyanate manufacture by-product HCl and carbon monoxide. Friere et al found that both the oxidation of anhydrous hydrogen chloride and the formation of phosgene could be carried out in the anode compartment of an electrochemical cell. This eliminated the need for multiple pieces of equipment to carry out these reactions. Moreover, no catalyst was needed to form chloride anions and subsequently make phosgene [7].

2.2 DEVELOPMENT OF NON-PHOSGENE ISOCYANATE MANUFACTURING ROUTES

Calculations of the temperature dependence of 14 gas-phase reaction equilibria of different reaction pathways to give methyl isocyanate in the gas-phase disclosed that besides the phosgenation of methyl amine several other synthesis strategies should be thermodynamically feasible at high temperature [22]. The idea of non-phosgene synthesis route for manufacture of isocyanates has been explored for quite a few years and many novel routes have been suggested and discussed in subsequent sections. However, none of these routes were more efficient than the phosgene process in order to implement them at a commercial level. In many cases the efficiency and stability as well as the lifetime of homogeneous or heterogeneous catalysts were the main issue. Some of the significant routes have been illustrated in Figure 2 and the following sections discuss them in more detail.

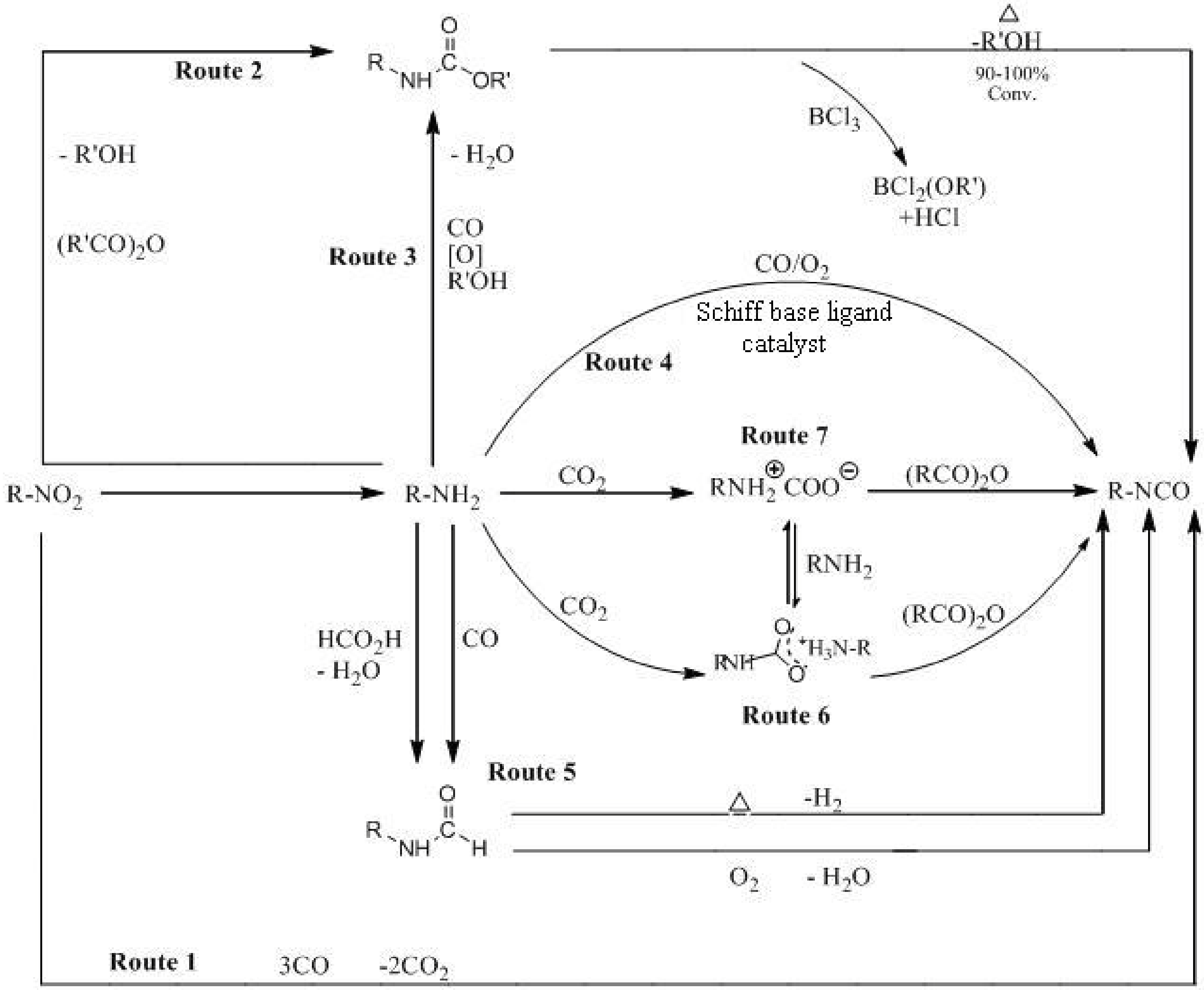


Figure 2. Synthesis strategies for production of isocyanate by non-phosgene routes

2.2.1 Reductive carbonylation of nitro compounds (Route 1)

The “dream reaction” leading to industrially relevant isocyanates will be a low-cost one-step synthesis starting from the corresponding nitro precursors, as this would eliminate the hydrogenation step of converting the nitro precursors to the corresponding amines [23]. The first simple catalytic system using Rh or Pd was reported by Hardy et al [24] but the yields reported for toluene diisocyanate were low (maximum 22.3%)

This process involves preparing an isocyanate by reaction of an aromatic nitro compound with carbon monoxide in the presence of a catalyst consisting of a noble metal and a Lewis acid. The amount of carbon monoxide needs to be atleast three times the moles of nitro group and the reaction is conducted in substantially anhydrous, hydrogen-free environment and at high pressure and elevated temperature. The temperature is maintained below the limit at which the starting materials and the product isocyanate decompose.

$$R\text{-}NO_2 \quad + \quad 3CO \quad \xrightarrow[\text{Pd (II) halide}]{\text{organic nitrile}} \quad R\text{-}NCO \quad + \quad 2\,CO_2 \qquad 2.1)$$

More efficient, but also more complex homogeneous catalytic systems consisting of Pd(II) salts, N-heteroaromatic compounds as ligands, and MoO_3 as co-catalyst followed soon. Reaction of 2,4-dinitrotoluene in o-dichlorobenzene containing diphenyl carbonate (DPC), $[Pd(C_5H_5N)_2Cl_2]$, and MoO_3 with 193 atm CO at 200 °C gave 56.8% 2,4-TDI at 84% catalyst recovery [25]. Ottmann et al was able to achieve yields of isocyanate up to 55% by using a catalytic system comprising of a mixture of noble metal base compound and an organophosphorus compound such as triphenylphosphine [26].

Recovery of the usually homogeneous catalyst systems, the need for promoters and insufficient yields to diisocyanates in comparison to the classic phosgenation route remained the roadblock for commercial utilization of this pathway. The other disadvantages of this direct route to the isocyanate are the extremely high catalyst loading, insufficient catalyst recovery and stability.

2.2.2 Carboxylation or Oxidative carbonylation of amine followed by thermolysis of the urethane / carbamate formed

The first step of formation of urethanes can be carried out by reaction of the amine either with an alkyl or aryl carbonate in the presence of a catalyst or with carbon monoxide and OH-containing compounds in the presence of a Pt-group metal compound and a halide as the catalyst.

2.2.2.1 Carboxylation of amine to urethane (route 2):

Activated and even inactivated carbonates are excellent carboalkoxylation or carboaroxylation reagents for urethane formation starting from aromatic amines (eq. 2.2), but their economical potential in comparison to CO_2 is lower.

$$\text{R-NH}_2 \quad + \quad (\text{CH}_3\text{CO})_2\text{O} \quad \longrightarrow \quad \text{R-NHCOO-R} \quad + \quad \text{CH}_3\text{OH} \qquad (2.2)$$

A number of workers have treated both aliphatic and aromatic amines with dialkyl carbonates to form urethanes that can be pyrolysed to isocyanates. Fu et al used a lead catalyst to achieve up to 95 % selectivity. However, in many cases the selectivity to the desired product dropped as the conversion increased to 100%. Aresta et al showed that inactivated carbonates like dimethyl carbonate or diphenyl carbonate were found to be excellent carboxylating reagents for aromatic amines in the presence of organophosphorus acids [27]. This methodology was highly selective in carbamate synthesis from 2,4-toluene diamine or 4,4-methylene diamine and methyl phenyl carbamate, but yields were still low. The reactions require a carbonate that is usually made from phosgene.

$$2\,CH_3OH + COCl_2 + 2\,NaOH \longrightarrow (CH_3CO)_2O + 2\,NaCl + 2\,H_2O \quad (2.3)$$

Insufficient yield or selectivity was the key problem of the carboxylation pathway in the past. Recent developments may have overcome these disadvantages. The only remaining roadblock may be the availability of the necessary carbonates at attractive prices, especially if made without the use of phosgene.

2.2.2.2 Oxidative carbonylation of amine to urethane (Route 3):

The most common oxidants [O] that can be used are oxygen, air, or the corresponding nitro precursors. Ikariya et al had obtained excellent results with monofunctional aromatic amines and heterogeneous catalysts. $PhNH_2$, Pd/C, KI, [O], and CO were autoclaved at 160 °C [28]. After work-up and separation of the catalyst, the filtrate was concentrated to give N,N - diphenylurea which was treated with MeOH to give $PhNHCO_2Me$ in 94% yield. Total removal of condensed water is the key in this process to obtain high yields of urethane [29].

$$R\text{-}NH_2 + R'OH + CO \xrightarrow{[O]} R\text{-}NHCOO\text{-}R' + H_2O \quad (2.4)$$

This route can be seen as a variant to the carbonate route described in Section 2.2.2.1. Valli et al had expressed that while making urethane they might have made carbonate in situ as shown in equation 2.5 & 2.6 [30].

$$2\,CH_3OH + CO + 0.5\,O_2 \xrightarrow[\text{bipyridyl}]{\text{Pd / clay}} (CH_3CO)_2O + H_2O \qquad (2.5)$$

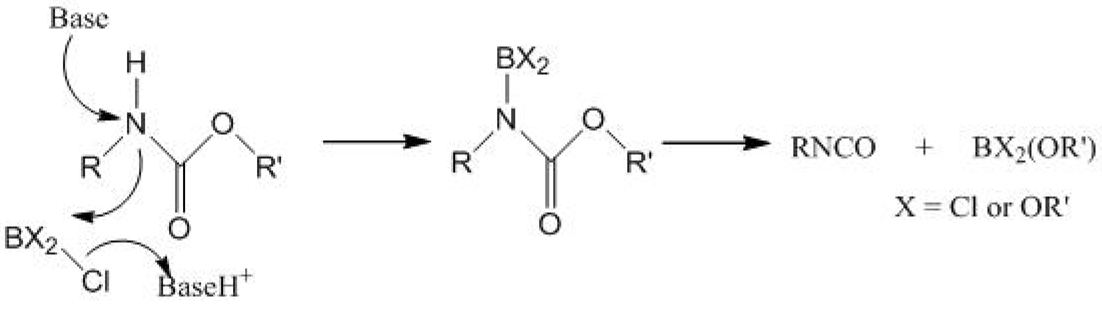
$$RNH_2 + CH_3OH + CO + 0.5\,O_2 \xrightarrow[\text{bipyridyl}]{\text{Pd / clay}} \text{R-NHCOO-}CH_3 + H_2O \qquad (2.6)$$

2.2.2.3 Thermolysis of carbamate / urethane formed:

Many urethane systems are designed as reactive systems, where the isocyanate and the alcohol compounds are mixed at the application site. The isocyanate is more valuable than the urethane for such applications. Urethanes can be converted into isocyanates in high yield and under mild conditions by reaction with a halogenated borane compound and a tertiary amine catalyst combination in a non-polar solvent. The borate by-product can readily be recycled to the borane [31].

$$\text{RNH-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-OR'} \xrightarrow{\Delta} \text{R-NCO} + \text{R'OH} \qquad (2.7)$$

The conversion of carbamate esters to diisocyanates of industrial importance is found to be possible by using BCl_3 in the presence of NEt_3. In this process, the reaction is simple in execution and work-up, and occurs under mild conditions affording isocyanates in good conversion (90 – 100 %) [32]. However, the rapid removal of the alcohol formed as a byproduct involves irreversible use of the alcohol and the BCl_3 used.



(2.8)

Thus even though the conversions to isocyanate prepared by this route can be good, the lack of a suitable strategy to separate the isocyanate formed restricts the use of this technology at an industrial level.

2.2.3 Oxidative carbonylation of amine to isocyanate (Route 4)

Serrano et al developed a one-pot catalytic process for making aromatic isocyanates based on the use of an immobilized Schiff base type of ligand catalyst that facilitates the oxidative carbonylation of aromatic amines to the corresponding isocyanates [33].

$$\text{R-NH}_2 + \text{CO} + \text{O}_2 \xrightarrow[\textbf{NaI}]{\substack{\textbf{Schiff base}\\ \textbf{ligand catalyst}}} \text{RNCO} \qquad (2.9)$$

TDI was synthesized by reaction of 10 g. of 2,4-toluenediamine with a mixture of CO/O_2 (19:1) in the presence of 7.6 g. of [Co-tert-butyl-Salen]/silica catalyst, 1.78 g. of NaI and 488 g. of 2,2,2-trifluoroethanol (TFE) as the solvent. The autoclave is pressurized to 40 bar and temperature is maintained at 120 °C for 3 hours. After 3 hours the reactor is cooled, depressurized and 97.8 g. 1,2-dichlorobenzene is added. The temperature is increased to 180 °C under atmospheric pressure. The TFE vapors are separated and condensed, and TDI is separated from the remaining liquid and purified to 99.9%. The overall yield obtained for TDI was 69.8%. The energy required for the separation of the large amount of solvents used in this process and the stability and regenerative ability of the catalysts needs to be studied before this route can be claimed as an effective alternative to the phosgenation route for manufacture of isocyanates.

2.2.4 Carbonylation of amine to formamide & dehydrogenation to isocyanate (Route 5)

A very promising field is the dehydrogenation of formamides to give isocyanates. Formamides are obtained via carbonylation of amines (eq. 2.9) [34] or reaction of amines with formic acid derivatives (eq. 2.10) [35]. The best selectivity reported for formation of formamide is 52.3 mole % and the maximum conversion of the amine used is 94.3 mole %.

$$\text{R-NH}_2 + \text{CO} \longrightarrow \text{R-NH-CHO} \qquad (2.10)$$

$$\text{R-NH}_2 + \text{HCOOH} \longrightarrow \text{R-NH-CHO} + \text{H}_2\text{O} \qquad (2.11)$$

Rao et al discovered that isocyanates could be prepared under strict temperature control by oxidative dehydrogenation of the corresponding formamides over Ag catalysts in an adiabatic reaction, or over Ag and Ag–Au mixtures under isothermal conditions [36]. Treating a formamide in the gas-phase with an oxygen-containing gas as shown in eq. 2.12 at a reaction zone temperature of > 300 °C in the presence of a catalytic amount of Cu and/or at least one metal of group IB or VIII for short contact times gave isocyanates in good yield (>85%) and selectivity (>90%) at high conversion (>95%) [37]. However, the yields for TDI synthesis using this methodology were far too low.

$$\text{R-NH-CHO} + \text{O}_2 \xrightarrow{\text{Ag-Au}} \text{R-NCO} + \text{H}_2\text{O} \qquad (2.12)$$

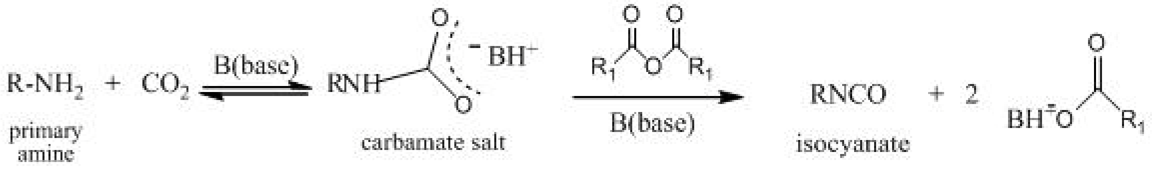
The direct dehydrogenation of a formamide was developed by Sofranco et al which involved heating formamides or derivatives in the presence of an N–H bond-activating to give the corresponding isocyanate [38] as shown in eq. 2.13.

$$\text{R-NH-CHO} \xrightarrow[\text{Na-CuO}]{\Delta} \text{R-NCO} + \text{H}_2 \qquad (2.13)$$

Acetanilide was placed above a catalyst bed (5% Na on CuO) in a tube reactor; the bed was heated to 600 °C and N_2 was swept through the tube. After 150 min, 36% conversion of acetanilide and 92% selectivity for phenyl isocyanate was observed. However, poor selectivity to formamides from amines in the first step and due to the lack of availability of large scale quantity of formamides as a raw material, this process cannot be used on an industrial scale.

2.3 CARBON DIOXIDE TO REPLACE PHOSGENE

The use of carbon dioxide as a phosgene replacement was explored and the conditions of synthesis of isocyanates from carbamate anions (generated from amines and carbon dioxide) with high selectivity were studied by McGhee et al using various dehydrating agents [1, 39]. Electrophilic dehydrating agents such as anhydrides can be used for direct generation of isocyanates from amines and carbon dioxide as follows.



(2.14)

The preferred bases included triethylamine, amidines and guanidines (such as CyTEG = N-cyclohexyl - N',N',N",N"- tetraethylguanidine). Dehydration of carbamate was carried out with phosphorus trichloride, phosphorus oxychloride, phosphorus pentoxide [40], acetic anhydride, benzoic anhydride, o-sulfobenzoic anhydride, trifluoroacetic anhydride (TFAA) [39]. McGhee et al also studied the possibility of making urethanes in situ by using alkyl chloride or aryl chlorides such as ethyl chloride and benzyl chloride [41, 42]. The results obtained are shown in Table 3.

Table 3. Conversion of amine to isocyanates with different dehydrating agents and bases

Amine	Anhydride	Base	% converted to -NCO
octylamine	acetic anhydride	CyTEG	40
octylamine	benzoic anhydride	CyTEG	65
octylamine	trifluoroacetic anhydride	CyTEG	95
octylamine	acetic anhydride	triethyamine	2
octylamine	benzoic anhydride	triethyamine	22
octylamine	trifluoroacetic anhydride	triethyamine	35
octylamine	$POCl_3$	triethyamine	95
octylamine	P_2O_5	triethyamine	97
octylamine	o-sulfobenzoic anhydride	triethyamine	95
cyclohexylamine	o-sulfobenzoic anhydride	triethyamine	100

All reactions were run in acetonitrile under 80 psig pressure of CO_2 at 0 °C. The phosphorus dehydrating agents led to a large amount of waste salts. Acetic anhydride gave some competing formation of amide. Though benzenesulfonic anhydride gave good yields, its by-product benzenesulfonic acid could not be converted to its anhydride thermally leading to issues related to recycling. Thus, further work was necessary to find the best no-waste system that gave high yields.

Another disadvantage of this process is that for every mole of isocyanate formed, two moles of salt of the nitrogenous base and the acid of the electrophilic dehydrating agent used are formed. In order to obtain higher yields of isocyanates, the process requires the use of strong bases such as guanidines, amidines, tertiary amines or mixtures thereof. This results in the formation of a salt of the base and the acid of the dehydrating agent used, which is difficult to split into the constituent acid and base. The acid needs to be further treated to obtain the dehydrating agent back so that the process can be feasible commercially.

2.3.1 Recycling strategy for the CO_2 process

The base used is liberated from the salt formed by addition of inorganic compounds such as alkali metal hydroxides or alkaline earth metal hydroxides to form the corresponding alkali metal or alkaline earth metal salt of the base salt [1].

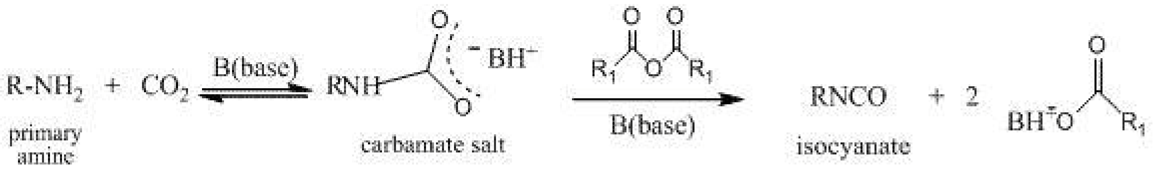
$$KOH + R_1COO^{\ominus}\,{}^{\oplus}HB \longrightarrow R_1COOK + BOH \qquad (2.15)$$

The first method for producing the organic acid from the alkali metal salt formed is by contacting the recovered alkali or alkaline earth metal salt with a cation exchange resin in proton form. The used resin has to be regenerated periodically by contacting it with a mineral acid capable of protonating the ion exchange resin and regenerating the acid form of the resin. The second method for producing the organic acid is by introducing the alkali metal or alkaline earth metal salt into an electro dialysis zone to produce the alkali metal or alkaline earth metal hydroxide and the organic acid. The organic acid is heated to suitable conditions of temperature and pressure to physically remove the water and produce the corresponding anhydride.

Perhaps due to unfavorable economics of the recycling strategy, this process did not proceed to pilot or larger scale applications.

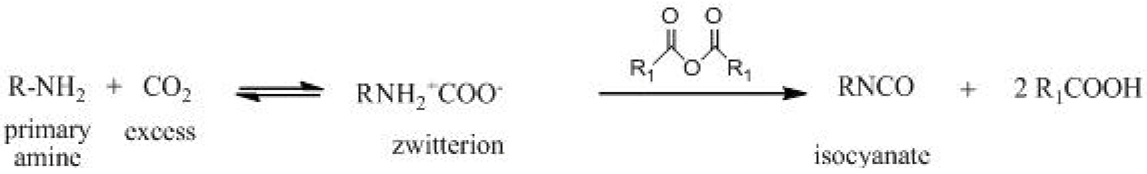
3.0 RESEARCH OBJECTIVE

The objective of this dissertation study is to develop a non-phosgene route to replace the current phosgenation route for manufacture of isocyanates. In order to achieve the same, the route developed by McGhee et al as described in equation 3.1 would be modified to eliminate the formation of salt as a by-product.



3.1)

This can be done by eliminating the use of the nitrogenous base and carrying out the carbonylation process in an excess of CO_2, leading to the formation of a zwitterion instead of a carbamate as shown in equation 3.2.



(3.2)

This route would be studied with the following objective –

- Identify the ideal conditions of temperature, pressure, type of solvent and type of dehydrating agent most suitable for this route
- Enable one pot synthesis

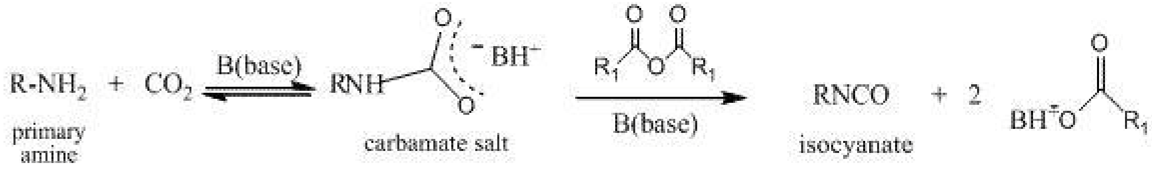
- Produce isocyanate with satisfactory yields
- Develop a separation strategy to isolate the isocyanate formed to avoid the reaction with the organic acid formed as the by-product
- Design the process to make it economically viable

Based on the results obtained from this analysis, the process would be simulated using Aspen Plus process simulator to compare its material and energy requirements with that of the conventional phosgenation route for manufacture of isocyanates. The results from the Aspen Plus would be used to identify any potential hot-spots for mass and energy consumption in the novel route and accordingly make changes to improve the process.

The second but equally important objective of this dissertation study is to perform a life cycle analysis to compare the environmental impacts of polycarbonate and its replacement Tritan ™. A detailed analysis would be performed to study the effect of using different functional units, different scenarios of internal recycling of unreacted raw material and the effect of using different allocation methods on the environmental impacts of these polymers.

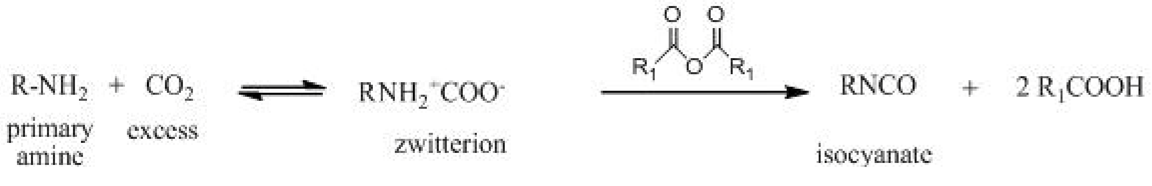
4.0 DEVELOPMENT OF LOW TEMPERATURE NON-PHOSGENE ROUTE

This study hypothesized that the zwitterion formed by the reaction of a primary amine with carbon dioxide when reacted with an anhydride, would lead to the formation of the corresponding isocyanate and acid (Route 7 in Figure 2 & eq. 4.2). It was the objective of this project to study and develop this non-phosgene route to replace the present phosgene route for manufacture of isocyanates. The main aspects of the study involved modifications to the route proposed by McGhee et al (Route 6 in Figure 2 & eq. 4.1), to eliminate the formation of salt as a by-product.



(4.1)

This was done by eliminating the use of a nitrogenous base & carrying out the carbonylation process in an excess of CO_2, leading to the formation of a zwitterion instead of a carbamate as shown below.



(4.2)

The details of this study have been explained in the following sections.

4.1 MATERIALS

All chemicals used in this project were obtained from Sigma-Aldrich, Fischer Scientific or Alfa Aesar. Water readily reacts with isocyanates with reactivity similar to that of alcohol to form a carbamic acid intermediate. The carbamic acid is unstable and spontaneously decarboxylates into an amine and carbon dioxide [43]. The amine formed reacts with another isocyanate group to produce a urea crosslink.

$$\text{R-NCO} + H_2O \longrightarrow \text{R-NHCOOH} \longrightarrow \text{R-NH}_2 + CO_2 \qquad (4.3)$$

$$\text{R-NCO} + \text{R-NH}_2 \longrightarrow \text{R-NHCONHR} \qquad (4.4)$$

Therefore, it is very important to carry out reactions involving isocyanates under anhydrous conditions. Hence, all the chemicals and solvents used were first treated with CaH_2 to strip off any residual water present in them.

The gases used in the experiments and Gas Chromatographic analysis were obtained from Penn Oxygen and had the grades as shown in Table 4.

Table 4. Grades of gases used in experiments and gas chromatography

Carbon Dioxide	Coleman Grade – 99.99 %
Hydrogen	Ultra High Purity – 99.999 %
Helium	Ultra High Purity – 99.999 %
Air	Zero Chromatographic – Water < 5 ppm

4.2 EXPERIMENTAL METHODS

4.2.1 Measurement of carbon dioxide solubility in solvents

The solubility data for CO_2 in acetone was obtained by studying the phase behavior at a given temperature for different weight fractions of CO_2 and acetone. This was carried out in a high pressure, variable-volume, windowed cell (formerly by DB Robinson and Associates, now Schlumberger) retained in a constant temperature air bath. Figure 3 shows the schematic behavior of the apparatus. Temperature range for the cell is -20 °C to 180 °C and it can be pressurized up to 10000 psi. The maximum volume of the cell is about 110 cc. To perform the phase behavior experiment, a known amount of acetone is placed on the piston inside the glass quartz cylinder above the piston. The piston can be moved up or down, thereby decreasing or increasing the volume of the sample chamber, by adding or withdrawing the overburden fluid (silicone oil) using a positive displacements pump.

CO_2 is added to the cell and constant pressure is maintained by withdrawing overburden fluid. When the required amount of CO_2 is added, the cell is pressurized and agitated using magnetically driven stirrer until the single phase is obtained at very high pressure. The cell is then slowly depressurized by withdrawing overburden fluid until two phases are observed. The pressure at which CO_2 bubbles begin to appear is noted. The system is pressurized again and agitated to obtain single phase and depressurized until the two-phase pressure is again observed. This process is repeated 3 to 4 times at each weight percent to obtain a consistent reading. [44, 45]

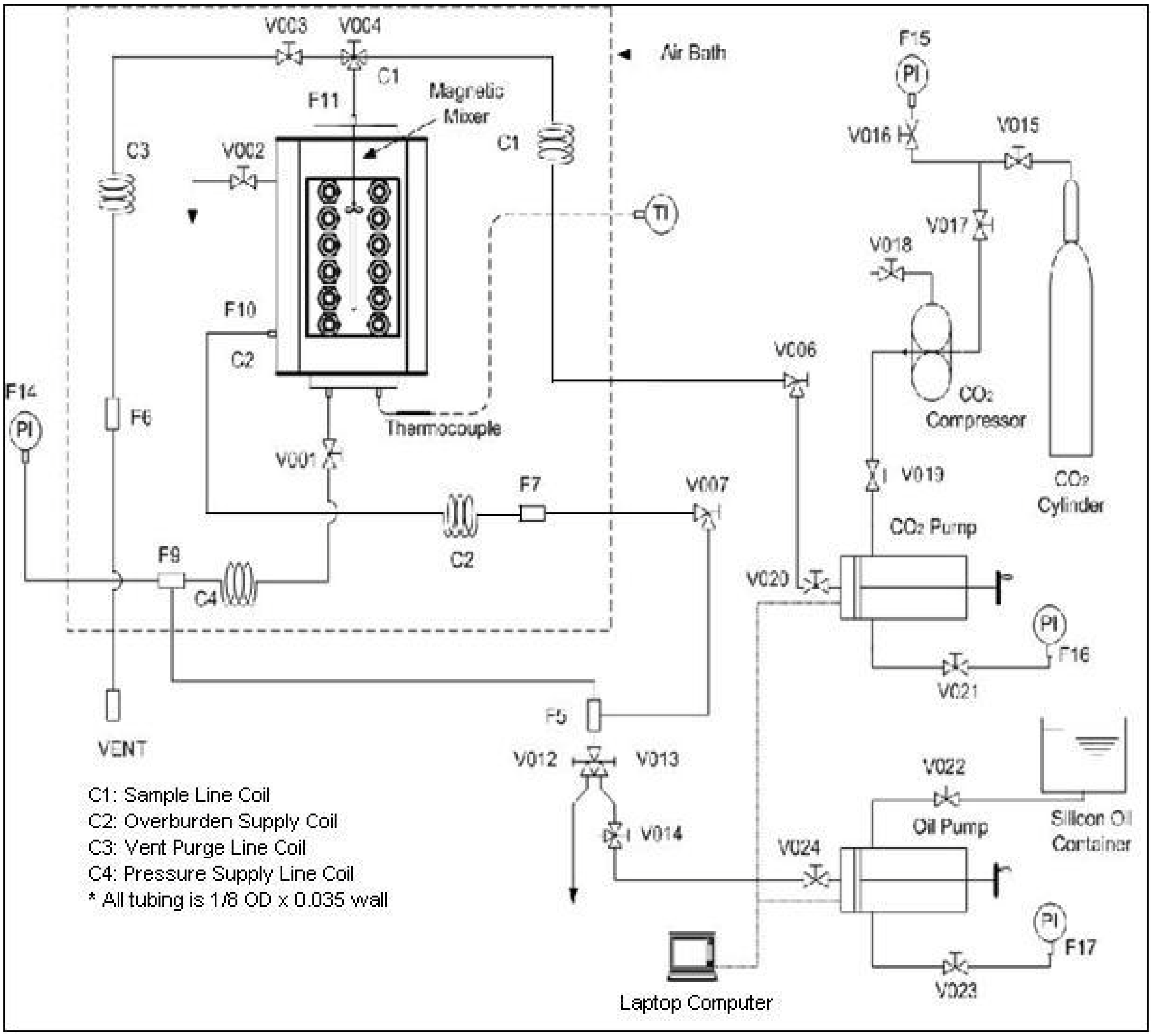


Figure 3. Schematic of phase behavior apparatus (Robinson Cell)

4.2.2 Measurement of CO_2 solubility in solvents at low temperature

Since, the lower limit for temperature in the Robinson Cell is -20 °C, a different procedure is used to measure the solubility of CO_2 at temperatures lower than that. The weight (A gm) of a 50 ml round bottom flask is measured. 20 ml of the solvent in which the solubility of CO_2 is to be measured is added to the round bottom flask and the total weight (B gm) is measured. Excess dry ice is then added to the 20 ml of solvent and the total weight (C gm) is measured when the last chunk of dry ice disappears indicating the maximum saturated solubility at the given temperature. The solubility (weight fraction) of CO_2 is then given by

$$S = \frac{CO_2 dissolved}{Solvent} = \frac{(C - B)}{(B - A)} \tag{4.5}$$

4.2.3 Synthesis of isocyanate from primary amine and CO_2 at low temperature

In a typical experiment, 20 ml of anhydrous acetone, 25 g of dry ice and 1 mmol (154 mg) of biphenyl as an internal standard for GC is added to a 250 ml round bottom flask. 2 g of CaH_2 is added to maintain anhydrous conditions throughout the reaction. A mixture of 5 ml of acetone and 25 mmol (1.832 g) of n-butylamine is added to the reaction vessel at the rate of 1ml/min. The solution is kept for ca. 12 min with constant stirring. A mixture of 5 ml acetone and 25 mmol (6.30 g) of anhydride is added at the rate of 1 ml/min. The reaction is allowed to proceed for ca. 12 min. The reaction mixture is brought to room temperature and an aliquot from the reaction mixture is analyzed by gas chromatography (GC) as described in Appendix A.2. The conversion to n-butyl isocyanate obtained using different anhydrides is discussed in Section 4.3.6.1. FT-IR (cm^{-1}): 895, 1130, 1177, 1265, 1448, 1644, 1689, 1785, 1835, 1874, 2276, 2337, 2932, 3054.

4.2.4 Synthesis of isocyanate from primary amine and carbon dioxide at low temperature and high pressure

The setup for this experiment is shown in Figure 4. In a typical experiment, 20 ml of anhydrous acetone and 1 mmol (154 mg) of biphenyl as an internal standard for GC is added to a specially designed glass reactor from Kimble-Kontes which can withstand an operating pressure upto 175 psi. 2 g of CaH_2 is added to maintain anhydrous conditions throughout the reaction. A pressure generator is filled with 17.5 ml of acetone and 6.405 gm of butyl isocyanate (concentration = 5 mmol butyl isocyanate / ml acetone) and the second pressure generator is filled with 17.5 ml of acetone and 22.05 gm of trifluoroacetic anhydride (TFAA) with a concentration of 5 mmol TFAA / ml acetone. CO_2 is added to this reaction mixture at the required pressure and the following cooling baths are used for different operating temperatures.

-78 °C	Dry ice + acetone
- 42 °C	Dry ice + acetonitrile
-20 °C	Dry ice + o-xylene
0 °C	Salt + ice

The solution is kept for ca. 10 min with constant stirring. A mixture of 5 ml of acetone and 25 mmol (1.832 g) of n-butylamine is added to the reaction vessel at the rate of 1ml/min from the first pressure generator. The time for which the solution is kept with constant stirring depends on the pressure and is ca. 12 minute for atmospheric pressure, 20 to 30 minute for 29 psi, 1 hour for 70 psi. A mixture of 5 ml acetone and 30 mmol of anhydride is added at the rate of 1 ml/min from the second pressure generator. The reaction is allowed to proceed for ca. 12 minute. The reaction mixture is brought to room temperature and an aliquot from the reaction mixture is analyzed by gas chromatography (GC) as described in Appendix A.2. The conversion to n-butyl isocyanate obtained using different anhydrides is discussed in Section 4.3.8. FT-IR (cm^{-1}): 895, 1130, 1177, 1265, 1448, 1644, 1689, 1785, 1835, 1874, 2276, 2337, 2932, 3054.

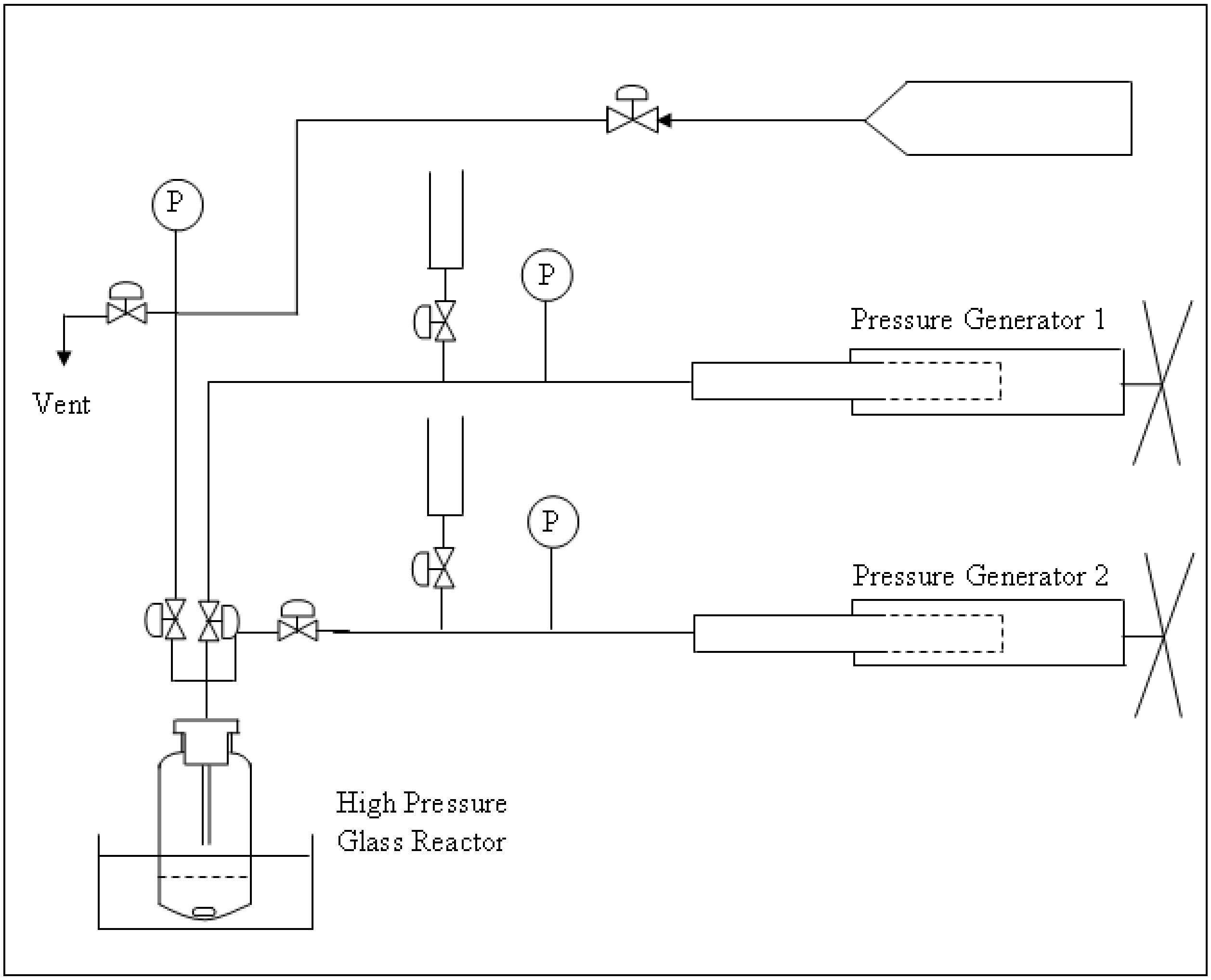


Figure 4. High pressure set-up for synthesis of isocyanate using the glass reactor for pressures upto 170 psi

4.2.5 Extraction of acid using polyvinyl pyridine & recovery by methanol

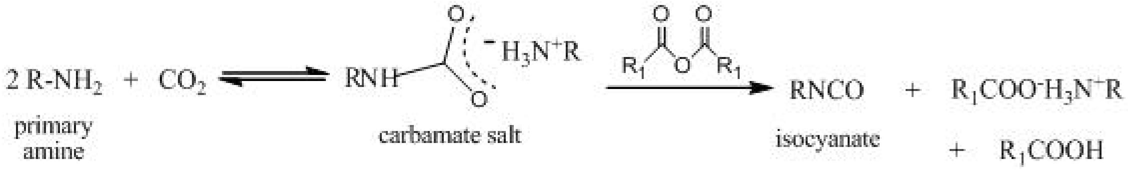
In a typical experiment, 10 mmol of polyvinyl pyridine (PVP) is added to 10 ml acetone in a 100 ml beaker. The reaction mixture is stirred for ca. 5 minute. The PVP is filtered and dried in an oven at 110 °C to remove any water present in the PVP resin. The dried PVP is added to a mixture of 10 ml of acetone and 10 mmol (1.14 g) trifluoroacetic acid with constant stirring for ca. 20 minute. The PVP is filtered and an aliquot of the filtrate is titrated against 0.05 N NaOH solution to calculate the amount of TFA present in the filtrate. This process is repeated twice to calculate the additional TFA adsorbed onto the PVP resin. The PVP saturated with TFA is filtered and is transferred to a beaker containing 10 ml of methanol with constant stirring for 20 minute. An aliquot of the methanol solution is titrated against 0.05 N NaOH solution to calculate the TFA recovered in the methanol solution. This process is repeated twice to calculate the amount of TFA desorbed into methanol from the PVP resin.

4.3 RESULTS AND DISCUSSION

4.3.1 Detailed description of the proposed process

In view of the considerable disadvantages of using a strong base (described in Section 2.3 and 2.3.1), we explored the possibility of eliminating the use of a separate base and let the primary amine act as the base, resulting in the formation of a carbamate salt . The pKa value of octylamine and butylamine are 10.65 and 10.8 respectively, which is very similar to that of triethylamine (pKa =10.7) that was used as one of the bases by McGhee et al [1]. The isocyanate yields obtained were similar to that obtained by McGhee by using triethylamine as the base. The comparison is shown in Table 5.

The reaction proceeds as follows,

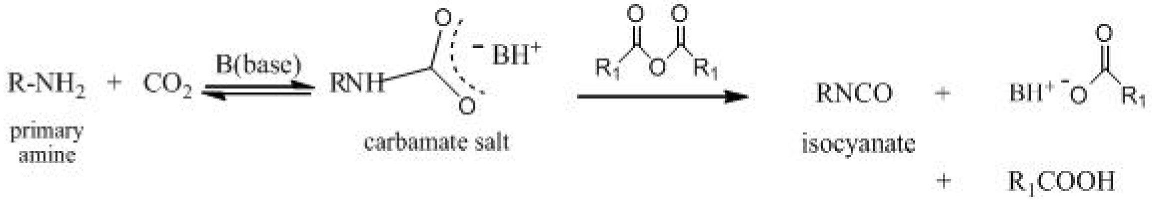


(4.6)

Table 5. Effect of strength of base on conversion to isocyanate

Amine	Base	pKa	Conversion to isocyanate (%)
n-octylamine	CyTEG	13.7	95 [39]
n-octylamine	triethylamine	10.78	35 [39]
n-octylamine	n-octylamine	10.65	21

Because of similar conversions as seen in Table 5, it was observed that the anhydride used in the second step is sufficient for the dehydration of the carbamate salt and the base used in the 2nd step only neutralizes the acid formed. If the reaction is carried out in conditions such that the isocyanate formed doesn’t react with the carboxylic acid formed as a byproduct then we can eliminate the use of a base in the 2nd step. Xiao et al. have studied the mechanism and the kinetics of the reaction between an isocyanate and a carboxylic acid and have concluded that the reaction proceeds at a much slower rate at low temperature [46]. Thus by carrying out the reaction at sufficiently low temperatures, it is possible to produce one mole of isocyanate with only one mole of salt formed instead of two moles of salt formed as a by-product as described by McGhee et al.



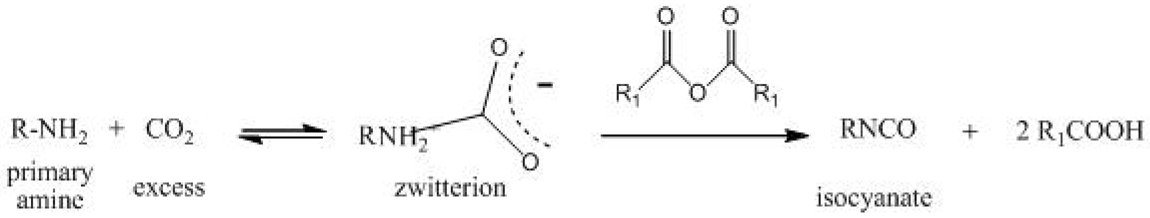
(4.7)

The formation of carbamate has been explained by the zwitterion mechanism and proceeds in the following two step manner [47, 48].

$$R\text{-}NH_2 \quad + \quad CO_2 \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad RNH^+COO^- \qquad (4.8)$$

$$RNH^{+}COO^{-} + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} RNCOO^{-}\,{}^{+}HB \tag{4.9}$$

So, if the reaction is carried out in a large excess of CO_2, it is possible to have a higher amount of the zwitterion intermediate present in the sample. We proposed that if an anhydride is added to this zwitterion intermediate, it will result in the synthesis of isocyanate as follows,



(4.10)

As mentioned earlier, if carried out at low temperatures and in an excess of CO_2, it may be possible to manufacture isocyanate without the formation of any salt as a by product. However, preliminary experiments (shown in Figure 5) show the presence of the IR peak 1685 cm^{-1} & 1685 cm^{-1} corresponding to the peak formed due to the presence of salt of primary amine and trifluoroacetic acid (TFA) and amide respectively (See Appendix A.1. for further details).

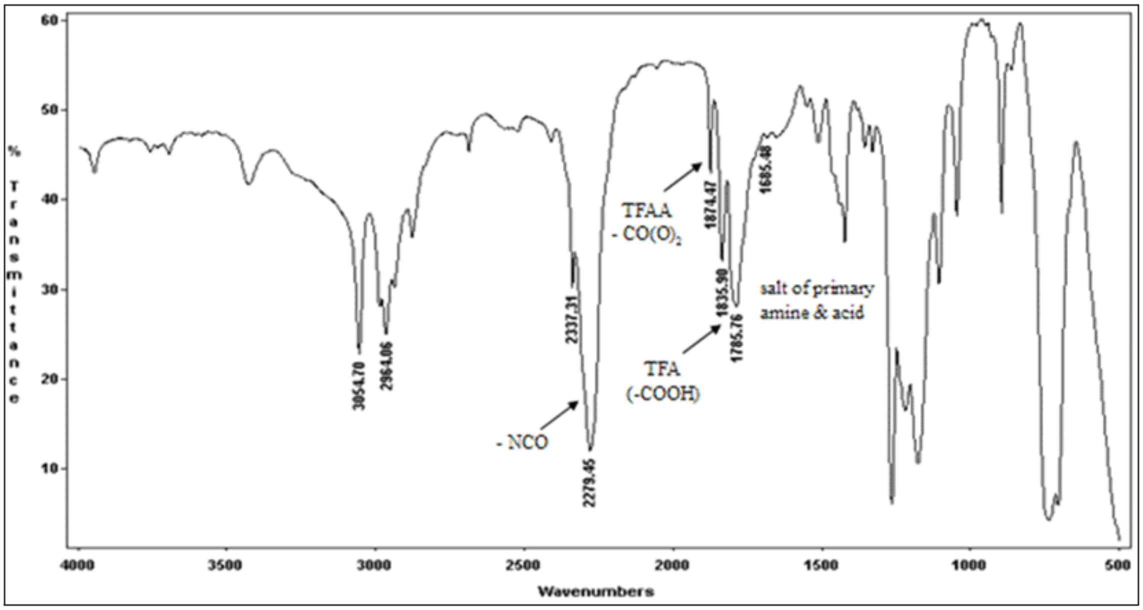


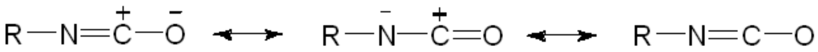
Figure 5. IR spectra of product mix when TFA is added to the reaction mixture formed when excess CO_2 is added to n-butylamine in acetone

This indicates that it is not possible to have the presence of the zwitterion intermediate only. Even in large excess of CO_2 some equilibrium quantity of the carbamate would be present in the reaction mixture. The primary objective of this study was to identify the conditions at which the reaction proceeds via the zwitterion route than the carbamate route.

4.3.2 Side Reactions

In order to achieve maximum possible yields, the possible side reactions were studied so that they could be minimized.

The high reactivity of isocyanates is prompted by their capability to undergo nucleophilic addition reactions with many substrates. The reactivity of the isocyanate group towards nucleophilic reactions can be best explained by considering the electronic structure of the isocyanate group and the effect of the substituents. The charge density is the greatest on oxygen and the least on carbon and the resonance structures are as follows.

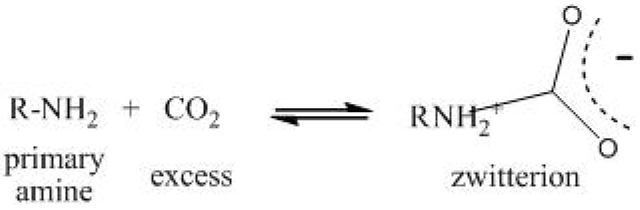


$$R-N=\overset{+}{C}-\overset{-}{O} \longleftrightarrow R-\overset{-}{N}-\overset{+}{C}=O \longleftrightarrow R-N=C-O$$

The reactions of isocyanates with active hydrogen compounds involve attack by a nucleophile at the electrophilic carbon of the isocyanate. Therefore, any substituent that is electron withdrawing will increase the positive charge on the carbon and thereby increase the reactivity of the isocyanate group towards nucleophilic attack. Conversely, electron donating groups will reduce the reactivity of the isocyanate group.

4.3.2.1 Reaction of amine with carboxylic acid and anhydride:

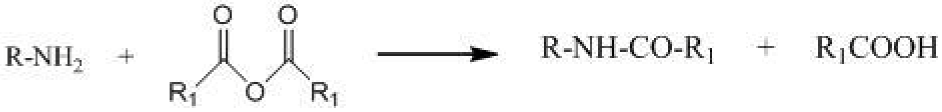
The formation of zwitterion is a reversible step and hence there will be an equilibrium concentration of the components involved as follows.



(4.11)

$$K = \frac{[RNH_2^+COO^-]}{[RNH_2][CO_2]} \tag{4.12}$$

Due to the presence of equilibrium, some primary amine would be present. As a result, the following side reaction can take place.



(4.13)

$$\text{R-NH}_2 + \text{R}_1\text{COOH} \longrightarrow \text{R-NH}_3^{+}\,{}^{-}\text{OOCR}_1 \tag{4.14}$$

These side products can be minimized by maintaining conditions that reduce the amine concentration.

1. <u>Low Temperature:</u> The formation of a zwitterion from amine and CO_2 is an exothermic reaction, hence the equilibrium constant K would be higher at lower temperatures according to the Van Hoff equation, where ΔH° is the standard enthalpy change of the reaction and R is the universal gas constant. As a result, the reaction would shift forward resulting in lower equilibrium concentration of amine

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.15}$$

$$[RNH_2] = \frac{[RNH_2^+COO^-]}{K*[CO_2]} \tag{4.16}$$

2. Excess of CO_2: As seen from the equation above, at a given temperature, an excess of CO_2 will suppress the amine concentration. Also, an excess of CO_2 will result in higher concentration of the zwitterion as it would suppress the formation of carbamate. Hence, a minimum of 10 times molar excess of CO_2 over amine concentration is used in the experiments.

4.3.2.2 Reaction of amine with the isocyanate formed:

Isocyanates react rapidly with amines forming urea without the need for any catalyst. Due to the absence of any significant steric hindrance and the electronegative effect of the aromatic ring, straight chain aliphatic amines react faster than aromatic amines. The higher the electronegativity of the aromatic ring substituents, the lower will be the reactivity of the amines with the isocyanate [49].

$$\text{R-NH}_2 + \text{RNCO} \longrightarrow \text{RNH-CO-NHR} \qquad (4.17)$$

As a result it is imperative to maintain reaction conditions such that we do not have any amine present in the reaction mixture.

4.3.2.3 Reaction of isocyanate with water:

The blowing reaction of isocyanates with water results in urea formation and carbon dioxide gas release. The reaction is exothermic and releases 47 kcal/mol of water consumed. The reactivity of isocyanate with water and primary hydroxyl group is comparable, however is much smaller than with amines [49].

$$\text{RNCO} + \text{H}_2\text{O} \longrightarrow \text{R-NH-COOH} \qquad (4.18)$$

$$\text{R-NH-COOH} \longrightarrow \text{R-NH}_2 + \text{CO}_2 \qquad (4.19)$$

$$\text{R-NH}_2 \quad + \quad \text{R-NCO} \longrightarrow \text{RNH-CO-NH-R} \qquad (4.20)$$

Hence, the presence of water in the reaction mixture is detrimental to the isocyanate yield as two moles of isocyanate are consumed for every mole of water. The solvents and the reactants are treated with CaH_2 to make sure that we have minimal moisture present in the reaction mixture.

4.3.2.4 Reaction of isocyanates with carboxylic acid:

Weak aromatic and aliphatic acids react with isocyanates to form mixed anhydrides.

$$\text{RNCO} \quad + \quad \text{R}_1\text{COOH} \longrightarrow \text{R-NH-CO-O-CO-R}_1 \qquad (4.21)$$

The anhydrides formed from strong acids such as trifluoroacetic acid spontaneously decompose to give carbon dioxide and an amide [50].

$$\text{R-NH-CO-O-CO-R}_1 \longrightarrow \text{RNH-CO-R}_1 \quad + \quad \text{CO}_2 \qquad (4.22)$$

Xiao et al have studied the kinetics of this reaction at different temperatures and in different solvents [46]. It was found that these reactions follow the rate law for 2nd order reactions and the rate constant was higher in polar solvents. Also, the equilibrium constant is higher at higher temperatures, indicating an endothermic reaction. Hence, in order to minimize the effect of this reaction on the yield of isocyanates, we carried out the reaction at – 78 °C.

The -NCO group reactivity depends on structure. The relative isocyanates reactivities with several active hydrogen-containing compounds are shown in Table 6 [49]. Figure 6 summarizes all the possible reactions that can take place while attempting to manufacture isocyanates via the proposed route.

Table 6. Relative reactivity of –NCO with different hydrogen containing compounds

Active hydrogen compound	**Typical Structure**	**Relative Reaction rates***
Primary aliphatic amine	$R-NH_2$	100
Secondary aliphatic amine	RR’NH	20 - 50
Primary aromatic amine	$Ar-NH_2$	200 - 300
Primary hydroxyl	RCH_2-OH	100
Water	HOH	100
Carboxylic acid	RCOOH	40
Secondary hydroxyl	RR’CH-OH	30
Urea	R-NH-CO-NH-R	15
Tertiary hydroxyl	RR’R”C-OH	0.5
Urethane	R-NH-CO-O-R	0.3
Amide	$RCO-NH_2$	0.1

(* uncatalyzed at 25 °C)

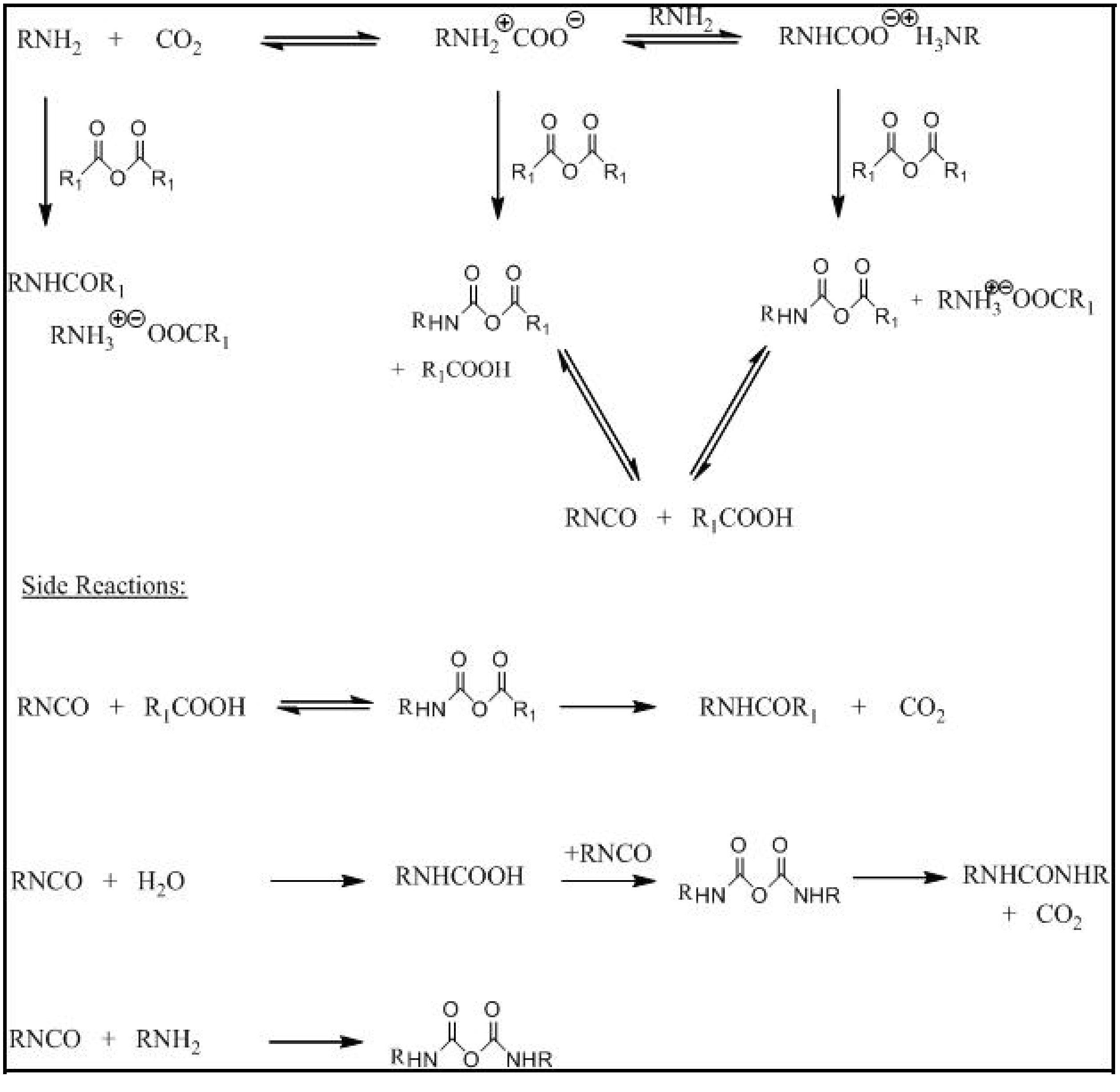


Figure 6. Proposed route and possible side reactions

4.3.3 Solvent selection

The parameters that were taken into consideration while selecting the most suitable solvent for the proposed process have been discussed in the following sections

4.3.3.1 Reaction with isocyanates:

As seen in Table 7, isocyanates react with compound having an active hydrogen present. For example, the reaction with alcohols proceeds as follows,

$$\mathrm{RNCO} + \mathrm{R_1OH} \longrightarrow \mathrm{R\text{-}NH\text{-}CO\text{-}O\text{-}R_1} \tag{4.23}$$

Due to similar reactions the use of all protic solvents as the reaction media can be eliminated. The major non-protic solvents that were explored were acetone, dichloromethane, acetonitrile and toluene.

4.3.3.2 Polarity:

Acetonitrile has been used as the solvent in prior literature references to synthesize isocyanates via the carbamate route suggesting that a polar solvent is the preferred solvent for this process [1, 39, 40, 51]. In order to verify the preference of polar solvents, we conducted preliminary test with n-octylamine, triethylamine as the base and trifluoroacetic anhydride as the dehydrating agent in different solvents of varying polarity. The IR spectra of the final reaction mixture indicated that the intensity of the isocyanate peak (2276 $\mathrm{cm^{-1}}$) in different solvents was in the following order – acetonitrile > acetone > dichloromethane > toluene. Though acetonitrile is the most polar of the solvents used, the minimum temperature that can be achieved in acetonitrile + dry ice mixture is – 42 °C. The minimum temperature obtained by acetone + dry ice mixture is -78 °C. As discussed later in Section 4.3.7, the effect of lower temperature was more pronounced than the effect of using more polar solvent. The conversion of n-butylamine to n-butyl isocyanate via the carbamate route was 94 % in the dry ice + acetone mixture at -78 °C, whereas it was 81 % in the dry ice + acetonitrile mixture at -42 °C. Thus, acetone worked as a better solvent giving higher conversions at lower temperatures despite its lower polarity compared to acetonitrile.

4.3.3.3 Solubility of CO_2:

As discussed in Section 4.3.1, in order to have the advantages of the zwitterion route, it is necessary to have an excess of carbon dioxide in the first step of the reaction (carbon dioxide with a primary amine). This can be achieved by adding dry ice to the solvent resulting in a single phase solution. The use of dry ice serves the additional purpose of lowering the temperature of the reaction mixture which is favorable for higher conversion of the zwitterion to isocyanate. This effect on the higher conversion to isocyanate at lower temperature is discussed in detail in Section 4.3.7. In order to minimize the amount of solvent used, it is would be preferable to have the solvent with the highest solubility of CO_2 at the reaction conditions.

Figure 8 summarizes the solubility of CO_2 in different solvents of concern at different temperatures obtained from the data in “Solubility Data Series – Carbon dioxide” [52]. The CO_2 solubility data for dichloromethane (at -78 °C) and acetone (at -78 °C) was obtained in the lab using the procedure described in Section 4.2.3. Figure 7 & 8 show the solubility of CO_2 as a function of polarity index, which is a relative measure of the degree of interaction of the solvent with various polar test solutes. Solvents with higher polarity index have higher solubility of CO_2 and the solubility increases exponentially with reducing temperature. However, acetonitrile cannot be used as a solvent below - 42 °C (freezing temperature). This precludes the use of acetonitrile as a solvent for the proposed route and we focused the work on using acetone and dichloromethane as solvents at low temperature (- 78 °C) for further analysis.

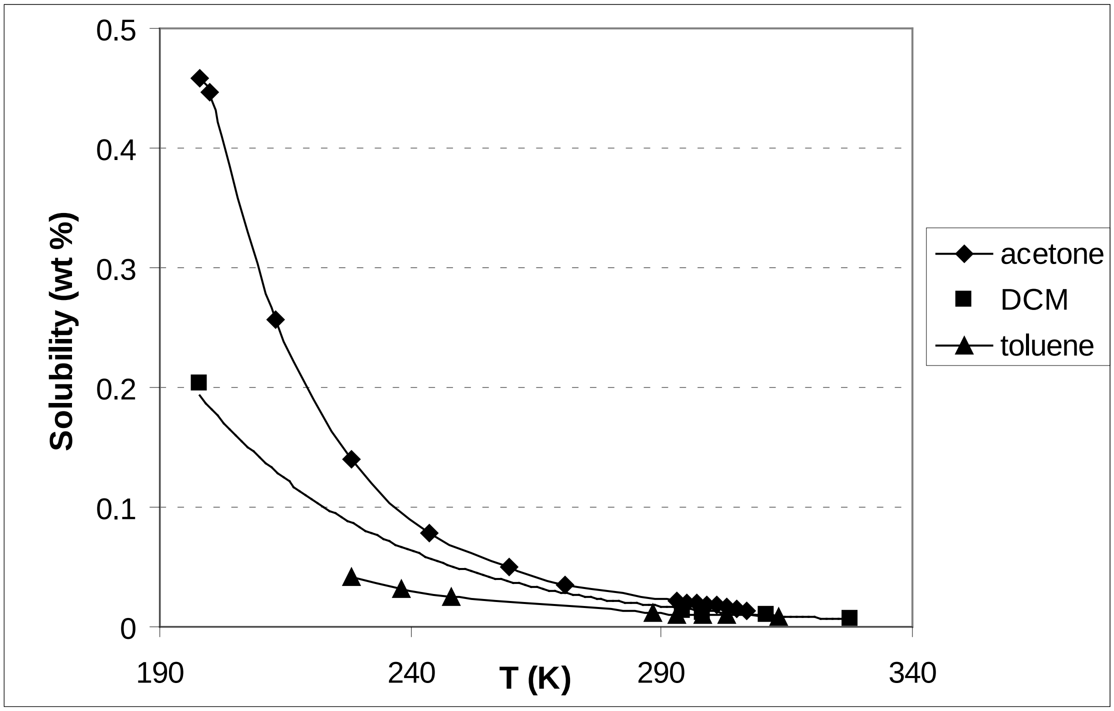


Figure 7. Effect of temperature on solubility of CO_2 in solvents (low temperature range)

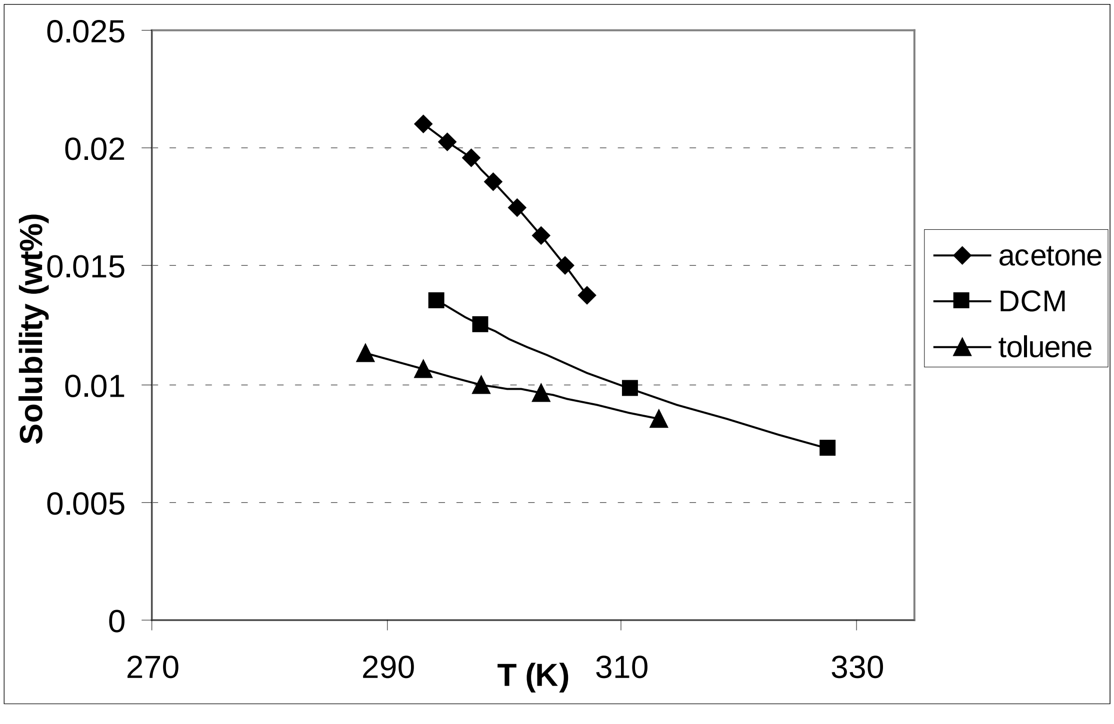


Figure 8. Effect of temperature on solubility of CO_2 in solvents

Table 7 shows the effect of polarity of the solvent on the solubility of CO_2 in that solvent. The solubility is compared to the polarity index and dielectric constant.

Table 7. Polarity and solubility of CO_2 in aprotic solvents

Solvent	Polarity Index	Dielectric Constant	Cold trap temperature with dry ice (°C)	Maximum solubility (wt percent) of CO_2 at cold trap temp
Acetonitrile	5.8	37	- 42 °C	-
Acetone	5.1	21	- 78 °C	0.459
Dichloromethane	3.1	9.1	- 78 °C	0.203
Toluene	2.4	2.4	- 45 °C	0.042

Since, the extent to which CO_2 would be present in the reaction mixture was a very important factor that would determine the stability of the zwitterion intermediate, the solubility of CO_2 was studied more in detail. The solubility data for CO_2 in acetone at 0 °C was obtained using the Robinson cell as explained in Section 4.2.1. Figure 9 shows the pressure required to completely dissolve the CO_2 present in the solvent (acetone). Figure 10 shows the decrease in the pressure required to dissolve the CO_2 in the solvent as the temperature of the system was reduced. This data was compared using the P-x and T-x relations obtained using Aspen Properties 2006 software. As seen from Figure 9, the experimental solubility data matched quite well with the predicted data using Aspen Properties. Hence, for further reference, Aspen Properties was considered as a reliable tool to predict the solubility of CO_2 in acetone at different conditions. The solubility data obtained using Aspen Properties is shown in Figure 11 and 12.

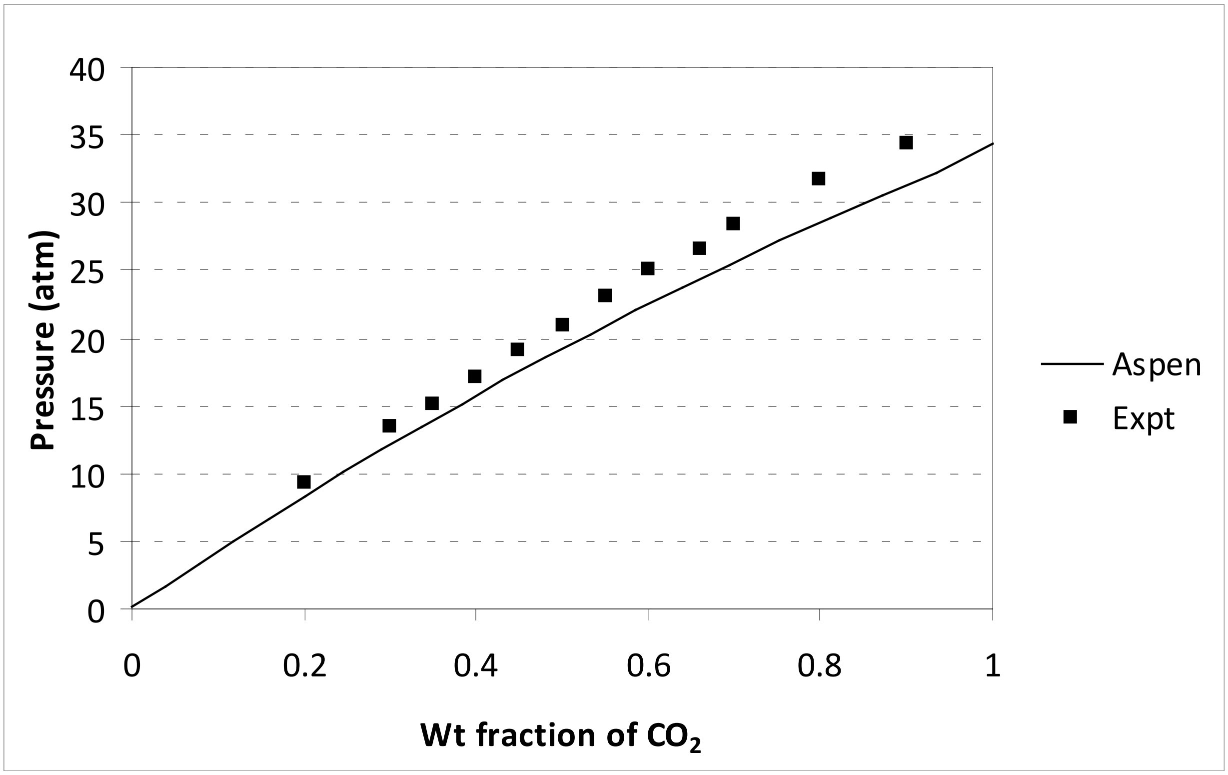


Figure 9. Comparison of results obtained using Aspen Properties with the experimental results obtained from the Robinson cell for the pressure required to achieve a single phase of CO_2 and acetone mixture at a constant temperature (T = 0 °C)

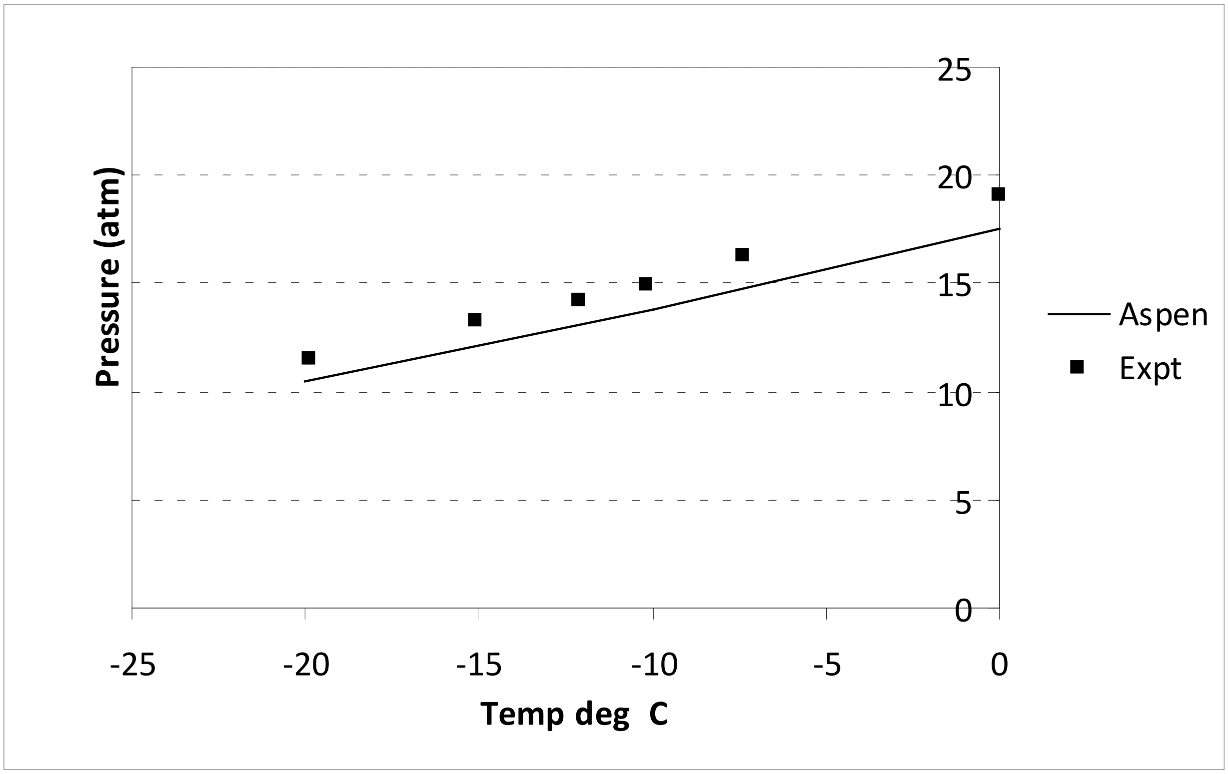


Figure 10. Comparison of results obtained using Aspen Properties with the experimental results obtained from the Robinson cell for the pressure required to achieve a single phase of CO_2 and acetone mixture at a constant CO_2 weight fraction of 0.45

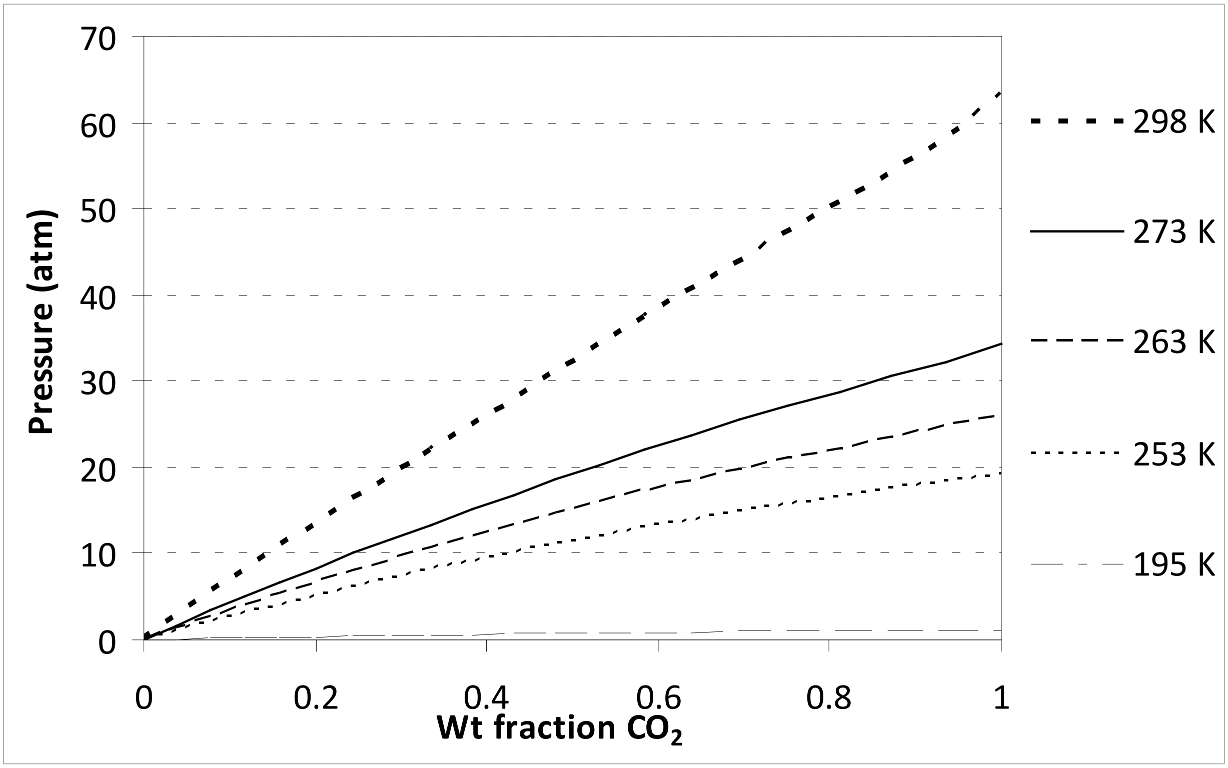


Figure 11. Aspen Properties results for pressure required to achieve a single phase of CO_2 & acetone mixture at a constant temperature of 298 K, 273 K, 263 K, 253 K & 195 K.

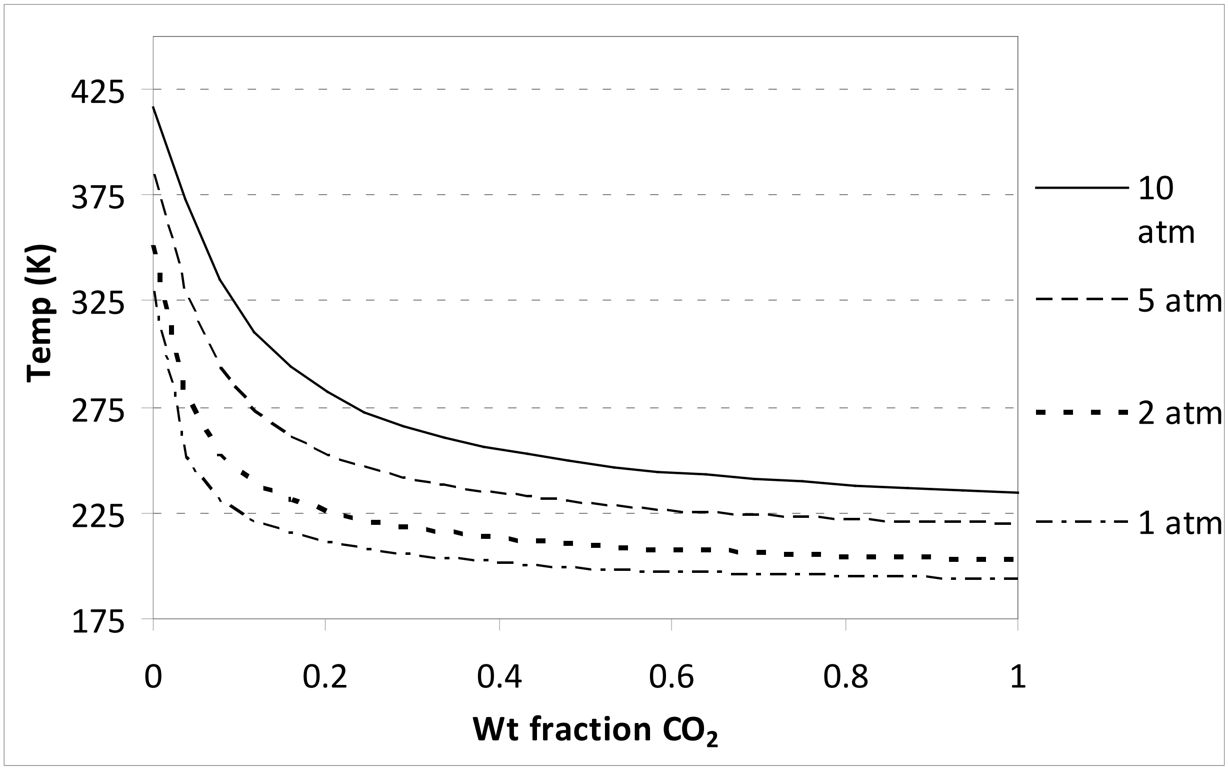


Figure 12. Aspen Properties results for the pressure required to achieve a single phase of CO_2 and acetone mixture at a constant pressure of 1 atm, 2 atm, 5 atm and 10 atm.

4.3.4 Selection of isocyanate and corresponding amine

Though diisocyanates such as methylene diphenyl diisocyanate and toluene diisocyanate are the most industrially relevant isocyanates, preliminary test of their corresponding amines would make it difficult to study the conversion of the –NH_2 group to –NCO group in isolation. Incase of diisocyanates, none or one or both the –NH_2 would be converted to the –NCO group making it difficult to monitor the exact conversion and selectivity of the amine species to the isocyanate species. Hence, mono isocyanates like n-butyl isocyanate and n-octyl isocyanates have been used for the purpose of this study. Prior literature data suggested that aliphatic amines resulted in higher conversion to isocyanates compared to aromatic amines [40-42]. This can be attributed to the lower basic nature of the aromatic amines due to the electron withdrawing effect of the phenyl group.

4.3.5 Concentration of products as a function of time

In order to study the progress of the reactions involved as a function of time, the IR peaks of n-butyl isocyanate (2276 cm^{-1}) and that of the amide (1709 cm^{-1}) formed by the reaction of the isocyanate with the carboxylic acid byproduct [46, 50] were monitored as soon as the dehydrating agent is added to the reaction mixture. The peak ratio of isocyanate and the amide peak with that of the CH_3 asymmetrical stretching peak (2929 cm-1) is reflective of the concentration of the respective components in the reaction mixture as the CH_3 peak strength remains unaffected throughout the reaction. Figure 13 shows how the peak ratio of isocyanate and amide vary as the reaction proceeds.

As seen in Figure 13, the isocyanate peak ratio initially increases rapidly. According to the mechanism proposed earlier, carboxylic acid is also formed as a byproduct which can react with the isocyanate. Hence, the increase in peak ratio of isocyanate gradually slows down and the peak ratio eventually decreases with time. At the same time, the peak ratio of the amide peak increases. Referring to the graph, we concluded that the ideal reaction time should be 5 to 15 minute, as that is the time when the peak ratio of the isocyanate peak is at its maximum value.

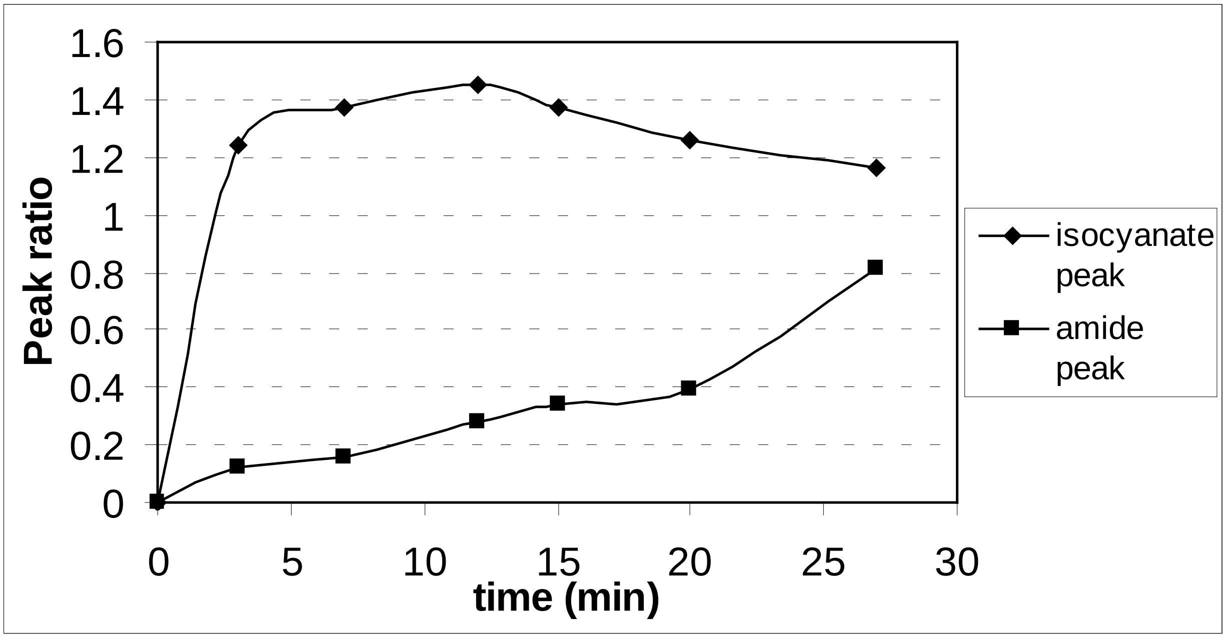


Figure 13. Infrared peak ratio of isocyanate and amide as a function of time

4.3.6 Selection of dehydrating agent:

A number of solid drying agents like CaH_2, $CaCl_2$, molecular sieves were evaluated as dehydration agents of the zwitterion or the carbamate. However, as seen in Figure 14, the absence of isocyanate peak (2277 cm^{-1}) on addition of CaH_2 indicates that there is no equilibrium with H_2O molecules present and the primary function of the dehydrating agent to be used is to undergo an electrophilic attack on the zwitterion or the carbamate and be able to form a suitable leaving group.

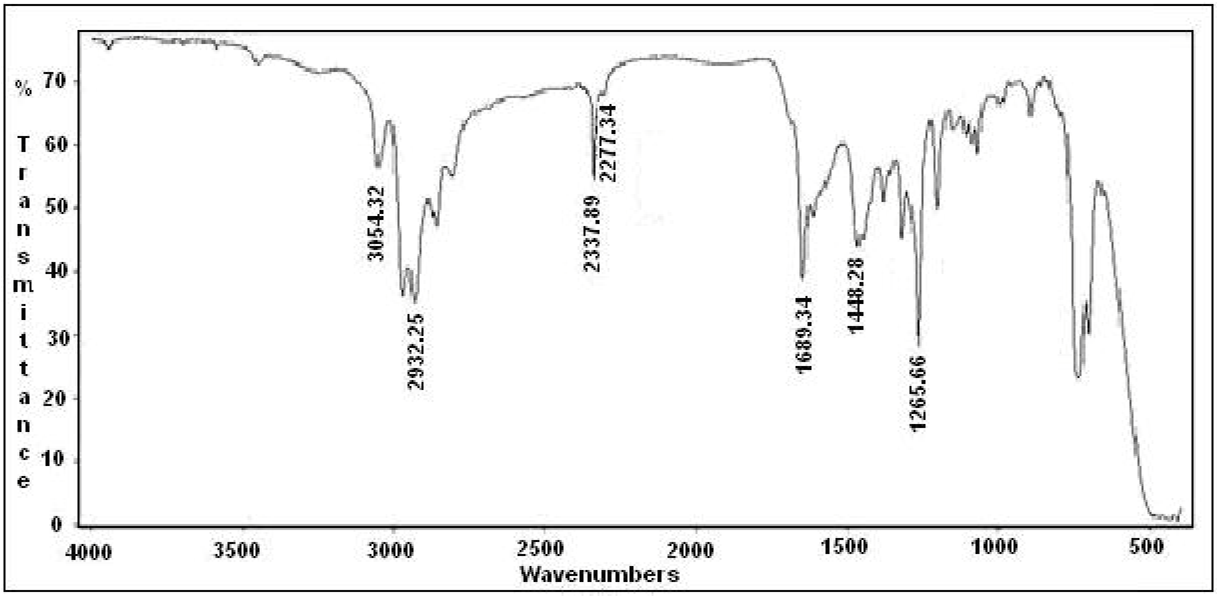


Figure 14. IR spectra of product mix with CaH_2 as dehydrating agent

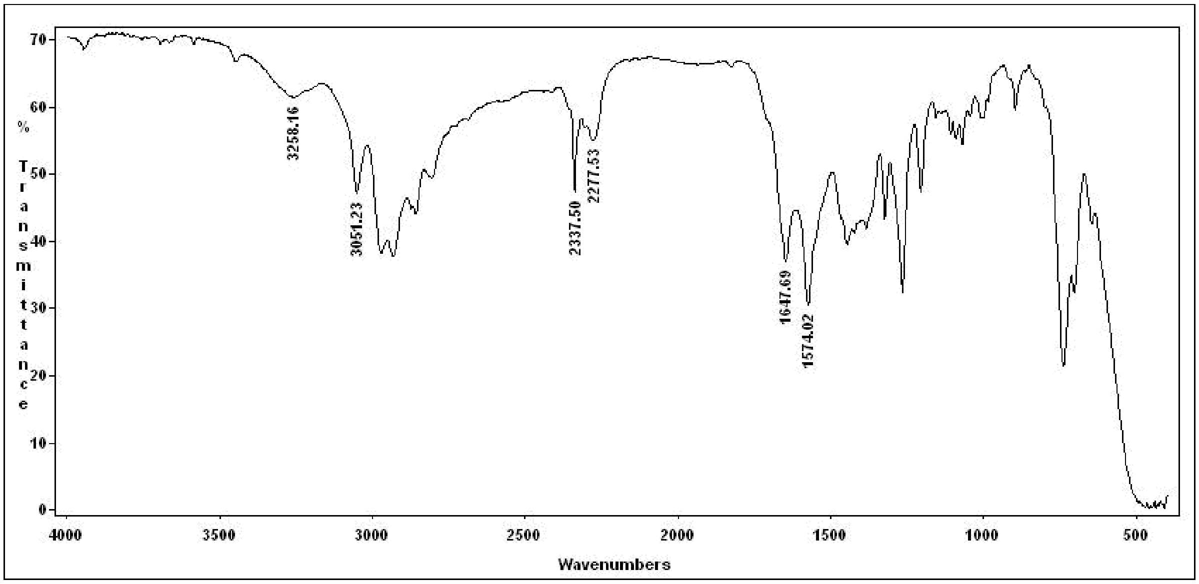


Figure 15. IR spectra of product mix with acetic anhydride as dehydrating agent

Anhydrides with strong electron withdrawing groups were found to be the most suitable as the dehydrating agent in the proposed process. As seen from figure 15 & 16, the intensity of the isocyanate peak (2277 cm^{-1}) is much stronger when trifluoroacetic anhydride is used as a dehydrating agent compared to acetic anhydride. The other reaction parameters were the same for both experimental runs.

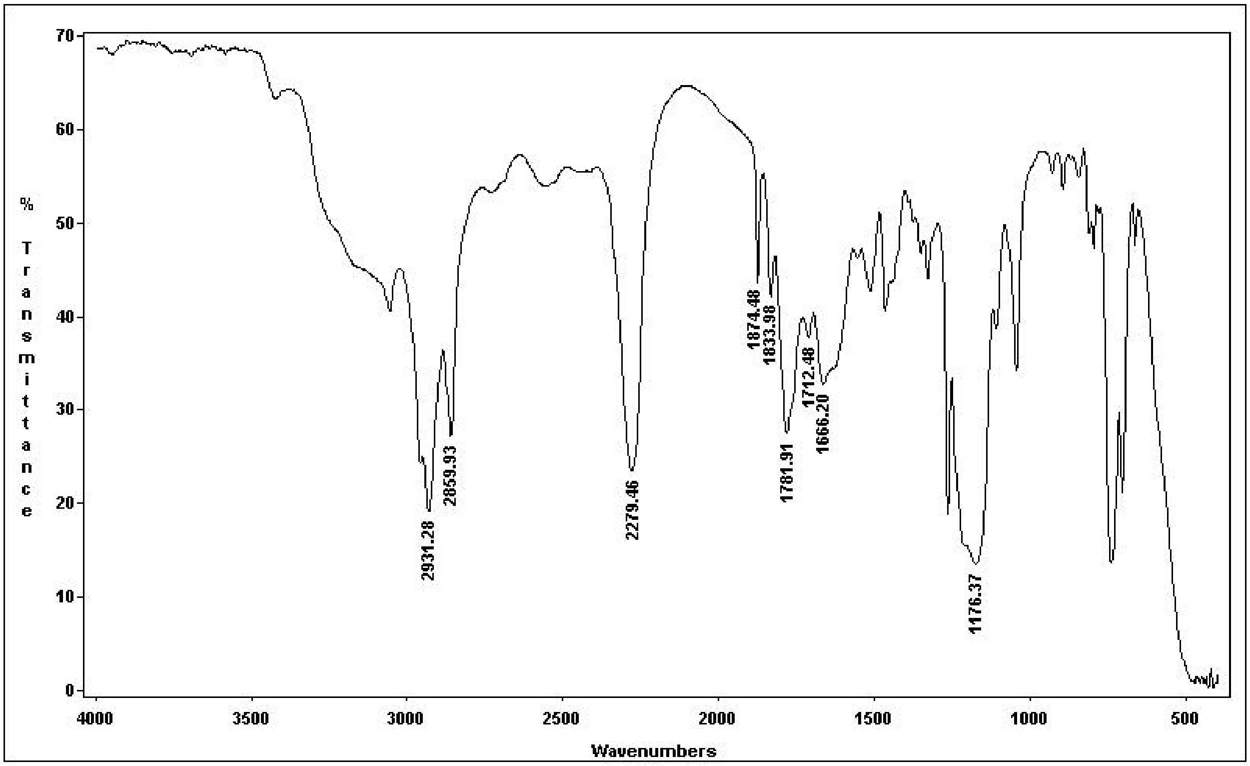


Figure 16. IR spectra of product mix with trifluoroacetic anhydride as dehydrating agent

Figure 17 shows the typical IR spectra of the reaction mix (carbamate present) vs. the product mix (isocyanate formed) when trifluoroacetic anhydride was used as the dehydrating agent. The isocyanate peak strength was significantly stronger for trifluoroacetic anhydride suggesting the strong electrophilic action of the anhydride due to the presence of the electron withdrawing fluorine groups.

Since recycling of di-acids (formed as a byproduct) to cyclic anhydrides would be relatively easier than linear anhydrides; preliminary tests were carried out with maleic anhydride, succinic anhydride and phthalic anhydride. However, neither of these cyclic anhydrides resulted in detectable amounts of isocyanates by IR spectroscopy.

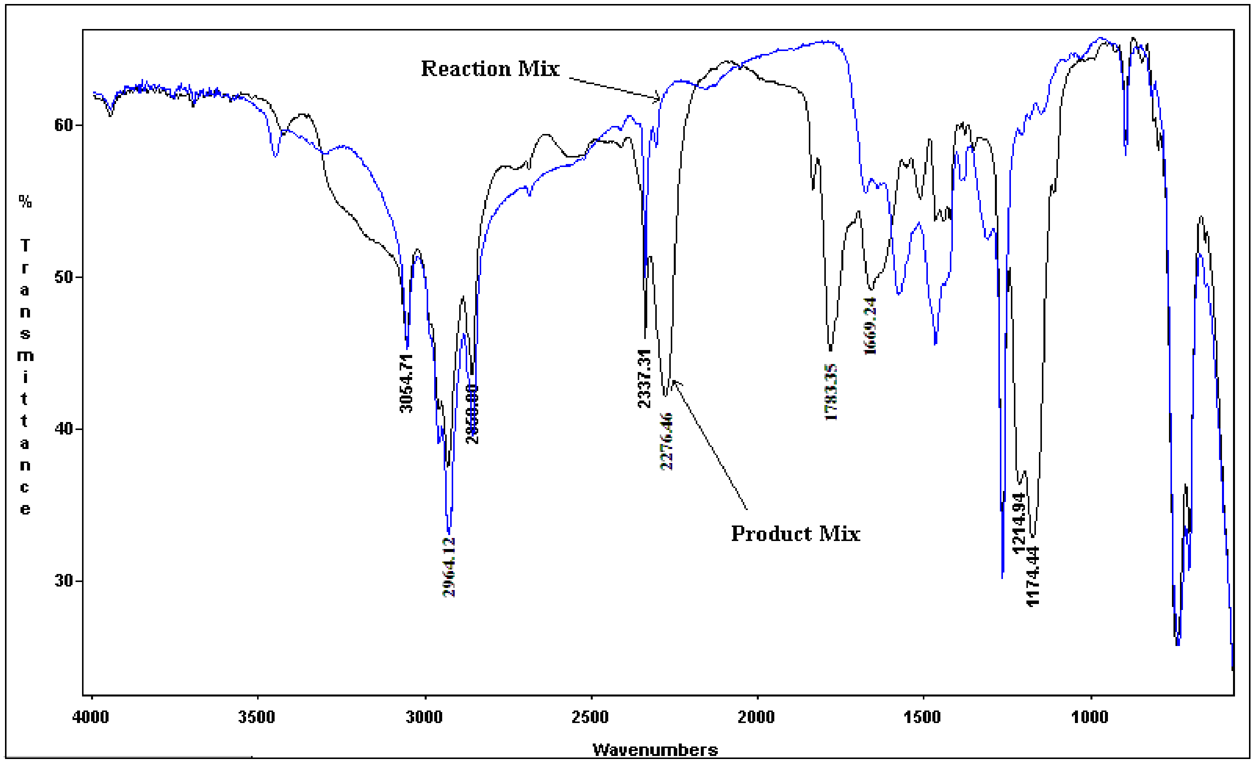


Figure 17. IR spectra of reaction mixture vs product mixture

4.3.6.1 Effect of the strength of acid of the anhydride used as dehydrating agent on conversion to isocyanate:

From the preliminary results shown in the IR spectras in Section 4.3.6, it was evident that organic anhydrides were ideally suitable as the dehydrating agents for the synthesis of isocyanates from primary amines and carbon dioxide. Also, the preliminary results showed higher selectivity to isocyanates when anhydrides with stronger electron withdrawing groups were used.

In order to test this effect further, a series of experiments with different anhydrides were carried out using the procedure described in Section 4.2.3. The selectivity to isocyanate using the different anhydrides used is shown in Table 8.

Table 8. Effect of using different anhydrides as dehydrating agents on selectivity to isocyanate

Dehydrating agent	**pKa of corresponding acid**	**Selectivity to isocyanate (%)**
Trifluoroacetic anhydride	0.27	76.52
Trichloroacetic anhydride	0.7	54.47
Dichloroacetic anhydride	1.48	50.36
2-methyl-6-nitrobenzoic anhydride	2.5	20.26*
Benzoic anhydride	4.12	3.41*
Acetic anhydride	4.76	5.16

* Amount of solvent (acetone) used was twice the amount used for other anhydrides because of low solubility.

This effect can be seen more clearly in Figure 18, where the selectivity to isocyanate is plotted against the pKa of the acid corresponding to the anhydride used as the dehydrating agent. The highest selectivity obtained was with trifluoroacetic anhydride at 76.52 %. All the reactions were carried out with acetone as the solvent, at -78 °C and atmospheric pressure.

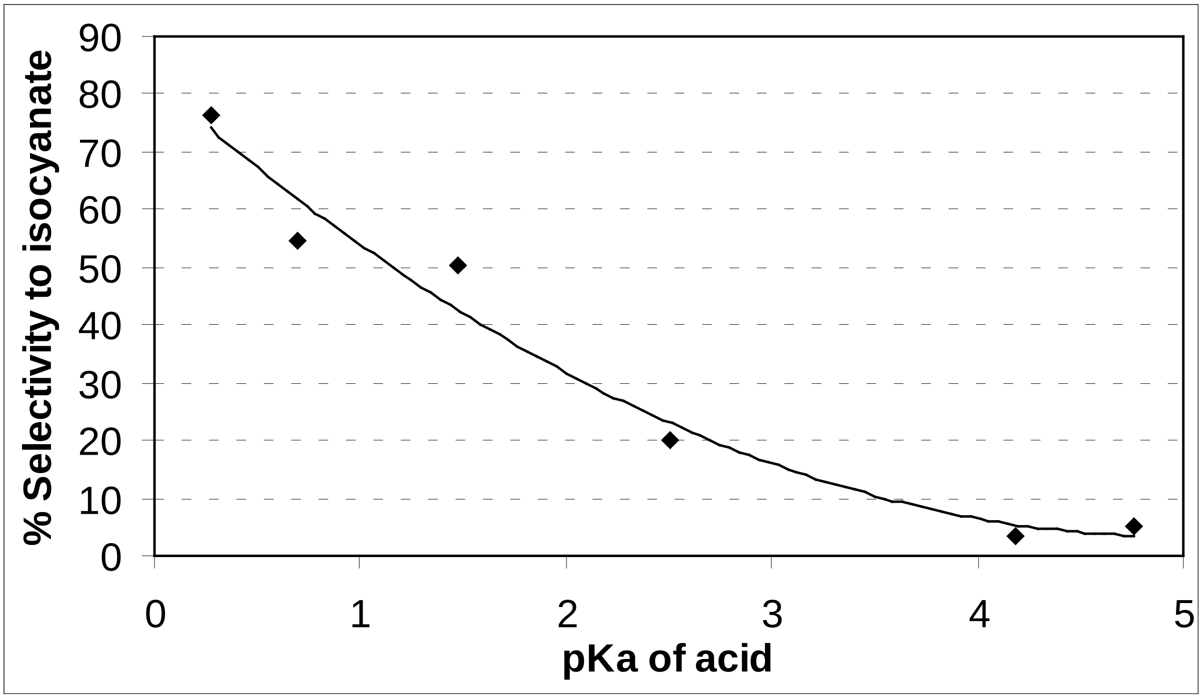


Figure 18. Percent selectivity to isocyanates as a function of the pKa of the acid of the corresponding anhydride used as the dehydrating agent

However, it is important to note that the selectivity to isocyanate is not exclusively dependent on the relative strength of the acid of the anhydride used, i.e. the electron withdrawing capability of the functional group attached to the anhydride. There are other factors such as the nature of the anhydride (linear anhydrides performed much better compared to cyclic anhydrides) and solubility of the anhydride in the solvent that also played a role. Cyclic aromatic anhydrides such as phthalic anhydride (pKa of acid - 2.89), 4-nitrophthalic anhydride (2 pKa values for the acid – 2.02 & 4.44), tetrachlorophthalic anhydride (pka of acid – 1.29) and 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) did not lead to any detectable selectivity to isocyanate. This could be attributed to the slower rate of hydrolysis of cyclic anhydrides compared to linear anhydrides. For example, the second order hydrolysis rate constant of phthalic anhydride is $6*10^{-6}$ liter/mol-sec, and the pseudo first order hydrolysis rate constant (due to excess of water used in the experiment) for acetic anhydride is $2.63*10^{-3}$ sec^{-1} [53-55].

Aromatic anhydrides with non-halogen electron withdrawing functional groups such as 2,4-dinitrobenzoic anhydride (pKa of acid – 1.43) had very low solubility in acetone or dichloromethane and almost negligible solubility at -78 °C. The experiments with these substituted benzoic anhydrides also resulted in negligible isocyanate concentration which were significantly lower compared to the trend seen in Figure 18. However, based on this trend, selectivity higher than the one obtained by using trifluoroacetic anhydride would not be expected with solvents which have higher solubility for these anhydrides. The pKa values were obtained from the work by Lian et al, Jover et al and Carlson et al who have published an extensive list of pKa values of phthalic acid and benzoic acid and their substituents [56-58].

4.3.6.2 Effect of pH of environment on conversion to isocyanate:

The higher selectivity to isocyanate by anhydrides whose acids had a low pKa value is due to the electron withdrawing potential of the functional groups or due to the acidic environment created by the low pKa acids. In order to understand the exact reason responsible for these higher conversions, a new set of experiments were conducted with addition of HCl in dioxane to make the environment acidic, and with varying contribution of acetic anhydride (AA) and trifluoroacetic anhydride (TFAA). The results are shown in Table 9.

In the presence of HCl, the conversions went down to zero implying a negative effect on efficiency of the synthesis route. The conversions obtained with varying ratios of acetic anhydride & trifluoroacetic anhydride resulted in selectivity lower than what would have been expected with only trifluoroacetic anhydride being present. Therefore, the desired effect of the presence of trifluoroacetic anhydride & acid creating a stronger acidic environment leading to higher overall selectivity was not achieved. Instead, the acetic anhydride negatively affected the selectivity by the reaction of trifluoroacetic anhydride.

Table 9. Conversion to isocyanate as a function of the acidity of the environment

Dehydrating agent	% Selectivity to isocyanate
AA + 1 ml 1M HCl in dioxane	0
AA:TFAA – 4:0	5.16
AA:TFAA – 3:1	7.22
AA:TFAA – 1:1	26.39
AA:TFAA – 1:3	33.15
AA:TFAA – 0:4	76.52

4.3.7 Effect of temperature:

As explained earlier in Section 4.3.3.3, the key strategy in the conversion of the primary amine to the corresponding isocyanate is maximizing the extent to which the process follows the zwitterion route. In order to have the maximum possible concentration of the zwitterion intermediate in the reaction medium, it is important to have CO_2 present in excess to the amine, which can be achieved at low temperatures. However, it is important to study the thermodynamic effect that low temperature has on the progress on the reaction.

4.3.7.1 Effect of temperature on formation of zwitterion intermediate

Referring to Figure 7 & 8, at lower temperature, the solubility of CO_2 in the solvent increases, increasing the extent to which CO_2 is in excess of the primary amine for a given amount of solvent. This shifts the equilibrium towards a higher concentration of zwitterion of primary amine and CO_2 compared to that of the carbamate salt. Hence, the 1st step of treating the amine with CO_2 is carried out at low temperature by adding dry ice to acetone (-78 °C) or dichloromethane (-78 °C).

At these temperatures and atmospheric pressure, primary amines spontaneously react with CO_2. The conversion of the primary amine was calculated by performing gravimetric analysis on the product mixture by bubbling CO_2 gas through the reaction mixture containing the primary amine and solvent. In order to avoid any loss of solvent due to the heat dissipated as a result of the exothermic reaction, a cold trap was attached to one of the arms of the 2-neck round bottom flask outlet and the flask was kept in a ice bath. The percent conversion was calculated using the formula given in equation 4.24.

$$\%Conversion = \frac{P}{S+A} x100 \tag{4.24}$$

Where,

S = Weight of solvent added initially to the reaction mixture

A = Theoretical weight of 25 mmol of primary amine & 25 mmol of CO_2

P = Weight of final product mixture

The conversion obtained was 100 % within the limits of experimental error, indicating complete reaction of all the primary amine present. In the presence of excess CO_2, the amine would be converted to either zwitterion or the carbamate but no amine would be left unreacted. In order to have CO_2 in large excess in the reaction mixture, the amine is added drop-wise with constant stirring. The molar excess in which CO_2 is present at reaction conditions in a given amount of solvent is given in Table 10.

Table 10. Molar ratio of CO_2 to amine in dichloromethane and acetone at -78 °C.

Solvent *	Theoretical CO_2 present	CO_2 / R-NH_2 molar ratio
Dichloromethane	6.7 g = 152 mmol	6.1
Acetone	14.7 g = 333 mmol	13.3

(*Solvent = 20 ml, n-butyl amine = 25 mmol)

4.3.7.2 Effect of temperature on dehydration of zwitterion/carbamate mix by anhydride to form isocyanate:

The effect of temperature is reflected in the excess to which CO_2 is present in a given quantity of solvent. This affects the equilibrium ratio of the zwitterion to carbamate present in the reaction mixture. Also, the dehydration of zwitterion / carbamate is an exothermic reaction and hence lower temperature results in higher conversion to isocyanate. This is because the equilibrium constant K would be higher at lower temperatures according to the Van Hoff equation similar to the exothermic reaction of amine with CO_2 as explained in section 4.3.2.1. In order to study this effect, we carried out the reaction in different cooling baths (solvent + dry ice) in two sets of experiments.

In the first set of experiments, the procedure described in Section 4.2.3 is followed for synthesis of isocyanates from primary amine, carbon dioxide and a dehydrating agent. The aim of this series of experiments was to synthesize isocyanates via the zwitterion route as much as possible instead of the carbamate route. Figure 18 describes the two competing reactions taking place in the system.

In the second set of experiments, the primary amine is completely converted to the carbamate to make sure there was no zwitterion present. This is achieved by slowly bubbling CO_2 through the primary amine. The white precipitate of the carbamate formed is then added to the solvent with constant CO_2 bubbling at a very low flowrate. A cooling bath of acetone + dry ice (for -78 °C), acetonitrile + dry ice (for -42 °C) and o-xylene + dry ice (for -22 °C) was used with acetone as the solvent in the reaction medium.

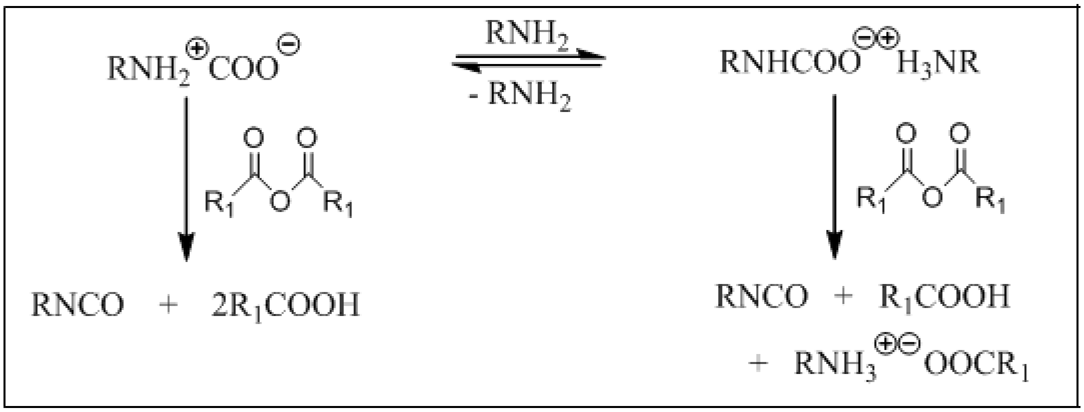
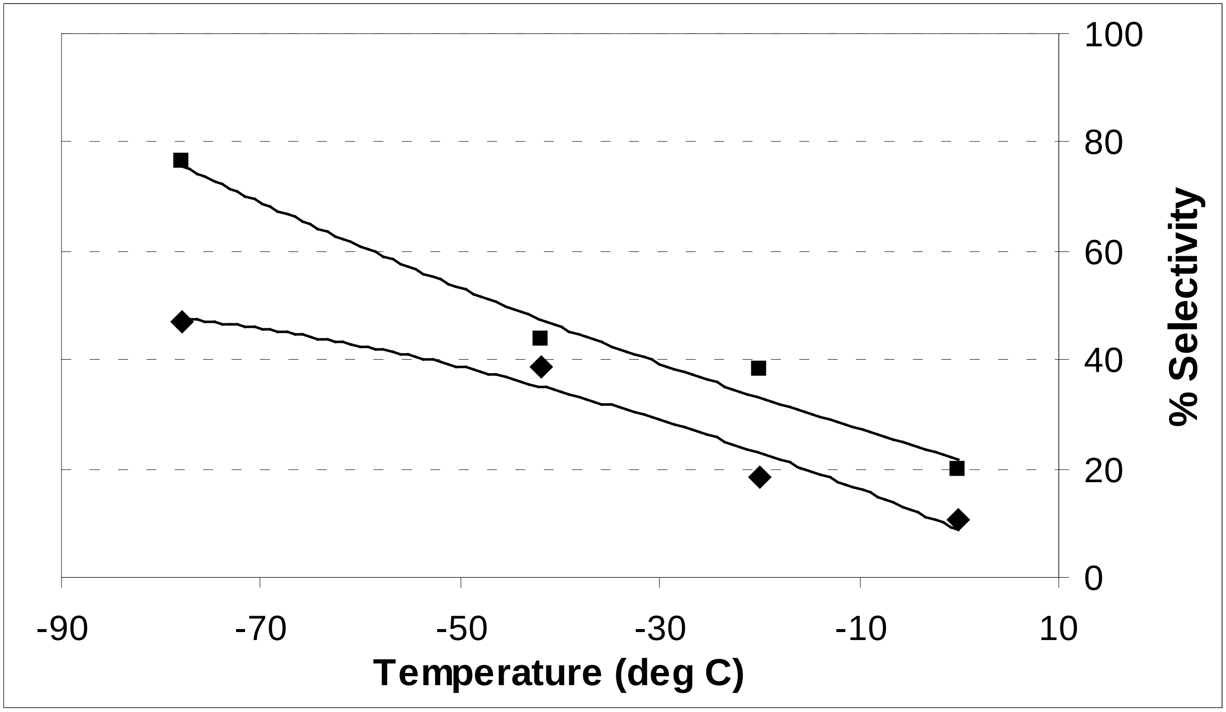


Figure 19. Competing formation of isocyanate via the zwitterion and the carbamate route

The selectivity via the zwitterion route should theoretically be twice that of the carbamate route. As seen in Figure 19, one mole of isocyanate is formed for every mole of amine via the zwitterion route. Whereas, two moles of amine are required every mole of isocyanate formed via the carbamate route. This is because the second mole of amine forms a salt complex with the acid of the anhydride used as the dehydrating agent. The selectivity to isocyanate obtained in these two series of experiment has been shown in Figure 20. The increase in the selectivity to isocyanate implies that by working at really low temperature and at excess CO_2 concentrations, the reaction does proceed via the zwitterion route. However, since the increase is not twice compared to the carbamate route, it can also be implied that there exists an equilibrium amount of carbamate present even at more than 13 times molar excess of CO_2 at the given conditions. The progress of the reaction via the carbamate route implied that though working at extremely low temperatures reduced the amount of salt formed, it was not possible to completely eliminate its formation.



Carbamate route (◆) zwitterion route (■)

Figure 20. Selectivity of isocyanate via the carbamate and the zwitterion route

4.3.8 Effect of pressure

In order to increase the selectivity further, experiments were carried out maintaining conditions favorable for the reaction to proceed via the zwitterion route. As seen in Figure 12, at a given temperature, the solubility of CO_2 in acetone increases with increasing pressure. Thus, an alternate approach to increase the amount of CO_2 dissolved in the solvent is to apply a higher pressure of CO_2 over the reaction mixture. The key to this step is to add the primary amine to the reaction mixture while it is in the pressurized state. In order to test if the formation of isocyanate could be increased further, series of experiments were carried out using the procedure outlined in

Section 4.2.4. A few changes to the procedure were employed which have been discussed further. Also, the set-up was slightly modified with the major change being the replacement of high pressure glass reactor (with a pressure limit of 175 psi) with an autoclave reactor (with a pressure limit of 2000 psi).A compressor was added to the CO_2 line to increase the pressure of CO_2 in the reactor to the desired value. These changes have been shown in Figure 21.

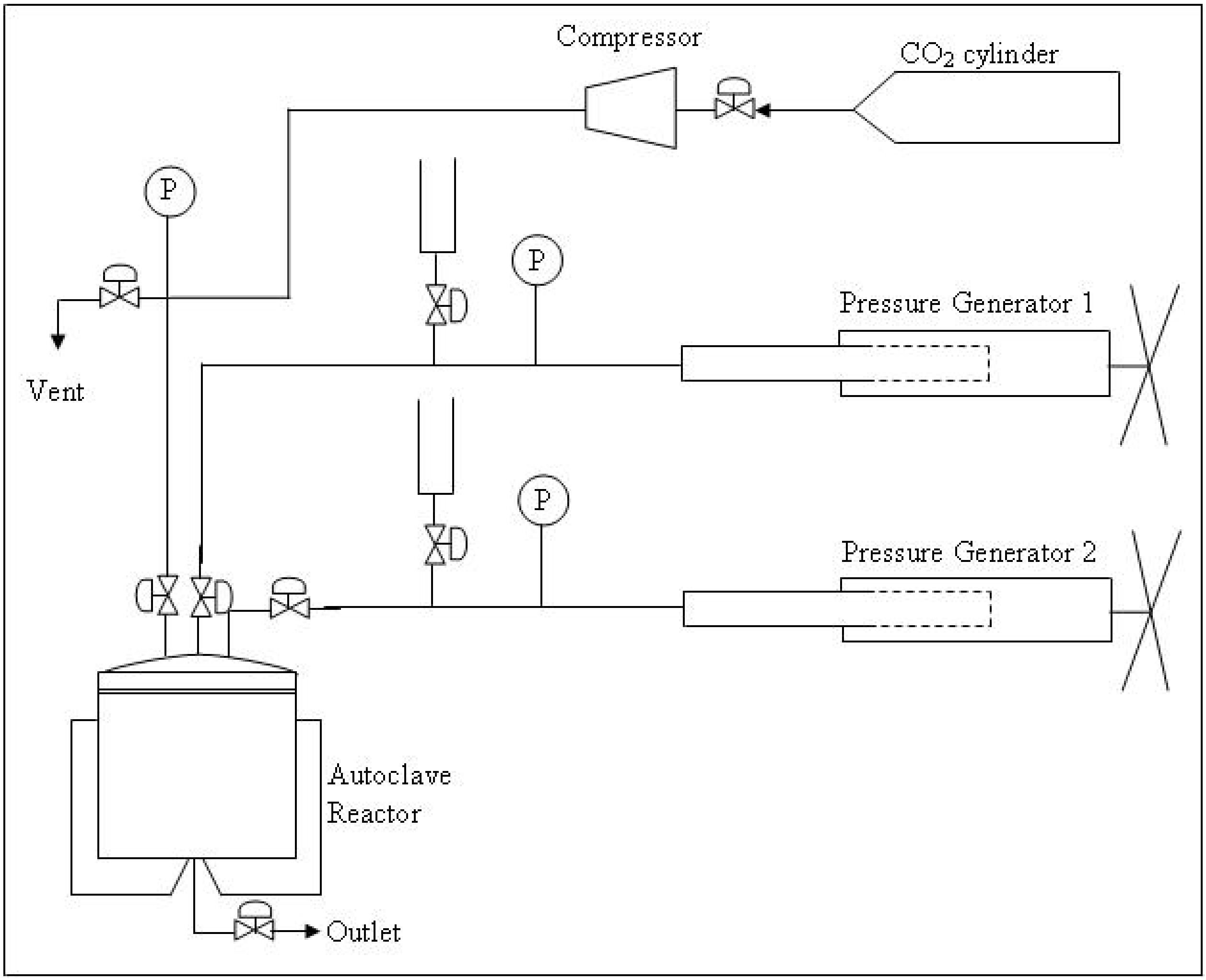


Figure 21. High pressure set-up for synthesis of isocyanate using the glass reactor for pressures up to 200 psi

The reactor is maintained at 0 °C and pressurized with CO_2 to the required pressure at which the reaction is to be studied. N-butylamine in acetone is then introduced into the reactor using a pressure generator. The dehydrating agent (trifluoroacetic anhydride) is then added using the 2nd pressure generator and the reaction is allowed to take place with constant stirring. After 5 minutes the reactor is depressurized and a sample of the reaction mixture is taken for IR analysis. The experiment is repeated for a reaction time of 12 minutes.

The progress of the reaction was studied by observing the IR spectra peak of n-butyl isocyanate (2276 cm^{-1}). The peak ratio of isocyanate peak with that of the CH_3 asymmetrical stretching peak (2968 cm-1) is reflective of the concentration of the respective components in the reaction mixture as the CH_3 peak strength remains unaffected throughout the reaction. This is because the concentration of the CH_3 species remains unchanged throughout the reaction. Figure 22 shows how the peak ratio of isocyanate varies as the reaction proceeds.

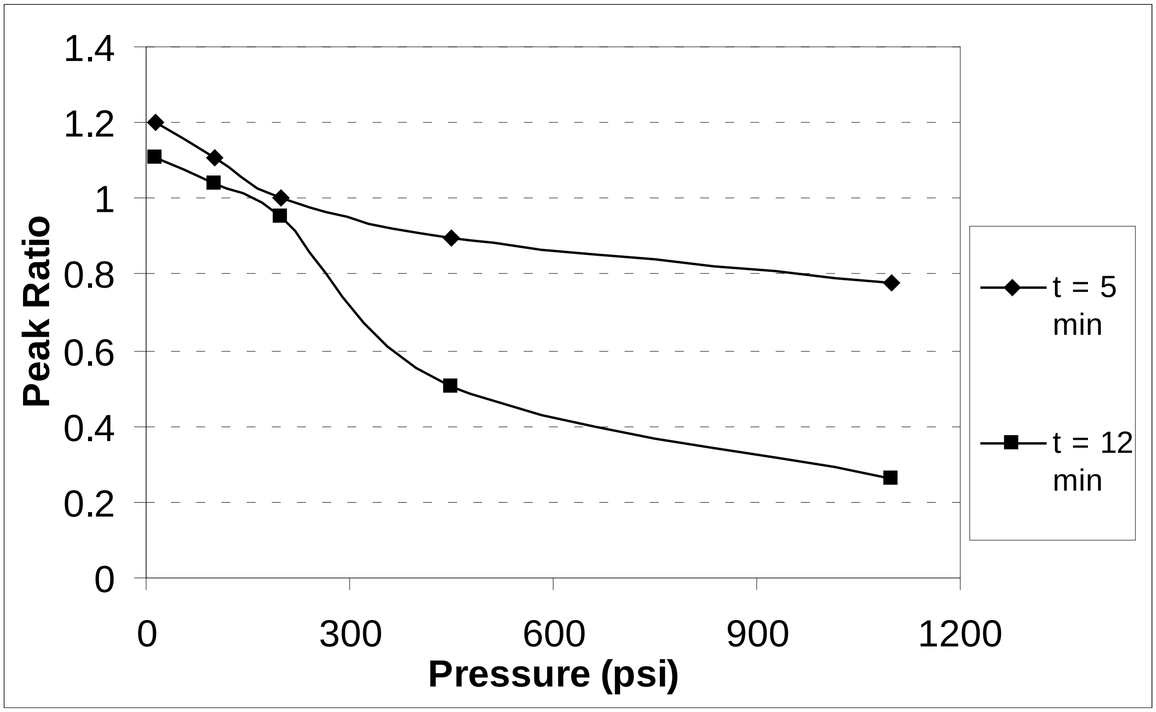


Figure 22. Effect of pressure on conversion of amine to isocyanate (reflected by peak ratio)

As seen in Figure 22, the isocyanate peak ratio reduces with pressure and is lower after 12 minutes compared to the peak after 5 minutes. This shows that the isocyanate gets used up with time due to the reaction with the carboxylic acid formed as byproduct. These results suggest that higher pressure appears to reduce the conversion of amine to isocyanate for a given time and also increase the extent to which the side reaction of the isocyanate with the carboxylic acid takes place. Thus, using higher pressure of CO_2 to increase the CO_2 dissolved in the solvent is not thermodynamically favorable for higher conversion to isocyanates.

The drop in the peak intensity of isocyanate was not significant in the moderately high pressure range (below 100 psi). This observation combined with the CO_2 solubility information from Figure 11 & 12 for low temperature and high pressure led to the next set of experiment. The procedure outlined in section 4.2.4 was followed to study the effect of pressure (0 psig to 70 psig) at -78 °C and the results are shown in Figure 23. However, the desired result of increase in selectivity to isocyanate by increasing the excess to which CO_2 is present in the system by increasing the pressure was not achieved. This can be attributed to not only the pressure effect observed in Figure 22 but also to the volume effect as shown in Figure 24.

At -78 °C, and high pressure, the solubility of CO_2 in acetone is so high that the volume of the solvent system almost increased by a factor of two due to the dissolved CO_2. This led to reduction in the concentration of the amine and hence the zwitterion present in the system, which is the limiting reactant because CO_2 was already in excess. As a result the rate at which isocyanate was formed was lower under pressure. In order to eliminate this volume effect the procedure in section 4.2.4 was slightly modified wherein, the CO_2 was allowed to equilibrate with the solvent at -78 °C and 1 atm. The pressure was increased using Argon instead of CO_2 and then the anhydride was added. Since, the solubility in acetone for Argon is negligible compared to CO_2, there was no significant increase in the volume. The isocyanate selectivity obtained is reported in Figure 23 and was found to be almost constant at moderately higher pressure. Thus the desired effect on the selectivity was not observed at higher pressure.

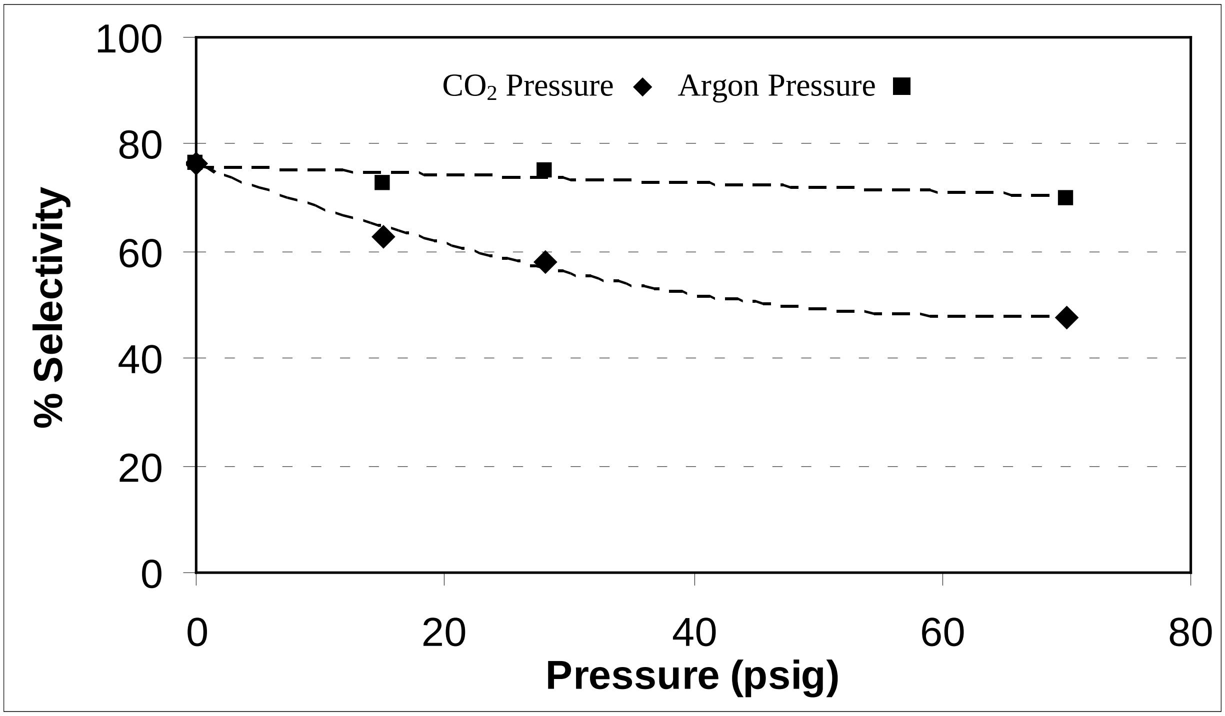


Figure 23. Selectivity to isocyanate under CO_2 pressure and under Argon pressure

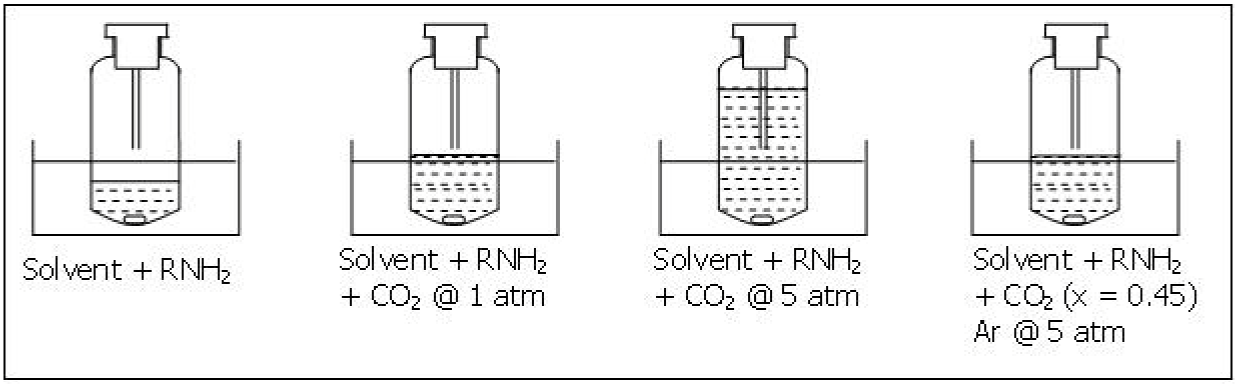


Figure 24. Volume effect due to the high solubility of CO_2 in acetone at high pressure

4.3.9 Separation of isocyanate

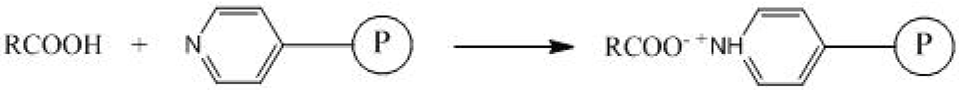
As discussed in the previous sections, the proposed low temperature route could be used to achieve satisfactory conversions to isocyanates starting from primary amines. However, separation of the isocyanate from the reaction mixture is inhibited due to the reaction of the isocyanate with the carboxylic acid formed as the by-product. Hence, it was observed that separation of n-butyl isocyanate (boiling point = 112 °C) even with vacuum distillation at 745 mm Hg vacuum did not give satisfactory yields. A residue containing a viscous mixture of the salt of n-butylamine and trifluoroacetic acid, and the amide formed by the reaction of n-butyl isocyanate and trifluoroacetic acid was left in the distillation flask.

Also, the solvents suitable for the proposed approach are low boiling compounds (Table 11). Hence, during the separation by distillation, the isocyanate is subjected to higher temperature for an extended time before the trifluoroacetic acid is separated.

Table 11. Boiling point of components present in reaction mixture

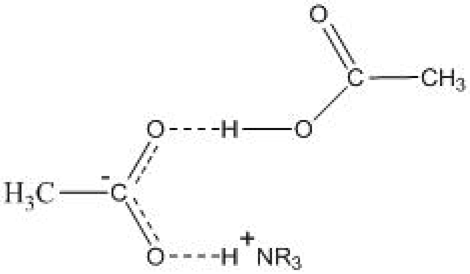
Compound	Boiling Pt (°C)
Dichloromethane	39
Trifluoroacetic anhydride	40
Acetone	56.5
Trifluoroacetic acid	72.4
Butyl isocyanate	118

Since the conventional methods for separation of isocyanate could not be used in the proposed process, the possibility of extraction of the trifluoroacetic acid at low temperature by a weak base and then distillation of the isocyanate from the reaction mixture was explored. Long-chain, aliphatic amines have been shown to be effective extractants for separation of carboxylic acids [59]. However, as shown in section 4.3.2.4, addition of an amine with reactive hydrogen will result in its reaction with the acid present as well as the isocyanate. Hence a polymer supported tertiary amine which is a weak base could be a suitable extractant for this process.



(4.25)

It has been reported earlier that a variety of carboxylic acids and aliphatic amines in various solvents behave in such a way that the first acid interacts directly with the amine to form an ion pair and the OH of the carboxyl of the second acid forms a hydrogen bond with the conjugated CO group of the carboxylate of the first acid as shown below [60].



Increasing acidity results in higher secondary loading of the carboxylic acid on the amine, hence for an extremely strong acid like trifluoroacetic acid, we might expect more than stoichiometric loading of acid over the base used for extraction [61]. The literature suggests that tertiary amines can act as effective adsorbents for organic acids [61-63]. Baniel et al had suggested that “diluent-swing extraction” can be an efficient strategy for extraction of carboxylic acids & their recovery using another solvent with higher affinity for the acids [64]. Based on the literature data available, polyvinyl pyridine (PVP) was chosen as the adsorbent for the extraction of TFA from acetone and methanol was used to recover the acid using the diluent swing strategy.

Preliminary studies were conducted to observe the adsorption of TFA on PVP wherein, a given quantity of dried PVP resin was added to a solution of TFA in acetone with constant stirring. The experiments were repeated with two different concentrations of TFA in acetone. The infrared spectra peak of the (-COOH) group was observed with time. As seen in Figure 25, the reduction in the peak intensity was observed with time indicating that the acid in the solution was getting adsorbed onto the resin matrix.

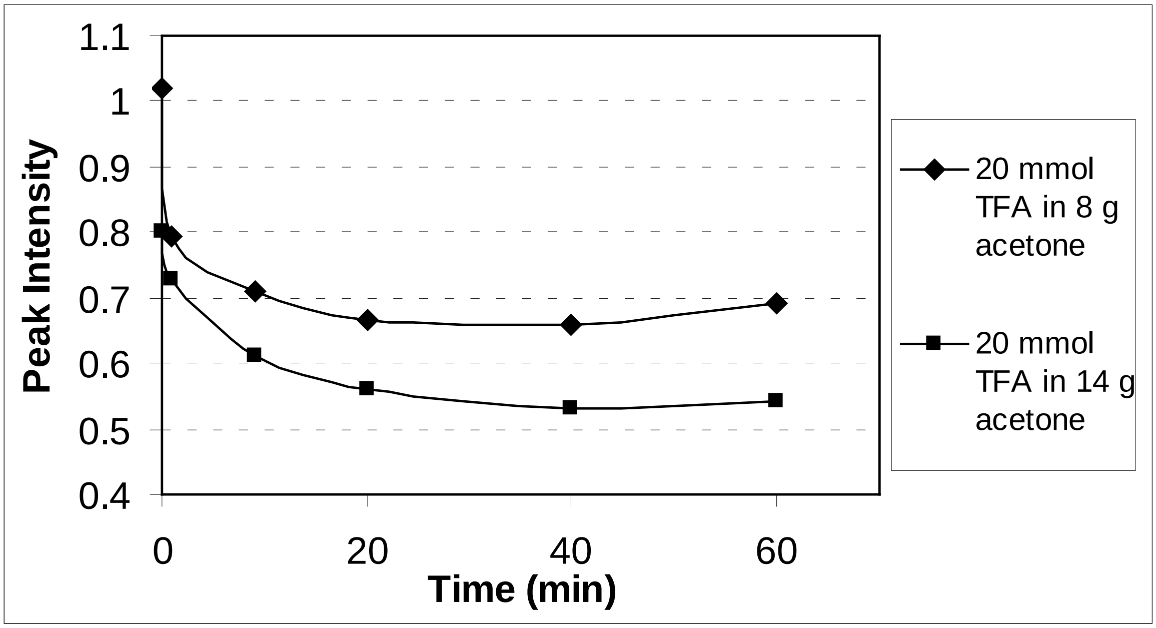


Figure 25. Change in the (-COOH) peak intensity in the infrared spectra due to adsorption of the acid on polyvinyl pyridine resin.

In order to quantify the extraction capacity of PVP for TFA, further experiments were carried out as described in Section 4.2.5. The adsorption of TFA on PVP and then its recovery using methanol was repeated in cycles on the same sample of PVP. This was done to check if this strategy can be used in a recyclable manner and whether it can be an effective TFA recovery option on a commercial scale. The repeated adsorption and desorption cycles have been shown in Figure 26. The total adsorption capacity of the PVP is more than 100 % which can be attributed to the H-bonding effect discussed earlier in this section.

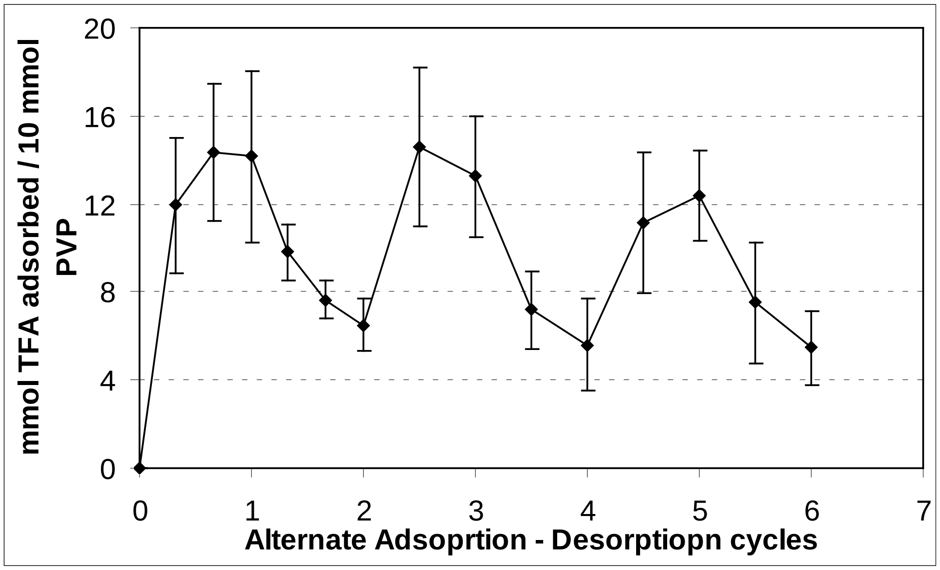


Figure 26. Adsorption – Desorption cycles of trifluoroacetic acid over polyvinyl pyridine

The recovery of TFA using methanol is shown in Figure 27. Since, recovery of TFA from the PVP resin decreases only marginally this strategy can be used in a cyclic manner for removal of TFA. The average capacity, defined as the amount of TFA extracted by PVP & subsequently recovered by methanol, was found to be 0.747 mol TFA/mol PVP over these cycles.

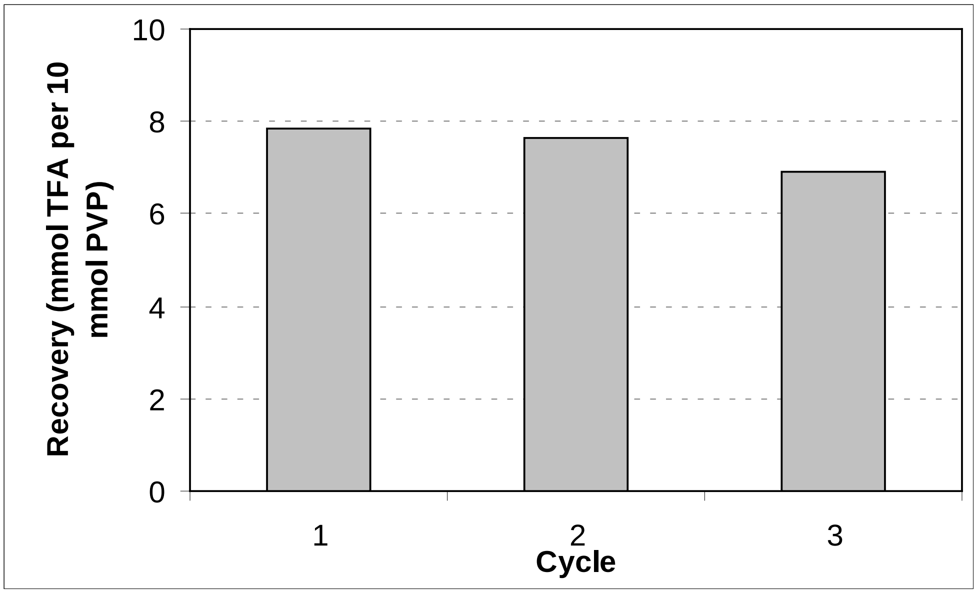


Figure 27. Recovery of trifluoroacetic acid in each cycle

The trifluoroacetic acid recovered by methanol can then be separated by conventional distillation. Lin et al has described a process to obtained trifluoroacetic anhydride by reactive distillation of trifluoroacetic acid with acetic anhydride [65]. Also, the salt of the acid and amine formed as the by-product in the main reaction can be recycled by exposing the salt to temperatures at which the salt dissociates to liberate the acid. DeVries et al has shown that salts of protic acids with weak bases can be dissociated to their constituent acid and bases on prolonged exposure to high temperature [66].

4.3.9.1 Effect of using PVP as an extractant for TFA on the conversion to isocyanate

If the trifluoroacetic acid formed as the by-product is continuously removed from the product mixture using polyvinyl pyridine, then as per the Le Chatelier's principle, the equilibrium would shift towards the product resulting in higher conversion to isocyanate. However, the presence of PVP in the reaction mixture would result in its reaction with the zwitterion to form the carbamate, forcing the reaction to proceed via the undesirable carbamate route. Hence, the PVP is added to the reaction mixture at the end of the reaction.

A series of experiments are carried our using the procedure described in section 4.2.4. The reaction is allowed to proceed for ca. 12 minute after the addition of trifluoroacetic anhydride and 50 mmol of PVP is subsequently added to the reaction mixture. The average selectivity to isocyanate when PVP was not added is 73.48%, 75.09% when PVP is left in the product mix for 5 minute and 72.88% PVP is left for 15 minute in different set of experiments. Within the limits of experimental error, no significant increase in the conversion to isocyanate was observed by addition of PVP. This implies that the reaction between zwitterion and trifluoroacetic acid would have gone to its completion and there would be no unreacted zwitterion present. Also, any TFA that is not extracted by PVP if allowed to stay in the system for a long time can potentially react with the isocyanate to form an amide as described in section 4.3.2.4.

4.4 SUMMARY

Based on the various experiments that were carried out to understand the synthesis of isocyanate from a primary amine, carbon dioxide and a dehydrating agent, it can be concluded that the ideal conditions for this reaction contingent on separation are given in Table 12,

Table 12. Ideal conditions for the novel non-phosgene route (contingent on separation)

Temperature	-78 °C
Pressure	Atmospheric
Solvent	Acetone
Reaction time	12 minute. (formation of zwitterion) 5-15 minute, preferably 12 minute (formation of isocyanate)
Dehydrating agent	Trifluoroacetic anhydride

Carrying out the reaction at low temperatures helped increase the excess to which the carbon dioxide was present in the system compared to the amine present. This resulted in significantly higher selectivity (76.52 %) to isocyanate as majority of the isocyanate was formed via the zwitterion route instead of the carbamate route. Also, using an anhydride with a strongly electron withdrawing group as the dehydrating agent gave higher selectivity to the isocyanate. An inverse relationship between the selectivity to isocyanate and the pKa of the acid of the anhydride used was established. The acid of the anhydride used as the dehydrating agent is formed as a by-product and can be extracted using a weak supported base such as polyvinyl pyridine. A brief overview of the schematic of the novel process compared to the conventional phosgene process is shown in Figure 28.

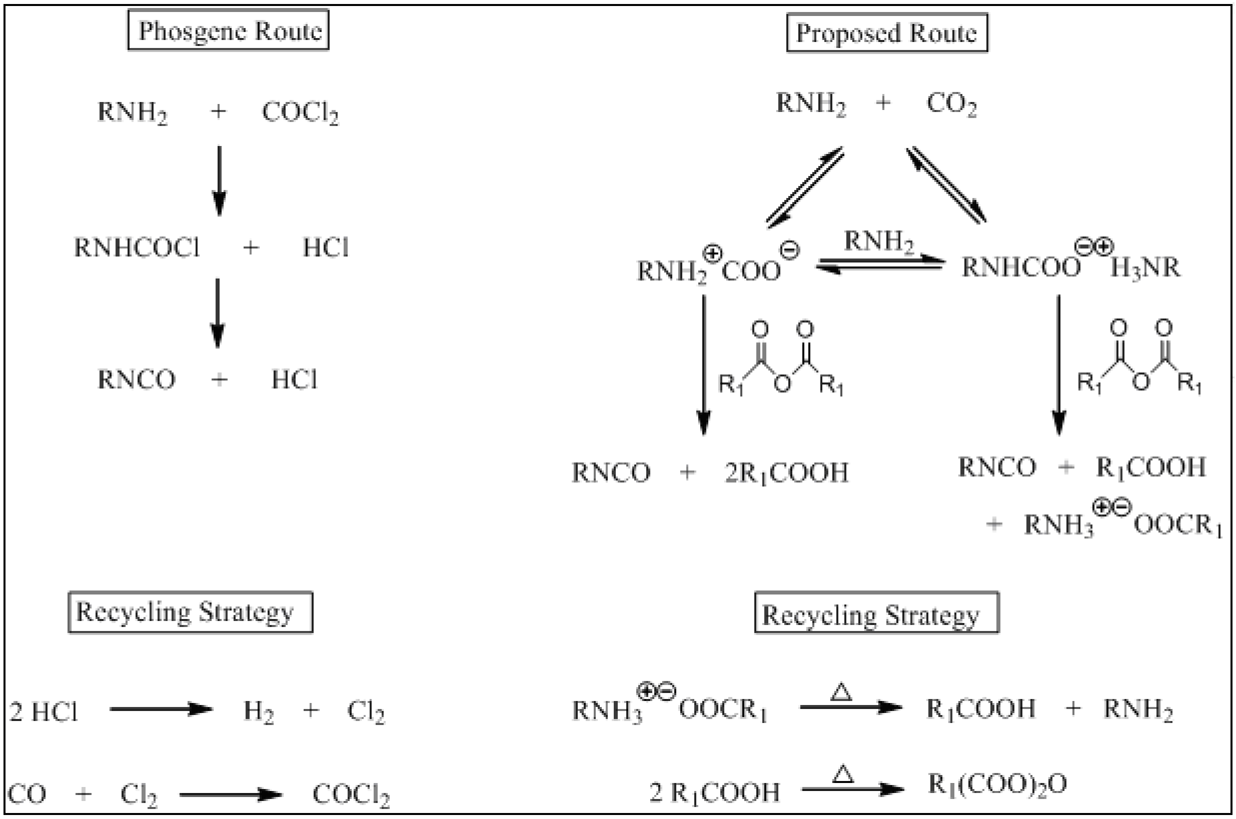


Figure 28. Brief overview of the traditional phosgene route and the novel non-phosgene route

In order to evaluate the technical feasibility of the novel non-phosgene route for manufacture of isocyanates, a detailed design of a commercial plant is simulated using Aspen Plus (process simulator) in Chapter 5. This study is performed to study the hot-spots for the energy consumption in a plant via phosgenation route and the novel route and compare the two routes for their energy consumption.

5.0 PROCESS SIMULATION OF THE PHOSGENE AND NON-PHOSGENE ROUTE FOR MANUFACTURE OF ISOCYANATES

Most of the non-phosgene routes for manufacture of isocyanates that have been described in section 2.2 have been claimed to be “greener” alternatives to the phosgenation route on the premise that they avoid the use of phosgene. However, it is important to note that avoiding the use of toxic chemicals and minimizing the potential for chemical accidents are only two of the twelve principles of green chemistry detailed in Table 2. When designing an alternate process, it is important to consider other factors such as atom economy, use of renewable sources of material, efficient recycle of chemicals used in the process, energy consumption etc. Prior approaches to alternatives to the phosgenation processes have only focused on higher yields at the lab scale but have not looked at these other factors in detail.

In an attempt to provide a holistic approach to green process design, this research study has incorporated an analysis to study the feasibility of the novel non-phosgene route at an industrial scale as discussed in section 4. In order to make any claims on the “greenness” of this route, it is important to compare it with the phosgenation route for the other factors mentioned earlier. It is important to provide a quantitative analysis for this comparison and not just subjectively discuss the advantages and disadvantages of these two routes.

“*When you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in* *numbers, your knowledge is of a meager and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science.*" This famous quote by Lord Kelvin (1824-1907) clearly stated the importance in using numbers in scientific studies.

This is also true in the field of green chemistry since whenever you talk about a green technology, the following question will be raised naturally: "So you think your process (or product) is green, how do you know?" [67] Quantitative comparison should be used as a tool to address this question. Given these issues surrounding the uncertainty in claiming a process to be "green", the energy requirements of the process at different operating conditions for the non-phosgene route are compared with the traditional phosgenation route by simulating a plant for isocyanate manufacture using Aspen Plus software.

Aspen Plus is a process simulation software which gives a model-based representation of the performance of various chemical processes. It predicts the behavior of chemical reactions using standard engineering relationships, such as mass and energy balances, rate correlations, as well as phase and chemical equilibrium data. By choosing the appropriate unit operations, thermodynamic models, reliable thermodynamic data and realistic operating conditions, Aspen Plus uses mathematical models to predict the performance of the cycle and actual plant behavior [68]. Aspen Plus contains data, properties, unit operation models, built-in defaults, reports and other features and capabilities developed for specific industrial applications. Using Aspen Plus, a successful simulation can be carried out by performing the following steps.

- Selecting and defining unit operation models for the simulation and placing them onto the flowsheet. This includes labeling the unit blocks from the Aspen Plus library, including user defined blocks.

- Linking the unit operations together using labeled streams. All material and energy streams must be identified, including the input and output streams.
- Specifying the global setup. This includes units of measurement, run type, input, mode, flow conditions, and so forth.
- Specifying all components that are involved in the process. This can be performed from the Aspen Plus component database, and non-database components.
- Specifying thermodynamic models for all unit blocks to represent the physical properties of the components and mixtures in the process, including properties that are not given in the Aspen Plus database.
- Specifying flow rate and thermodynamic conditions of all feed streams.
- Specifying the operating conditions of all unit operations.
- Performing the simulation; normal, automatic, troubleshooting, or on-demand case.
- Performing model analyses, flowsheet options and sensitivity analyses.

The process synthesis procedure decomposes the design problem into a hierarchy of decisions, as follows [69]:

Level 1: Batch vs. Continuous
Level 2: Input-Output Structure of the Flow Sheet
Level 3: Recycle Structure of the Flow Sheet and Reactor Considerations
Level 4: Separation System Specification
    Level 4a: Vapor recovery system
    Level 4b: Liquid recovery system
Level 5: Heat Exchanger Network

The complete process is always considered at each decision level, but additional fine structure is added to the flow sheet as we proceed to the later decision levels. As per the guidelines set by Douglas for process synthesis, the input information required to develop a process flow sheet and a base-case design is [69]:

A. Reactions
  1. The stoichiometry, temperature, and pressure of each reaction.
  2. A correlation of product distribution vs. conversion (and temperature).
  3. The catalyst for each reaction.
  4. The desired phase condition of each reaction step.

B. Products
  1. Desired production rate and product purity.
  2. Product price or price vs. purity.
  3. Value of all byproducts as chemicals or fuel.

C. Raw materials
  1. Composition, temperature and pressure of all raw materials.
  2. Prices of all raw material streams, or price vs. purity.

D. Constraints
  1. Explosive limits and safety considerations.
  2. Coking limits, polymerization or decomposition limits, etc.

E. Plant and site data
  1. Utilities-fuel, steam levels, cooling water, refrigeration.
  2. Waste disposal facilities and costs.

These guidelines were followed to simulate the performance of a plant for manufacture of isocyanate by the traditional phosgenation route and the novel non-phosgene route. Maximum possible information regarding part A (reactions), B (products), C (raw material), E (utilities) was obtained for these process. However, part D (constraints) has not been taken into consideration for the design of the process simulations due to the lack of availability of the data required to specify these constraints for some of the components. The details of these simulated models and the operating conditions are discussed in section 5.1 and 5.2.

5.1 ISOCYANATE MANUFACTURE VIA PHOSGENATION ROUTE

The manufacture of isocyanate via the phosgenation route described in section 1 was divided into four parts for ease of analysis of the results and to determine any hot-spots for energy consumption in the process. These four parts and the various references used to simulate them were –

1. Isocyanate manufacturing unit [70-77].
2. Distillation columns for separation of products [77-82].
3. Recovery of chlorine from hydrogen chloride [7, 83-87].
4. Manufacture of phosgene from recycled chlorine [17, 88-90].

These units have been simulated based on prior literature data and best possible engineering judgment. A brief schematic of the entire plant is given in Figure 29.

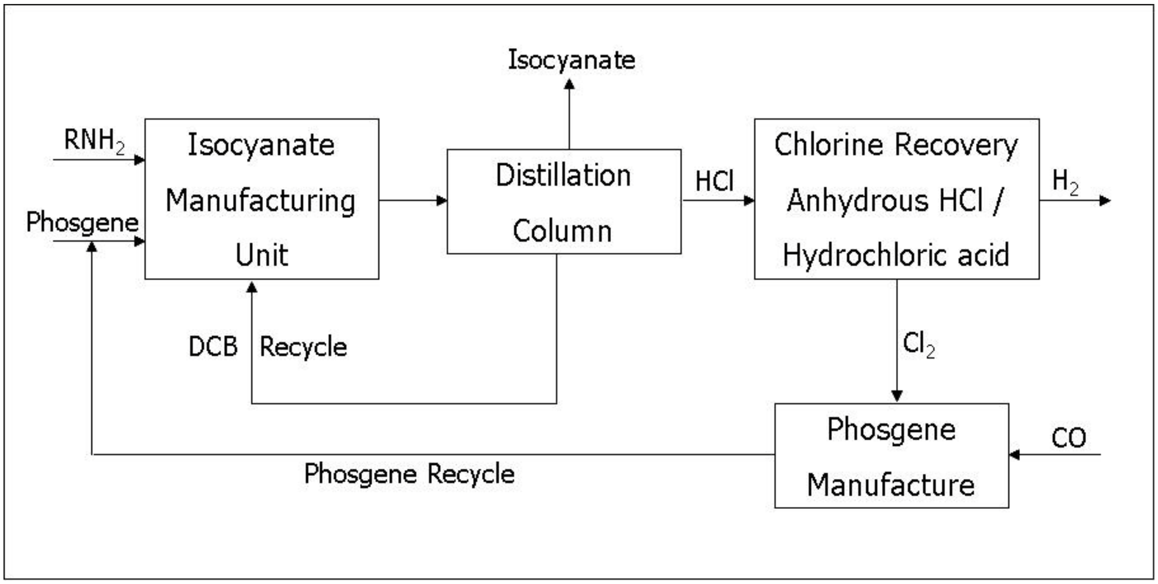


Figure 29. Schematic representation of isocyanate manufacturing plant via phosgenation route

5.1.1 Isocyanate manufacturing unit

As described in section 1.0, the manufacture of isocyanate via the phosgenation route involves reaction of a primary amine with chlorine in two steps; formation of the carbamoyl chloride and then its dissociation to an isocyanate and hydrogen chloride. The solvent used in this process is o-dichlorobenzene. The process flow diagram for this section of the plant is shown in Figure 30.

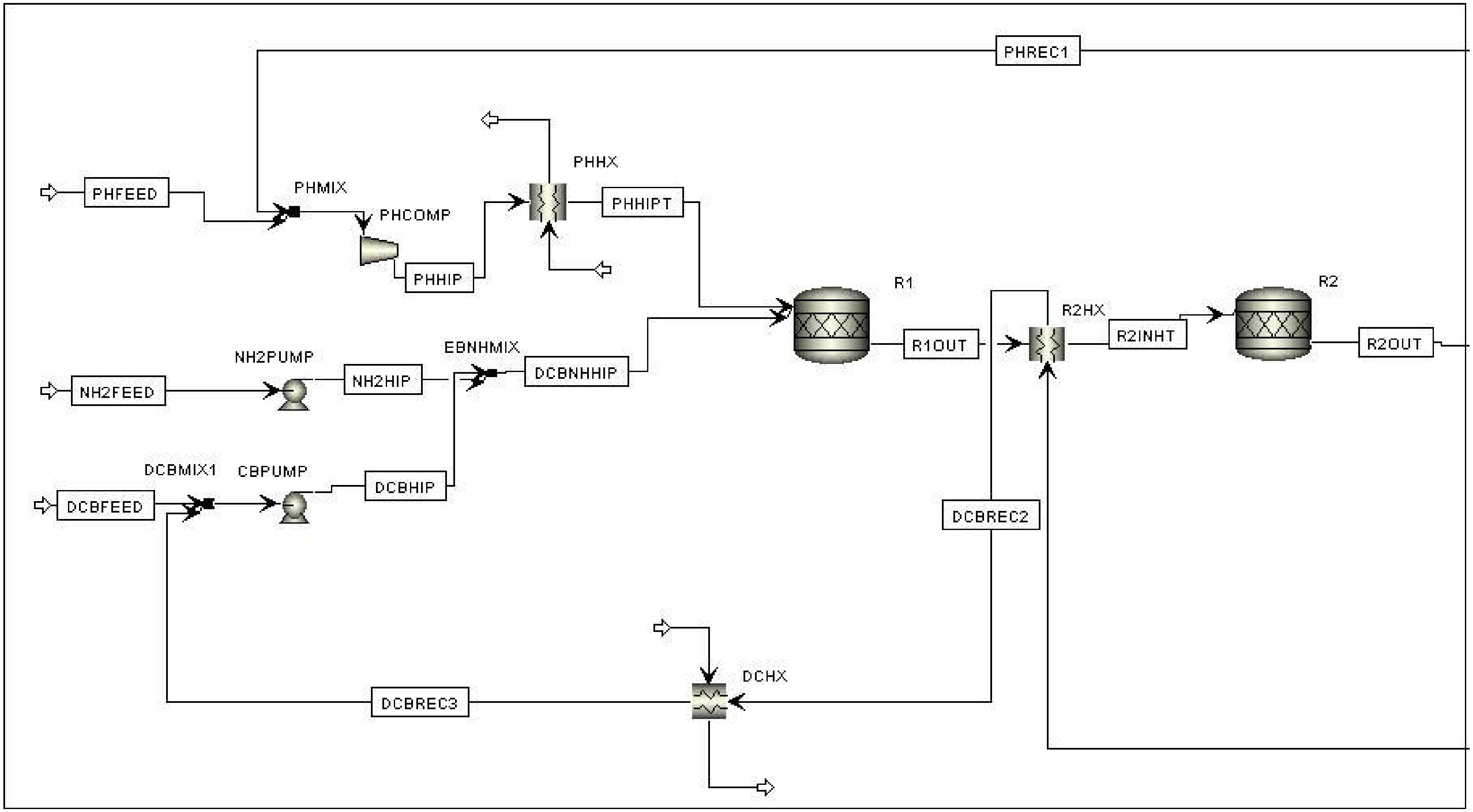


Figure 30. Process flow diagram for the isocyanate manufacturing unit (phosgenation route)

The main components that were included to simulate this process were the reactors, pumps, compressors and heat exchangers. The pumps (EBPUMP & NH2PUMP) are designed to increase the pressure of the n-butylamine and dichlorobenzene to 30 psig, which is the pressure at which the main reactions are carried out. Compressor (PHCOMP) is designed to increase the pressure of the gaseous phosgene (fresh + recycled) to 30 psig. Heat exchanger (PHHX) raises the temperature of the phosgene stream (PHHIPT) to 90 °C which is the temperature at which reactor (R1) operates. The heat exchanger that reduces the temperature of the recycled dichlorobenzene stream (DCBREC3) is designed such that the temperature of the combined stream of amine and solvent is at 90 °C. The “Design Spec” tool in Aspen is used for this heat exchanger design.

The first step in the synthesis of isocyanate takes place in the reactor (R1) operates at 90 °C and 30 psig. The product stream of R1 goes through the heat exchanger (R2HX) where it gains heat from the dichlorobenzene recycle stream, which raises its temperature to 145 °C. The dissociation of the carbamoyl chloride takes place in reactor (R2) at 145 °C with 91.5 % conversion of the amine to isocyanate. The rest of the amine is converted to n-butyl formamide by-product. Since, n-butyl formamide was not available in the component database in Aspen and the its thermodynamic properties required to add it the database were not available, it was replaced with tert-butylformamide to be used as a surrogate for the analysis. Tert-butylformamide was chosen because it had physical properties similar to that of n-butyl formamide.

The input parameters for the various units in the manufacture section are outlined in Table 13. The stream tables with the stream flow and conditions for this section are given in Appendix B1.

Table 13. Input parameters for equipments in the isocyanate manufacturing unit

Block	Type	Input Considerations
NH2PUMP	Pump	Discharge Pressure – 30 psig
CBPUMP	Pump	Discharge Pressure – 30 psig
PHCOMP	Compressor – Positive displacement	Discharge Pressure – 30 psig
PHHX	Multi-stream heat exchanger	Cold stream (PHHIPT) outlet temperature – 90 °C
DCBHX	Multi-stream heat exchanger	Hot stream (DCBREC3) outlet temperature – 106.6 °C
R2HX	Multi-stream heat exchanger	Cold stream (R2INHT) outlet temperature – 145 °C
R1	Stoichiometric Reactor	Temperature – 90 °C, Pressure – 30 psig Butylamine to carbamoyl chloride (91.5 % conv.) Butylamine to tert-butyl formamide (8.5 % conv)
R2	Stoichiometric Reactor	Temperature – 145 °C, Pressure – 30 psig Carbamoyl chloride to butyl isocyanate (100 % conv.)

5.1.2 Distillation columns

Distillation columns allow for final products to be isolated and purified. Column size and operating conditions also play a large role in the economic feasibility of a plant. Therefore, column sequencing becomes an integral part of plant design with respect to product quality and long-term economic viability. The crucial significance of column sequencing has led the chemical industry to adopt general guidelines for separation sequencing known as column heuristics. One such set of guidelines is given in Table 14.

Table 14. Distillation column sequencing guidelines

1. Remove corrosive materials early	Less expensive material for column construction
2. Remove reactive components or monomers quickly	Prevents reactions or polymerization of products
3. Remove final products as distillates	Avoids bottoms or waste in products
4. Remove recycle streams as distillates, particularly if they are recycled to a packed column	Avoids bottoms or waste in recycle
5. Remove more plentiful components first	Allows for smaller, less expensive columns
6. Remove the lightest components first, if an extremely volatile component is present	Easy separation performed before difficult separations
7. Perform difficult separations last	Easier to tightly control temperature and pressure in smaller columns
8. Obtain the recycle stream early	Reduces flow rate through columns and overall column size and energy cost
9. Minimize the number of vacuum columns	Less expensive to run at atmospheric pressure

If heuristics are followed properly, columns can be made with less material to reduce cost, the products can be separated with minimum impurities and further reactions to undesirable products can be eliminated.

Based on these guidelines, a series of five distillation columns were used to separate out the isocyanate formed as a product and recycle the unreacted phosgene and the solvent back to the manufacturing unit. The process flow diagram for this section of the plant is shown in Figure 31. The primary distillation column (PRIDC) separates the volatile phosgene and hydrogen chloride as the distillate stream and butyl isocyanate, dichlorobenzene (DCB) and heavies (amide) form the bottom products. The distillate stream (PHHCLLP) is sent to the next distillation column (PHHCLDC) where the separated hydrogen chloride at the distillate goes to the chlorine recovery unit. Phosgene collected at the bottom of this distillation column is sent back as a recycle stream to the manufacturing unit.

The bottom stream (ISODCH) from the primary distillation column, goes to a secondary column where the isocyanate is recovered as a product as the distillate and the solvent and heavies form the bottom product. The isocyanate stream (ISOHT) is sent to a heat exchanger (HXPI) to be cooled down to its storage temperature (21 °C). The mass fraction of the solvent is much higher than that of the heavies in stream DCBH1. In order to avoid drying up of the column at the bottom, solvent and heavies are separated in a series of two distillation columns (DCBDC1 & DCBDC2) so that similar flows in the distillate and bottom streams are maintained. The operating conditions and design parameters for these distillation columns are given in Table 15 & 16.

The stream tables with the stream flow and conditions for this section are given in Appendix B2.

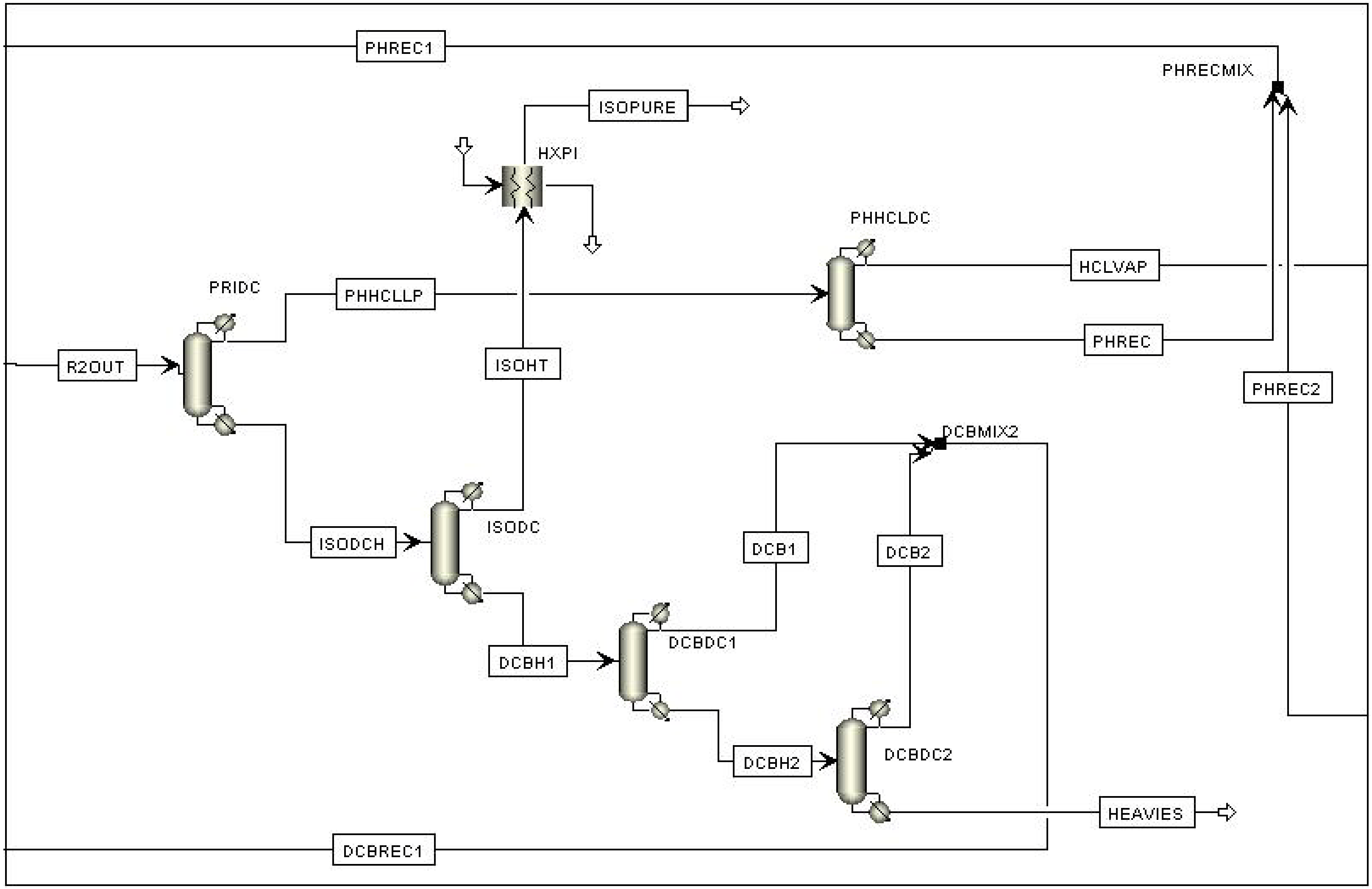


Figure 31. Process flow diagram for distillation columns (phosgene route)

Table 15. Design parameters for distillation columns (phosgene route)

Unit	Feed Stream	Distillate	Bottom	Specified Light Component	Specified Light Recovery	Specified Heavy Component	Heavy Recovery	Pressure
PRIDC	R2OUT	PHHCLLP	ISODCH	Phosgene	0.999	But-NCO	0.001	0.5 atm
PHHCLDC	PHHCLLP	HCLVAP	PHREC	HCl	0.99	Phosgene	0.01	2 atm
ISODC	ISODCH	ISOHT	DCBH1	But-NCO	0.999	DCB	0.001	1 atm
DCBDC1	DCBH1	DCB1	DCBH2	DCB	0.8	Heavies	0.1	1 atm
DCBDC2	DCBH2	DCB2	HEAVIES	DCB	0.99	Heavies	0.1	1 atm

Table 16. Operating conditions for distillation columns (phosgene route)

Unit	Recycle ratio	Stages	Feed stage
PRIDC	1.533	7	4
PHHCLDC	0.558	5	4
ISODC	1.658	16	9
DCBDC1	1.049	11	6
DCBDC2	1.760	23	8

5.1.3 Chlorine recovery unit

As discuss in section 1.0, the standard recycling strategy to treat the hydrogen chloride that is formed as a by-product is to convert it to hydrogen and chlorine via electrolysis. For the analysis of this chlorine recovery unit, the two scenarios studied are –

1. Electrolysis of hydrochloric acid
2. Electrolysis of anhydrous hydrogen chloride

The disadvantage with electrolysis of hydrochloric acid is that it needs to be carried out at an elevated temperature (80 °C) and requires an additional unit for absorption of the hydrogen chloride gas into water. Also, the energy requirement in the electrolytic cell for electrolysis of hydrochloric acid is about 17.5% more than that required for anhydrous electrolysis. The disadvantage with anhydrous electrolysis is that additional oxygen is required to make the conversion of HCl to chlorine and hydrogen thermodynamically favorable. Also, the hydrogen formed reacts with the oxygen and hence cannot be used as a source of energy. In order to study these effects on the total energy consumption both these cases were simulated.

In both the cases, the hydrogen chloride vapors obtained from the distillation columns unit are mildly contaminated with phosgene. These vapors are sent through a carbon filter (CFILTER) to remove any phosgene present in the stream and recover pure hydrogen chloride vapors. For the hydrochloric acid electrolysis, these vapors are then contacted with water at 65 °C in an absorber (HCLABS) to make hydrochloric acid with 22 wt % concentration (HCL22). The hydrochloric acid is fed to the electrolytic cell (ELECTRO1 & ELECTRO2). Since, Aspen library does not have a default model for an electrolytic cell, a combination of a stoichiometric reactor (ELECTRO1) and a separator (ELECTRO2) is used to mimic the electrolysis process.

The concentration of the hydrochloric acid reduces to 17 wt % and its temperature goes up to 80 °C as a result of the electrolysis. The separator represents the separation at the anode (CL2IN), cathode (H2) and the remaining electrolyte (HCL17). The remaining acid which is at a higher temperature goes through a heat exchanger (WTHX) to reduce its temperature to 65 °C before being sent back to the absorber as a recycle. The process flow diagram for this section of the plant is shown in Figure 32.

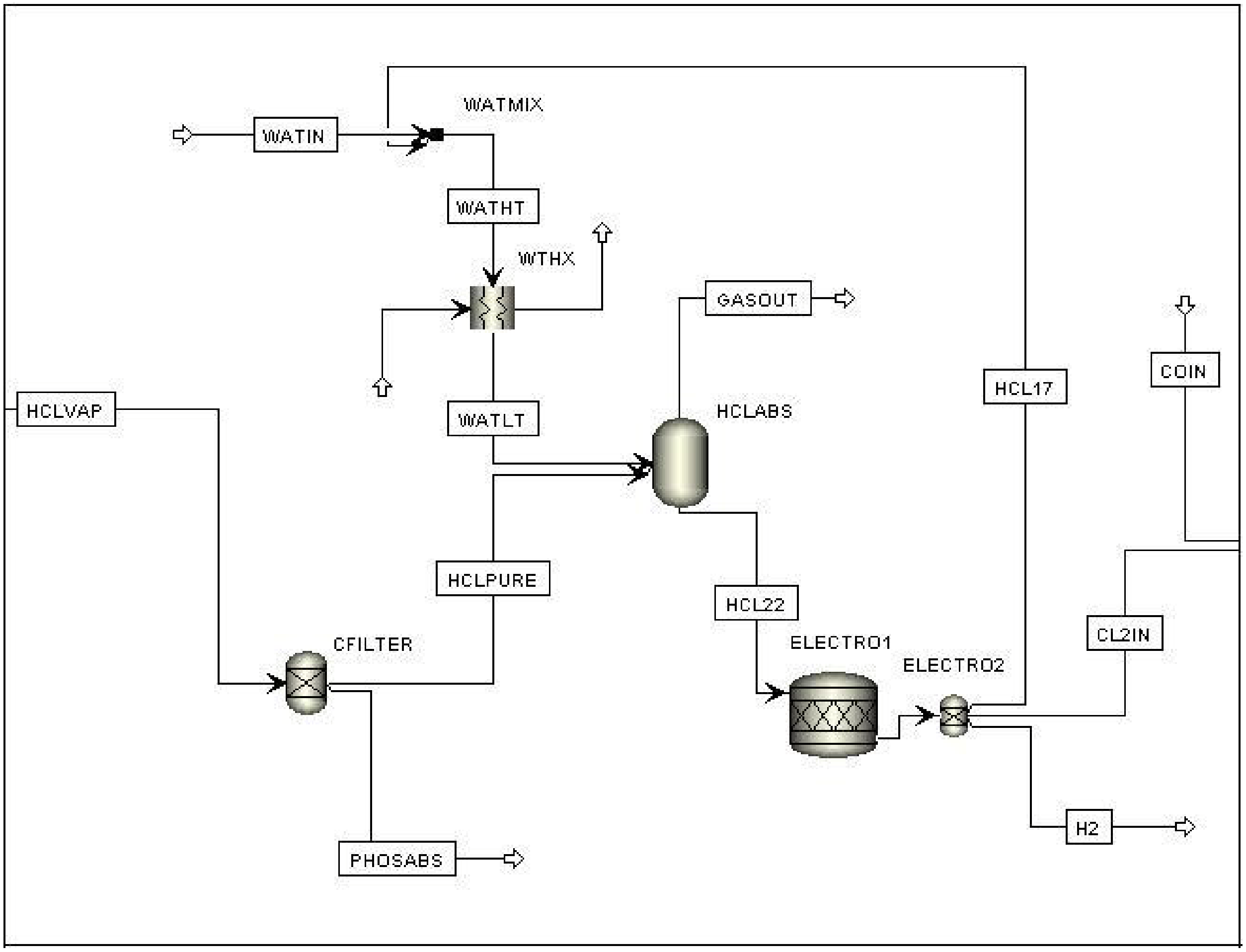


Figure 32. Process flow diagram for chlorine recovery unit from hydrochloric acid

For the electrolysis of anhydrous hydrogen chloride, the HCl vapors are sent directly to the electrolytic cell along with an oxygen stream (O2IN). There is no need for an absorber and a heat exchanger in this case. The process flow diagram is shown in Figure 33. The stream tables with the stream flow and conditions for this section are given in Appendix B3 (hydrochloric acid electrolysis) and B4 (anhydrous hydrogen chloride electrolysis).

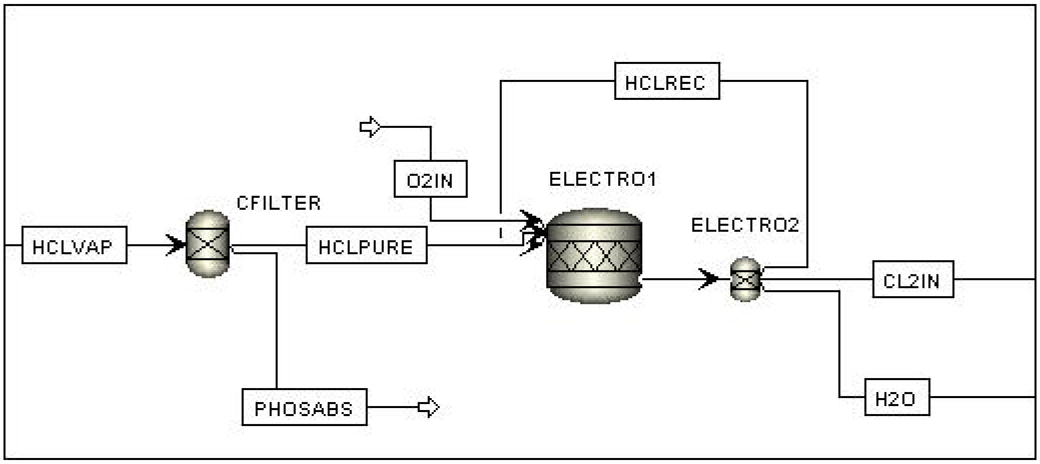


Figure 33. Process flow diagram for chlorine recovery unit from anhydrous hydrogen chloride

5.1.4 Phosgene manufacturing unit

Phosgene is manufactured by passage of carbon monoxide and chlorine over activated carbon. This reaction is highly exothermic and carbon monoxide is added in stoichiometric excess to keep the chlorine content of the phosgene as low as possible.

The chlorine from the chlorine recovery unit and carbon monoxide is pre-heated to 105 °C in heat exchanger (PHX1) before being sent to the first reactor (PHR1) which is a heat exchanger in the form of a nest of tubes filled with activated charcoal. The formation of phosgene starts as soon as the mixture comes in contact with the activated charcoal. The heat of the reaction is removed using diphenyl benzene at atmospheric pressure. The product gas leaving the first reactor is cooled to 100 °C in the heat exchanger (PHX2) and transferred to the second reactor (PHR2) which is a conventional nest of tubes filled with active charcoal. This reactor is operated at a constant temperature of 100 °C to ensure establishment of the phosgene equilibrium. The gaseous products are cooled down to 0 °C in the heat exchanger (PHX3) and sent to a flash drum to separate the unreacted carbon monoxide and phosgene that is recycled back to the isocyanate manufacturing unit. The operating conditions for the phosgene manufacturing unit are given in Table 17, the process flow diagram in Figure 34 and the stream tables in Appendix B5.

Table 17. Input parameters for equipments in phosgene manufacturing unit

Block	Type	Input Considerations
PHX1	Multi-stream heat exchanger	Cold stream (PHHIPT) outlet temperature – 105 °C
PHX2	Multi-stream heat exchanger	Hot stream (DCBREC3) outlet temperature – 100 °C
PHX3	Multi-stream heat exchanger	Hot stream (DCBREC3) outlet temperature – 0 °C
PHR1	Plug flow reactor with counter-current coolant	Rate controlled reaction: $Cl_2 + CO \longleftrightarrow COCl_2$
PHR2	Isothermal plug flow reactor	Temperature – 100 °C
PHFLSH	Two-outlet flash drum	Temperature – 0 °C, Pressure – 1.5 atm

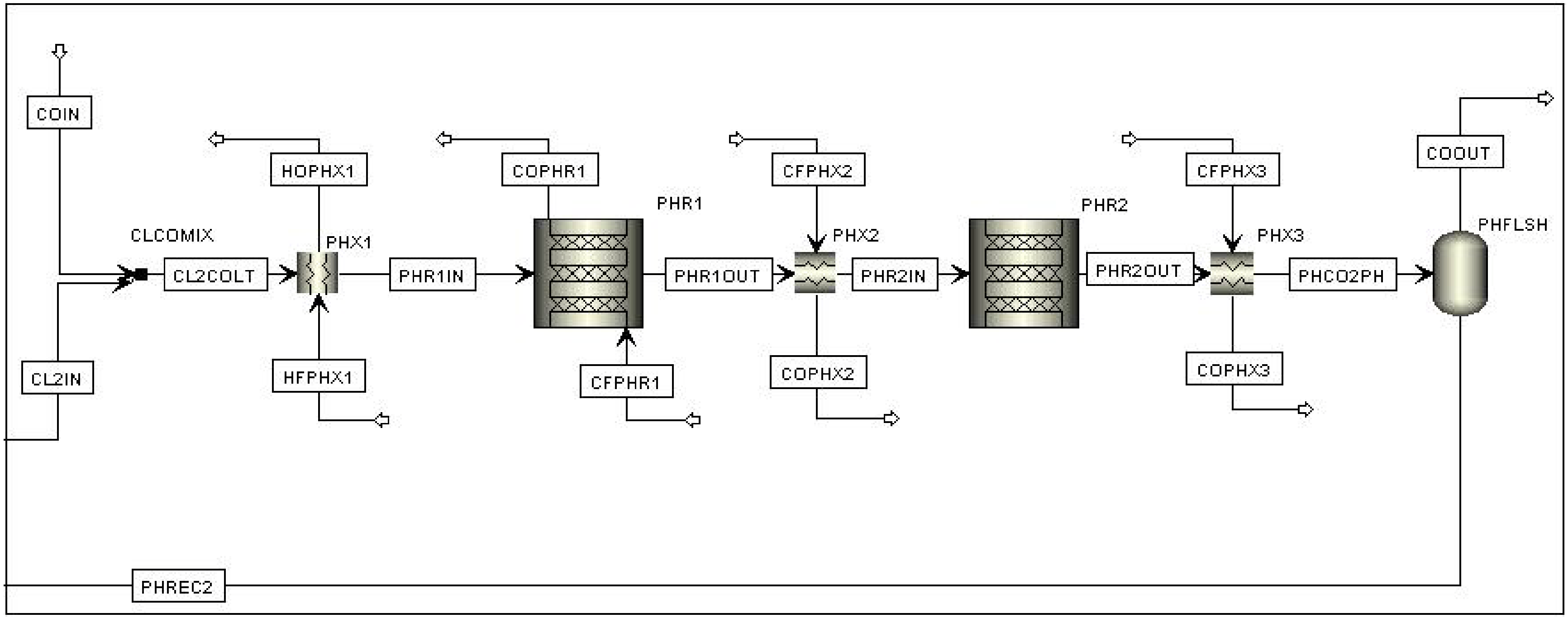


Figure 34. Process flow diagram of phosgene manufacturing unit

5.2 ISOCYANATE MANUFACTURE VIA NOVEL NON-PHOSGENE ROUTE

As described in section 4, isocyanate can be manufactured from a primary amine, carbon dioxide and trifluoroacetic anhydride at very low temperatures using acetone as the solvent. Similar to the process described in section 5.1, a plant is simulated for the manufacture of isocyanate via this route. The entire plant is divided into four units for ease of analysis, identification of hot-spots for energy consumption and comparison with the phosgene route as follows

1. Isocyanate manufacturing & acid adsorption unit (refer section 4.3.1 to 4.3.8).
2. Distillation columns for separation of products.
3. Trifluoroacetic anhydride recovery unit (refer section 4.3.9) & [65, 91, 92] .
    - Acetic anhydride from acetic acid unit [93-98].
4. Dry ice manufacturing unit [99-102].

These units have been simulated based on prior literature data and best possible engineering judgment. A brief schematic of the entire plant is given in Figure 29.

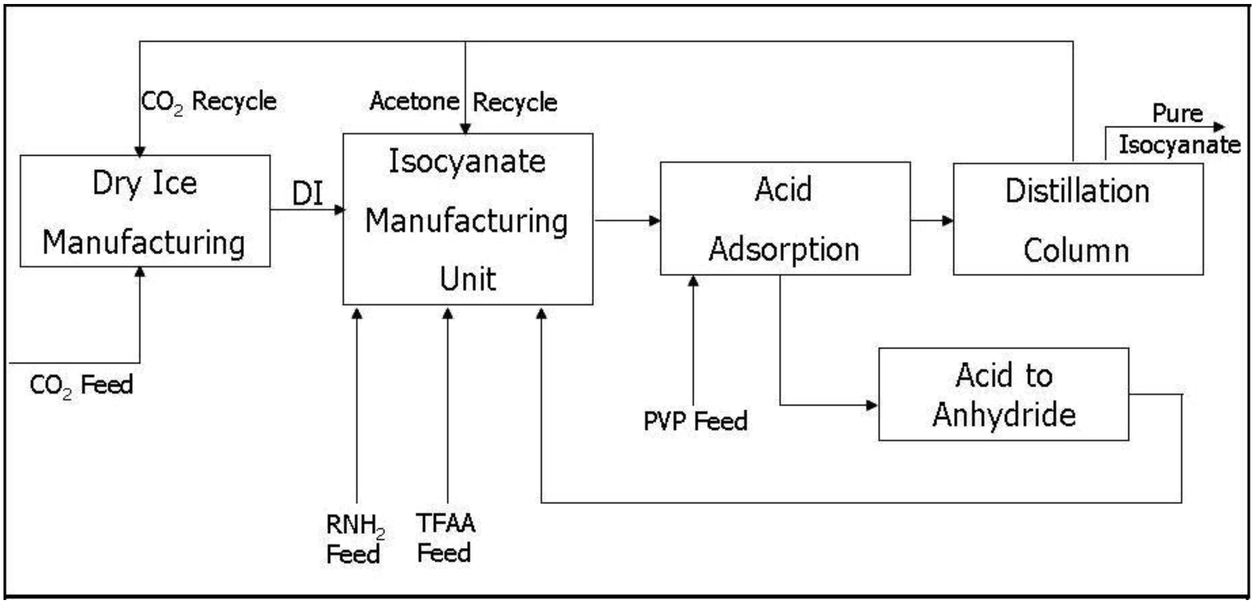


Figure 35. Schematic representation of isocyanate manufacturing via non-phosgene route

5.2.2 Isocyanate manufacturing & acid adsorption unit

This unit has three mixers (NH2AMIX, DIAMIX & TFAAMIX) that add the required quantity of acetone as described in section 4.2.3 to n-butylamine, dry ice and trifluoroacetic anhydride (TFAA) respectively. The amine stream (NH2ACET) comes in contact with the dry ice – acetone stream (DIACET) in reactor R1ZI, which is maintained at -78 °C and atmospheric pressure. The first step of formation of a mixture of zwitterion intermediate and carbamate takes place in this reactor. The outlet stream (R1ZIOUT) from R1ZI and the TFAA stream (TFAACET) is sent to the reactor (RMAIN), where the formation of isocyanate, salt and amide by-product takes place. The products are then sent through the filter (FILTER1) to filter out the salt formed. The filtrate containing butyl isocyanate, acetone, dissolved CO_2, trifluoroacetic acid and butyl formamide is sent to the acid adsorption unit (TFAABS) where the acid gets adsorbed on the poly-vinyl pyridine (PVP) resin. The acid loaded resin matrix is filtered out in the filter

(FILTER2). The operating conditions for this unit are given in Table 18, the process flow diagram in Figure 36 and the stream tables in Appendix C1.

Table 18. Input parameters for equipments in isocyanate manufacturing & acid adsorption unit

Block	Type	Input Considerations
R1ZI	Stoichiometric Reactor	Temperature – -78 °C, Pressure – 1 atm Butylamine to zwitterion (59.04 % conv.) Butylamine to carbamate (34.06 % conv.)
RMAIN	Stoichiometric Reactor	Temperature – -78 °C, Pressure – 1 atm Zwitterion to butyl isocyanate (100 % conv.) Carbamate to butyl isocyanate (100 % conv.) Butylamine to butyl formamide (100 % conv.)
TFAABS	Stoichiometric Reactor	Temperature – -78 °C, Pressure – 1 atm 100 % trifluoroacetic acid adsorbed on 28.7 wt % excess of polyvinyl pyridine

Trifluoroacetic anhydride is not available as a component in the Aspen plus database. It is therefore defined using the physical and thermodynamic properties given in Table 19.

Table 19. Properties of trifluoroacetic anhydride

Property	**Value**
Chemical formula	$C_4F_6O_3$
Molecular structure	$(CF_3CO)_2O$
Molecular weight	210.03
Boiling point	40 °C
Specific gravity @ 60 °F	1.52
Standard enthalpy of formation	-90500 kJ/kmol
Standard Gibbs energy of formation	-105000 kJ/kmol
Antoinne vapor pressure coefficient (Temp units – K, property units – mmHg)	A = 6.64084 B = 1202.32 C = 52.9
Ideal gas heat capacity polynomial coefficients (Temp units – K , property units – J/kmol.K)	A = 230.31 B = -332.586 C = 105.187

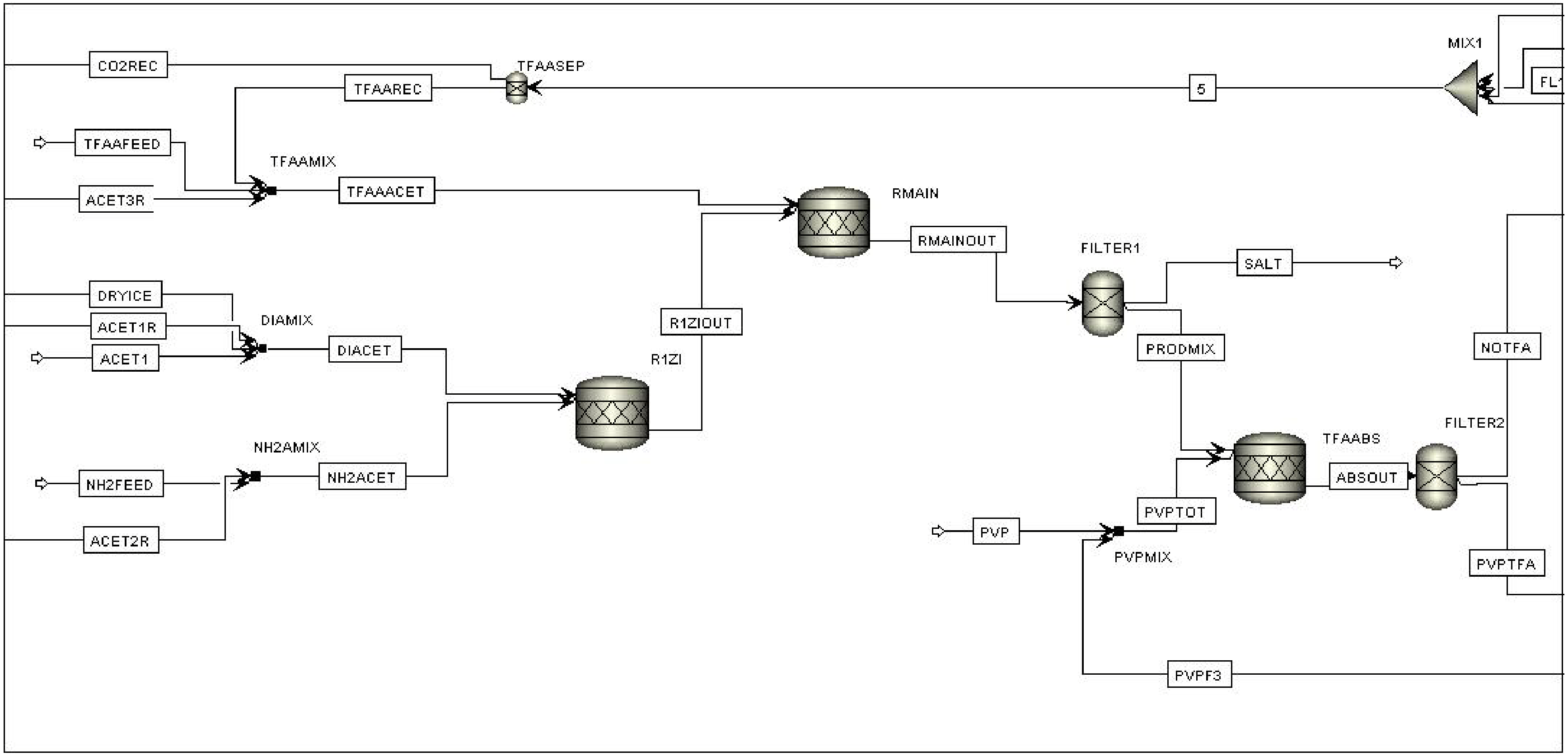


Figure 36. Process flow diagram of isocyanate manufacturing & acid adsorption unit

5.2.3 Distillation columns for separation of products

The filtrate from FILTER1 containing butyl isocyanate, dissolved CO_2, acetone and tert-butyl formamide is sent to a flash drum (FLASH1) operating at 0 °C and 1 atm. A significant portion of CO_2 is sent back to the dry ice manufacturing unit through the vapor stream (FL1TOP). The liquid stream (FL1BOT) is sent to the primary distillation column (DCISOACE) where acetone from the distillate is recycled back the isocyanate manufacturing unit. The mixture of butyl isocyanate and the formamide is sent to the second distillation column (DCISOAMI). Pure isocyanate is obtained as the distillate stream and the formamide is obtained as the bottom product. The process flow diagram for this section of the plant is shown in Figure 31. The operating conditions and design parameters for these distillation columns are given in Table 15 & 16 and the stream tables are given in Appendix C3.

Table 20. Operating conditions for distillation columns (non-phosgene route)

Unit	Recycle ratio	Stages	Feed stage
DCISOACE	0.259	17	7
DCISOAMI	0.155	21	11

Table 21. Design parameter for distillation columns (non-phosgene route)

Unit	Feed Stream	Distillate	Bottom	Specified Light Component	Specified Light Recovery	Specified Heavy Component	Heavy Recovery	Pressure
DCISOACE	FL1BOT1	DCISOACE	ISOAMIDE	Acetone	0.999	But-NCO	0.01	1 atm
DCISOAMI	ISOAMIDE	ISO	AMIDE	But-NCO	0.999	Amide	0.001	1 atm

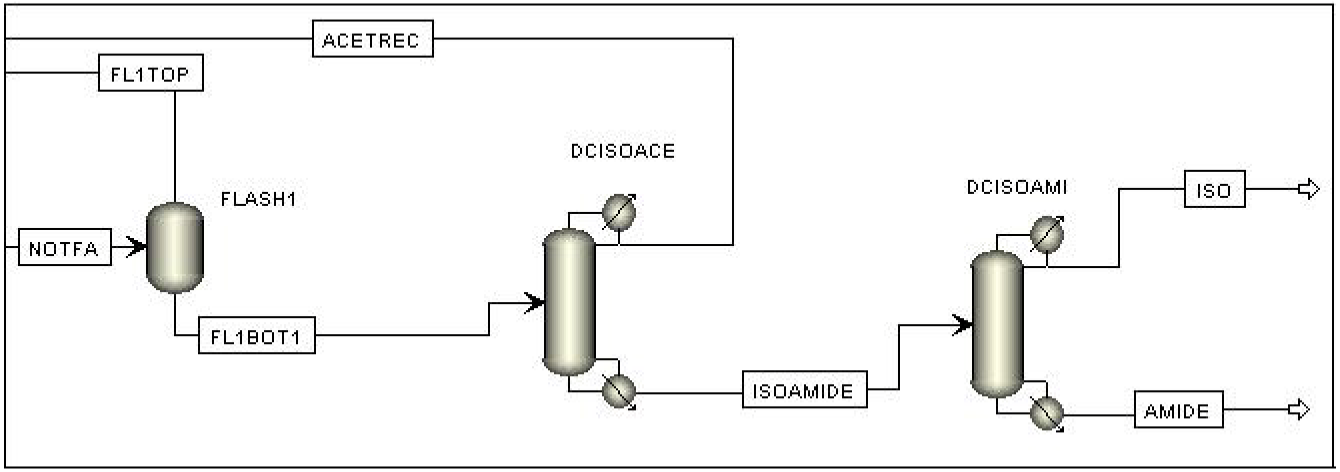


Figure 37. Process flow diagram of distillation column unit (non-phosgene route)

5.2.4 Trifluoroacetic anhydride recovery unit

This unit involves stripping of the adsorbed trifluoroacetic acid (TFA) on the polyvinyl pyridine (PVP) resins by methanol in a stripper unit (STRIPPER). The methanol requirement used to design this process is based on the experiments discussed in section 4.2.5 and 4.3.9. The unloaded PVP stream (PVPF3) obtained from the filter (FILTER3) is recycled back to the acid adsorption unit. The filtrate comprising of methanol and TFA forms an azeotropic mixture as shown in the T-xy chart in Figure 38 obtained using Aspen Properties [68].

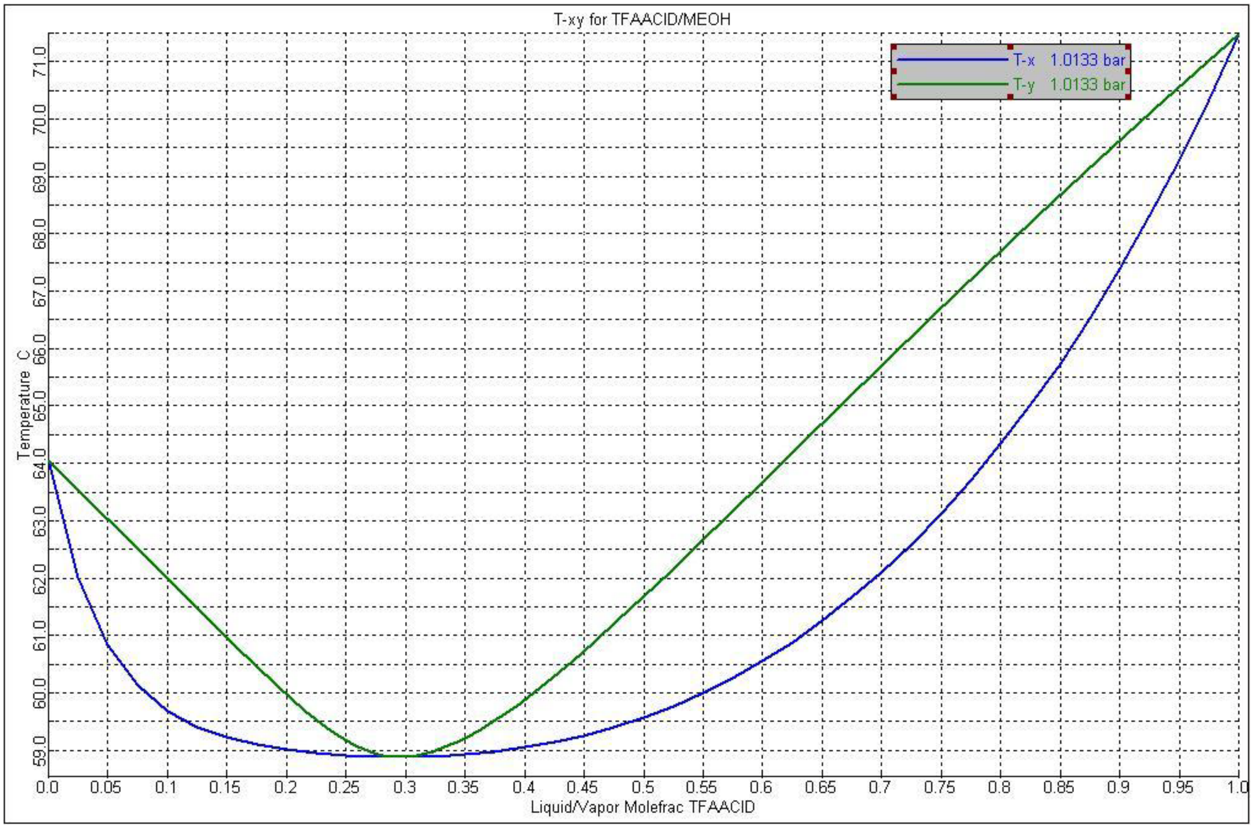


Figure 38. T-x-y chart for a methanol and trifluoroacetic acid mixture

As a result of the azeotropic nature of the liquid stream, a simple distillation design described in the previous sections using the Winn-Underwood-Gilliland method could not be used. A “RadFrac” column, which is used for rigorous 2 or 3 phase fractionation in single columns, was used. The sensitivity analysis tool was used to determine the ideal operating conditions for the best possible separation of methanol and TFA. These conditions are shown in Table 22.

Table 22. Operating conditions for separation of methanol and trifluoroacetic acid

Design Parameter	Value
Number of stages	15
Feed stage	6
Condenser	Total condenser
Reboiler	Kettle
Distillate rate	600 kg/hr
Molar reflux ratio	0.1

The pure methanol stream obtained as the bottom product of the distillation column (DCMETTFA) is recycled back to the stripper unit. The distillate stream containing concentrated TFA in methanol is cooled to 60 °C in a heat exchanger (HXTA) before being sent to the reactor (TFAARECO). The heat recovered by cooling the distillate stream is used to heat the acetic anhydride stream to 60 °C in a heat exchanger (HXAA). The user-defined properties given in Table 19 were not sufficient to simulate a reactive distillation unit for the formation of trifluoroacetic anhydride. This process was approximated by having the reactor TFAARECO and distillation units (TFAAFL & DCMETAA). The acetic anhydride reacts with trifluoroacetic acid in the reactor to give trifluoroacetic anhydride and acetic acid as the product. The operating conditions for the equipments in this unit are given in Table 23 and the process flow diagram is shown in Figure 39. The stream tables are given in Appendix C4.

Table 23. Input parameters for equipments in trifluoroacetic anhydride recovery unit

Block	**Type**	**Input Considerations**
HXTA	Multi-stream heat exchanger	Hot stream (CTFAOUT) outlet temperature – 60 °C
HXAA	Multi-stream heat exchanger	Cold stream (CAAOUT) outlet temperature – 0 °C
TFAARECO	Stoichiometric Reactor	Temperature – 60 °C, Pressure – 1 atm TFA to TFAA (94 % conv.)
TFAAFL	Two-outlet flash drum	Temperature – 10 °C, Pressure – 1 atm
DCMETAA	Distillation Column using Winn – Underwood – Gilliland method	Distillate – METREC2, Bottom – AACID Methanol recovery – 0.99 Acetic acid in distillate – 0.001 Reflux Ratio – 0.292 Number of stages – 16, Feed stage - 10

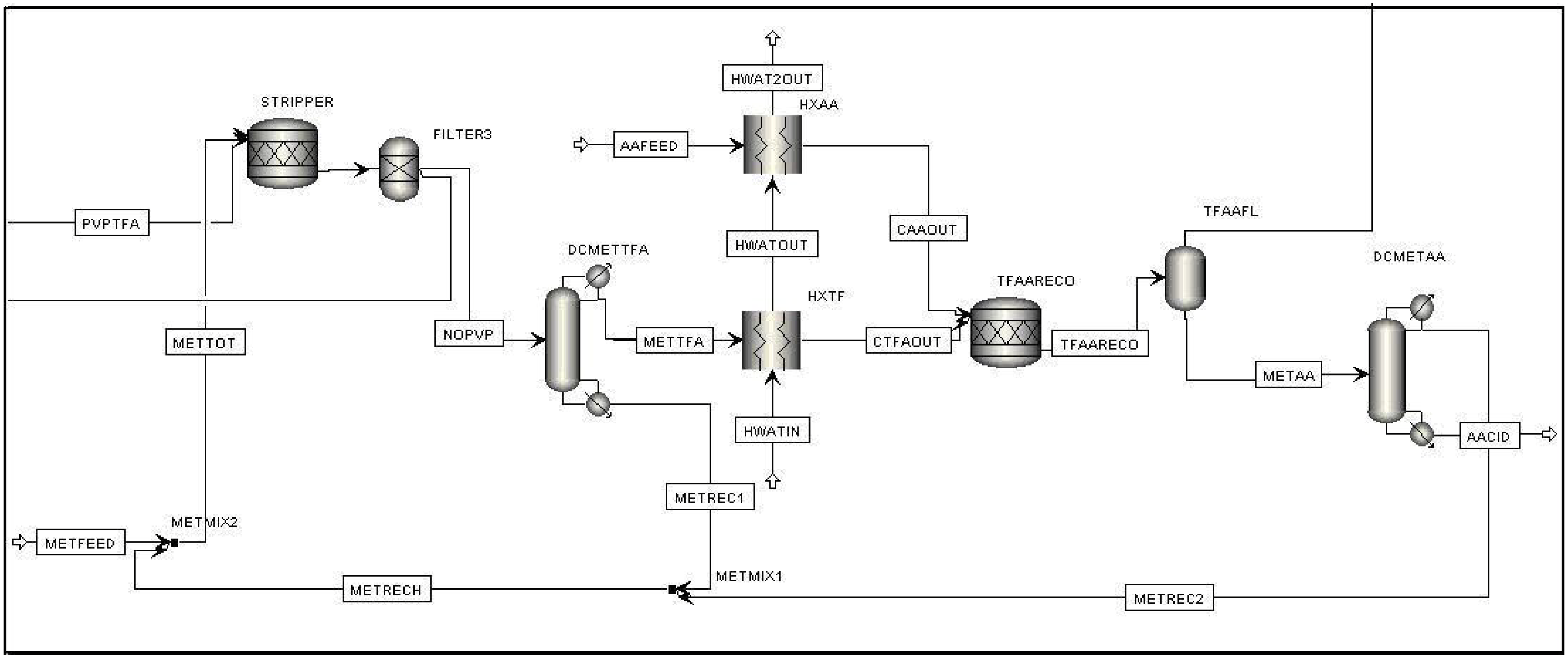


Figure 39. Process flow diagram of trifluoroacetic anhydride recovery unit

5.2.4.1 Recovery of acetic anhydride from acetic acid

The current commercial route for manufacture of acetic anhydride is through carbonylation of methyl acetate by carbon monoxide in the presence of rhodium as the catalyst [98].

$$CH_3COOCH_3 + CO \longrightarrow (CH_3CO)_2O \qquad (5.1)$$

This process replaced the acetic acid-ketene based process that was used until the 1970's because of the high energy cost associated with the ketene process. However, since the by-product obtained from the trifluoroacetic anhydride recovery unit (section 5.2.4) is acetic acid, the ketene process is used to simulate the acetic anhydride recovery unit.

$$CH_3COOH \xrightarrow{\Delta} CH_2CO + H_2O \qquad (5.2)$$

$$CH_2CO + CH_3COOH \longrightarrow (CH_3CO)_2O \qquad (5.3)$$

The kinetics of this process has been studied by Blake et al and Padmanabhan et al [96, 103, 104] and a number of patents have been filed for various improvements in the process [105-110]. The cracking of acetic acid needs to be carried out at 700 °C. Hence, a part of the acetic acid stream is pre-heated to 700 °C in the heat-exchanger (AAHX) using natural gas. It is then sent to a subsequent cracking zone (AAR1), where the acetic acid gets pyrolyzed to ketene and water. The water formed cannot be separated from the product mixture of water and unreacted acetic acid by regular distillation process. Ethyl acetate is therefore added to this stream in a three phase separator (KWSEP). The vapor phase stream (KETVAP) primarily consisting of ketene, the first liquid phase stream (EAACID) contains ethyl acetate and acetic acid and the second liquid phase stream (WATER) contains water. The vapor and first liquid phase streams are sent to the second reactor (AAR2) along with a stream of ammonia, which acts as a catalyst for the formation of acetic anhydride from acetic acid and ketene. The product stream is cooled down in a heat exchanger (AAX2) and then sent to a flash drum (AAFL) where the unreacted ketene vapors are separated. The liquid stream (FLBOT) is sent to a distillation column (AADC) where ethyl acetate is obtained as the distillate and acetic acid as the bottom product. The operating conditions for the equipments in this unit are given in Table 24 and the process flow diagram is shown in Figure 40. The stream tables are given in Appendix C5.

Table 24. Input parameters for equipments in acetic anhydride recovery unit

Block	Type	Input Considerations
SPLP	Stream splitter	Splits the acetic acid stream in the ratio 84.12 : 15.88
AAHX	Multi-stream HeatX	Cold stream (ACIDHOT) outlet temperature – 700 °C
AAR1	Stoichiometric Reactor	Temperature – 700 °C, Pressure – 358 mbar Acetic acid to ketene (59.44 % conv.)
KWSEP	Three phase separator	Temperature – 5°C, Pressure – 1 atm
AAR2	Stoichiometric Reactor	Temperature – 50 °C, Pressure – 358 mbar Acetic acid + ketene to acetic anhydride (99 % conv.)
AAX2	Multi-stream HeatX	Hot stream (R2PROD) outlet temperature – 8 °C
AAR2	Distillation Column using Winn – Underwood – Gilliland method	Distillate – EA, Bottom – AANHY Ethyl acetate recovery – 0.995 Acetic anhydride in distillate – 0.005 Reflux Ratio – 1.312 Number of stages – 12, Feed stage – 6

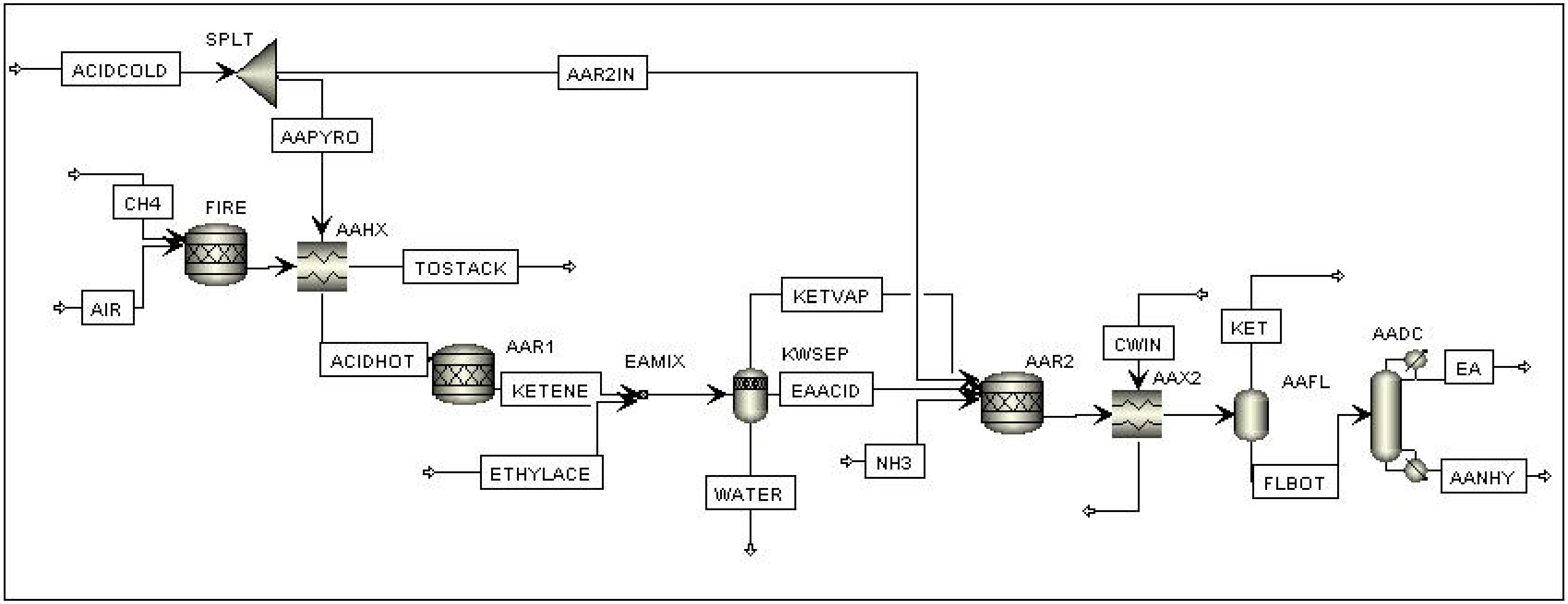


Figure 40. Process flow diagram of acetic anhydride recovery unit

5.2.5 Dry ice manufacturing unit

The standard process for making dry ice involves liquefying the carbon dioxide followed by subsequent expansion at atmospheric pressure. As a result of the sudden expansion, the temperature drops down and flakes of solid CO_2 are formed. Blocks of dry ice are produced using a hydraulic press. Liquefaction of carbon dioxide requires the pressure to be in the range of 15 to 25 atm and the temperature to be in the range of 261 to 296 K [101]. However, as seen in Figure 41, as the pressure of carbon dioxide increases, the temperature increases drastically too. Figure 42 shows that by reducing the temperature of CO_2 to -10 °C it is possible to get liquid CO_2 at about 27 atm.

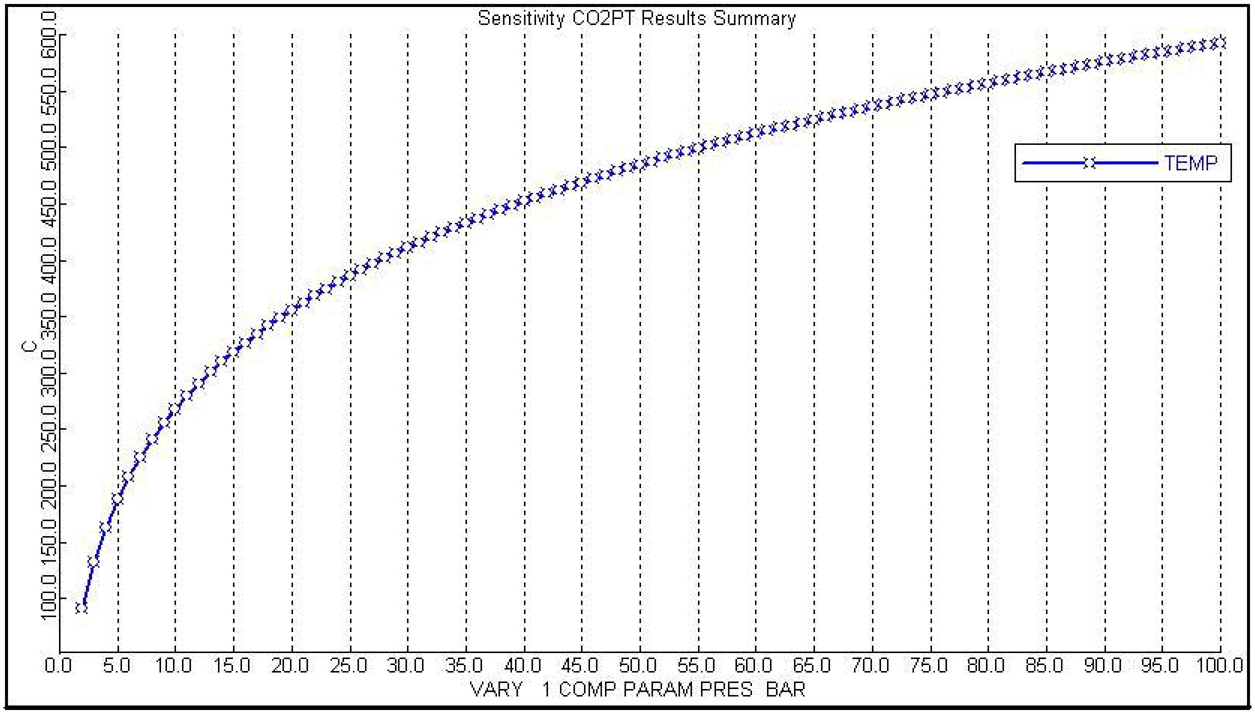
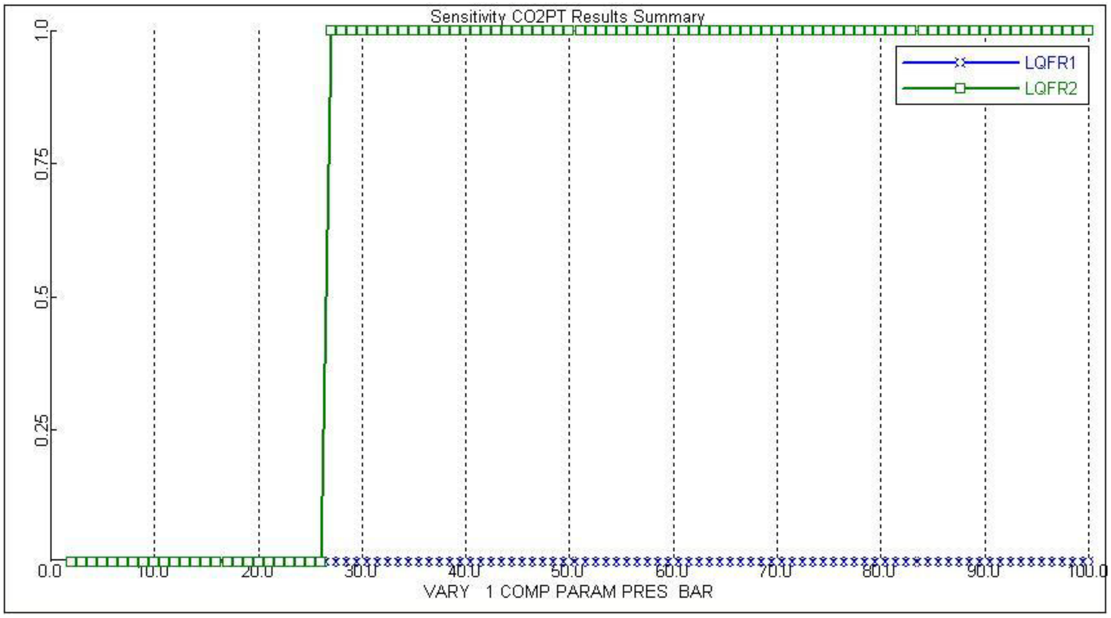


Figure 41. Pressure vs. temperature curve for carbon dioxide



(LQFR1 – Liquid fraction of CO_2 at temperature corresponding to pressure as shown in Figure 41, LQFR2 – Liquid fraction of CO_2 when cooled to -10 °C)

Figure 42. Liquid fraction vs pressure for carbon dioxide

Hence, the pressurization of CO_2 needs to be done in a step-wise manner with intermittent cooling. A multi-stage compressor is used to simulate this process in Aspen. It was observed that the total energy requirement of the compression and cooling went down with increasing number of stages (Figure 43). Based on these results, a five stage compressor was used to liquefy CO_2 by pressurizing it to 20 atm at -20 °C.

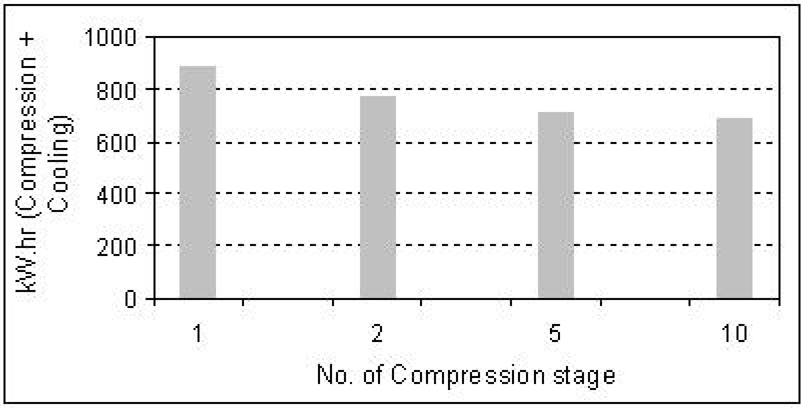


Figure 43. Energy consumption vs Number of stages in a multi stage compressor

Based on these initial observations, the dry ice manufacturing unit was designed as shown in Figure 44. The recycled CO_2 and acetone is sent to a flash drum (CO2SEP) where the gaseous CO_2 (CO2G) is separated from the CO_2 dissolved in acetone (ACECO21). The recycled and fresh gaseous CO_2 is liquefied in a 5 stage compressor (COMP1 & COMP2) to 20 atm at -20 °C. The liquefied CO_2 is decompressed (EXPANDER) to atmospheric pressure and is recycled to the isocyanate manufacturing unit. The stream tables for this unit are given in Appendix C2.

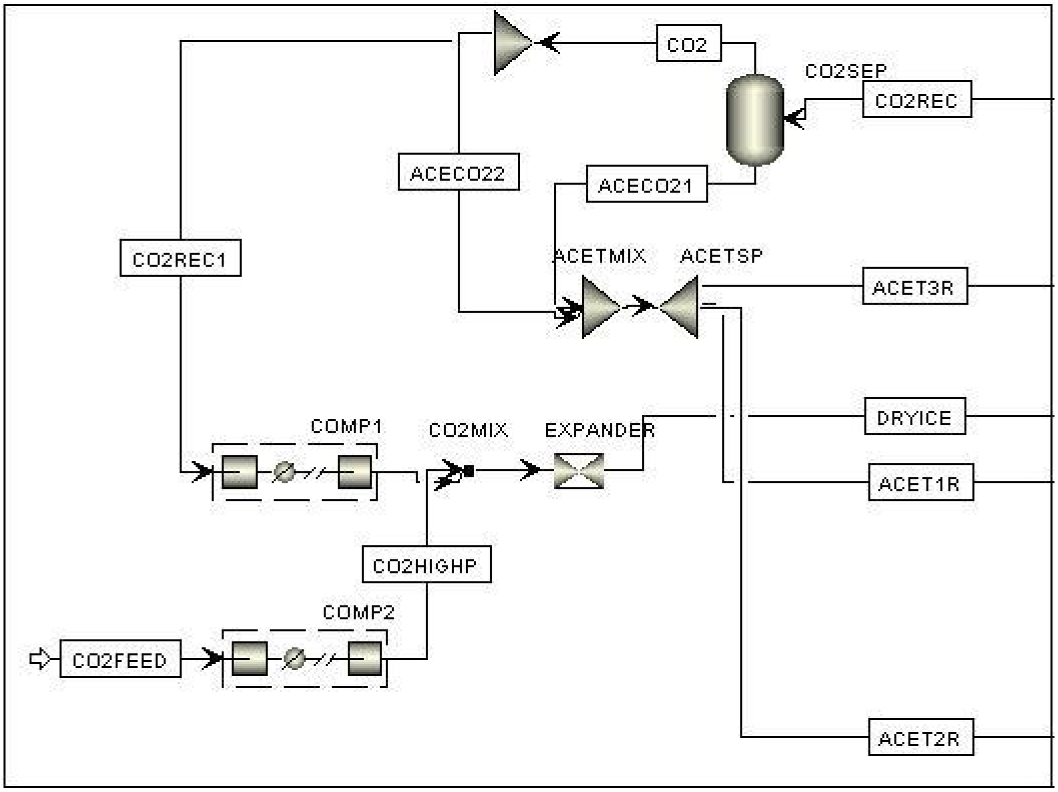


Figure 44. Process flow diagram for dry ice manufacturing unit

5.3 RESULTS AND DISCUSSIONS

The isocyanate plant via the phosgenation route was designed with an input flowrate of 250 kg/hr of n-butylamine. Based on the conversions and efficiency of separation techniques, the isocyanate obtained as the product was at 312.36 kg/hr with 99.3 % purity. The plant via the novel non-phosgene route was designed with an input flowrate of 138.89 kg/hr of n-butylamine and the isocyanate obtained as the product was at 145.68 kg/hr with 97.6 % purity. The results for the non-phosgene plant were scaled to an output of 312.36 kg/hr so that the two processes are compared effectively.

5.3.1 Raw material consumption comparison

The raw material requirement for the manufacturing 312.36 kg/hr of isocyanate via the phosgenation route with hydrochloric acid electrolysis, anhydrous hydrogen chloride electrolysis and the non-phosgene route is reported in Table 25. The total raw material required is minimum for the phosgenation route by anhydrous hydrogen chloride electrolysis followed by the hydrochloric acid route. The major contributing raw material for this route is the butylamine and carbon monoxide (used in the manufacture of phosgene). The electrolysis of anhydrous hydrogen chloride does not use any water; however, oxygen contributes a significant extent to the total raw material consumption. The major contributor to the non-phosgene route is the butylamine, carbon dioxide, trifluoroacetic anhydride and acetic anhydride. The use of the trifluoroacetic anhydride and n-butylamine can potentially be reduced recovering the acid from the salt formed. The acetic anhydride used can be reduced by recovering the acetic acid formed as discussed in section 5.2.4.1. The results for the additional processing unit are discussed later in section 5.3.3.

Table 25. Raw material consumption for different route for manufacture of isocyanate

Component	**(kg/hr)**
Butylamine	250.00
Phosgene	4.65
Carbon monoxide	95.81
Dichlorobenzene	5.65
Water	121.72
Total	477.83
Phosgene Route **(HCl acid electrolysis)**	

Component	**(kg/hr)**
Butylamine	250.00
Phosgene	4.65
Carbon monoxide	95.81
Dichlorobenzene	5.65
Oxygen	54.69
Total	410.80
Phosgene Route **(anhydrous HCl electrolysis)**	

Component	**(kg/hr)**
Butylamine	299.84
CO_2	138.06
Trifluoroacetic anhydride	110.90
Acetone	7.54
Methanol	6.55
Polyvinyl pyridine	16.00
Acetic anhydride	283.68
Total	862.57
Non-phosgene Route	

5.3.2 Energy consumption comparison

For a production capacity of 312.36 kg/hr of butyl isocyanate, the energy requirement was obtained from the Aspen process designs for the different equipments used to simulate the three routes considered. The energy requirement is categorized into electricity for pumps, compressors and electrolytic cells and heating and cooling requirement for reactors, heat exchangers, distillation columns and flash drums. The energy requirement for each of the individual equipments is given in Appendix D1 (phosgenation route) and D2 (non-phosgene route), and the summary is provided in Figure 44. For the phosgenation route, the four categories considered are isocyanate manufacture (Iso Manufac), distillation columns (DC), chlorine recovery and phosgene manufacture (Phos manufac). For the non-phosgene route the four categories considered are isocyanate manufacture (Iso manufac), distillation columns and flash drums (DC & Flash), trifluoroacetic anhydride recovery (TFAA Recovery) and dry ice manufacture.

By shifting from the hydrochloric acid electrolysis to anhydrous hydrogen chloride electrolysis for the recovery of chlorine, a significant amount of energy can be saved since the cooling of the recycled acid from 80 °C (electrolysis temperature) to 65 °C (acid absorption temperature) is not required. Also, anhydrous hydrogen chloride electrolysis is more efficient than hydrochloric acid electrolysis as it reduces the electricity consumption by 15 %. However, the disadvantage with anhydrous electrolysis is that water is formed at the cathode instead of hydrogen. Hence, the hydrogen cannot be utilized further for energy production and utilization. The combined energy consumption for the phosgenation route by electrolysis of hydrochloric acid is 1743.95 kW.hr and electrolysis of anhydrous hydrogen chloride is 1393.47 kW.hr.

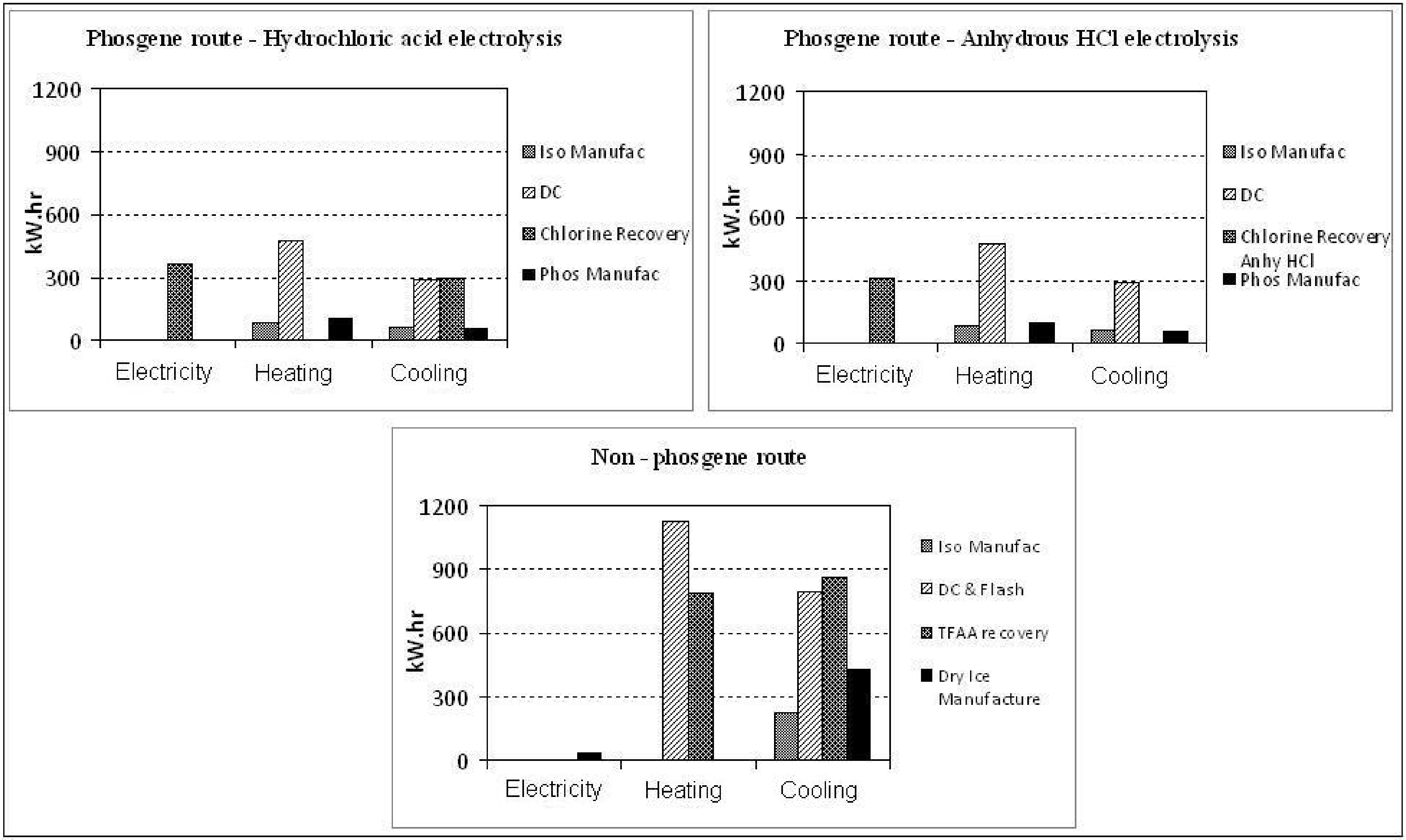


Figure 45. Energy consumption comparison between the phosgene and non-phosgene routes

The total energy consumption for the non-phosgene route is 3955.74 kW.hr. The main contributors to the energy consumption are the distillation columns (46.07 %) and the trifluoroacetic anhydride recovery units (41.08 %). Surprisingly, the energy consumption in the dry ice manufacturing unit was not significant (6.16 %). The reason for the lower energy consumption was that the recycled CO_2 and acetone was already at a low temperature (- 47.3 °C). Hence, the dry ice required was only to reduce the temperature further to -78 °C.

The reason for high energy consumption in the distillation units is the selection of acetone as the solvent, which has a lower boiling point (56.5 °C) than the product butyl isocyanate (112 °C). As a result, significant amount of energy is used in distilling the acetone before the isocyanate can be separated from the amide byproduct. However, it should be noted that the selection of acetone as the solvent was depended on a number of factors as discussed in section 4.3.3.

The high energy consumption in the trifluoroacetic anhydride recovery unit is due to the azeotropic distillation used for the separation of trifluoroacetic acid and methanol and further separation of acetic acid and methanol. In order to reduce the energy consumption in the separation of methanol and TFA, the effectiveness of propanol as an alternative to methanol in the extraction of TFA from PVP resin can be studied. Ethanol is not considered as it forms an azeotropic mixture with TFA whereas propanol does not.

5.3.3 Acetic anhydride recovery

Since, acetic anhydride contributed a significant part (32.88 %) to the raw material use in the manufacture of isocyanate via the non-phosgene route; an additional unit for its recovery from the acetic acid by product was studied as described in section 5.2.4.1. The option to recover the acetic anhydride was compared to the option to sell the acetic acid formed and buy fresh acetic anhydride. This comparison was based on the economic potential of the two options, where,

Economic Potential = Product value + Byproduct value – Raw material cost – Production cost

The comparison was performed for the option of the treatment of 142.24 kg/hr of acetic acid to acetic anhydride with the option of selling 142.24 kr/hr of acetic acid as a by-product. The prices of the commodities used are given in Table 26 [111-113].

Table 26. Price of chemicals and commodities

Commodity	**Price**
Acetic acid	0.38 $ / lbs
Acetic anhydride	0.49 $ / lbs
Methyl acetate	0.54 $ / lbs
Methane	3.92 $ / Mcf
Heating (Natural Gas)	3.81 $ / MMBtu
Cooling (Electric chiller)	10.03 ¢ / kW.hr

The raw material flowrate, product flowrate, electricity, heating and cooling requirement was obtained from the Aspen simulations for the two options and the economic value was calculated as shown in Table 27 & 28.

Table 27. Economic value of buying fresh acetic anhydride and selling acetic acid byproduct

Commodity	**Quantity**	**Value ($)**
Acetic anhydride (buy)	131.40 kg/hr	- 141.91
Acetic acid (sell)	142.24 kg/hr	+119.13
Economic value ($)		**- 22.78**

Table 28. Economic value of recovery of acetic anhydride from acetic acid

Commodity	**Quantity**	**Value**
Acetic anhydride (buy)	15.77 kg/hr	- 17.04
Methyl acetate (buy)	3.10 kg/hr	- 3.69
Methane (buy)	8.62 kg/hr	- 1.75
Heating	11.67 kW.hr	- 0.15
Cooling	117.64 kW.hr	- 11.80
Economic value ($)		**- 34.43**

As seen from this analysis, it would make more economical sense sell the acetic acid by-product instead of recovering the anhydride via the ketene process. The result of this analysis was not surprising since the ketene process has already been replaced by the carbonylation of methyl acetate process as an industrial route for manufacture of acetic anhydride due to inherent high cost of the former process. As a result, the recovery of acetic anhydride unit was not included in the mass and energy consumption analysis in section 5.3.1 & 5.3.2.

5.4 SUMMARY

The quantitative analysis based on the raw material and the energy requirement obtained from the Aspen Plus simulations was very useful in comparing the novel non-phosgene route with the commercial phosgene route. At the present state of development of the novel route, it requires significantly more amount of raw material and energy compared to the phosgene route. However, this analysis identified the hot-spots for higher raw material and energy consumption in the process developed. The process that contributes significantly to the high energy requirement for the non-phosgene route is the separation of the acetone from the product stream and the separation of trifluoroacetic acid and its recovery to trifluoroacetic anhydride. Based on this study, some of the potential areas that can be targeted to make the process more efficient would be,

1. Exploration of polar aprotic solvents such as acetone, which would have a high solubility for carbon dioxide, have low freezing temperatures for higher conversion to isocyanate and boiling point higher than the isocyanate for lower energy requirement for separation by distillation.
2. Molecular design of new anhydrides which have strong electron withdrawing groups (for high pKa value of the acid) and can also be efficiently recovered from their corresponding acid. This would reduce the energy associated with the anhydride recovery unit.
3. Development of an effective process to recover the amine and acid from the salt formed as the byproduct. The recycling of these raw materials would reduce the overall material requirement for the process.

The industry has significantly improved the process for the recovery of the phosgene from hydrogen chloride formed as the byproduct in the phosgenation route by shifting from electrolysis of hydrochloric acid to electrolysis of anhydrous hydrogen chloride. Thus, the mere replacement of hazardous chemicals such as phosgene would not necessarily guarantee a green alternative process for manufacture of isocyanates. The new reagent that is used to replace phosgene should be equally effective and can be recycled effectively to make the process greener.

This research study demonstrated the importance of the application of chemical engineering fundamentals to chemistry in the development of a new process. The simultaneous validation of the effectiveness of a newly developed process at an industrial level is equally important, because what might seem to be the best option at a lab-scale might not necessarily be the most efficient option at the industrial scale.

6.0 LIFE CYCLE ASSESSMENT TO COMPARE THE ENVIRONMENTAL IMPACTS OF POLYCARBONATE WITH TRITAN

Polycarbonates are thermoplastic polymers that have functional groups linked together by carbonate groups (-O-CO-O-) in a long molecular chain. They can easily be worked, molded and thermoformed and hence are widely used in the modern chemical industry. Bisphenol A (BPA) based polycarbonate (PC) is one of the most versatile and widely used engineering thermoplastics on the market. Their interesting combination of features such as high temperature resistance, sterilizability, impact resistance and optical properties position them between commodity plastics and engineering plastics.

Polycarbonates are appealing to manufacturers and purchasers of food storage containers due to its clarity, toughness, or light weight, especially when compared to silica glass. Polycarbonate is therefore seen in the form of single use and refillable plastic water bottles. However, it is possible that these polymers fall out of their equilibrium under certain conditions and some residual BPA is leached out into the contents of these bottles. For example, BPA appeared to leach from polycarbonate animal cages into water at room temperature and may have been responsible for enlargement of the reproductive organs of female mice [114]. A study on exposure of pregnant rats to BPA at 2.5 to 1,000 μg per kilogram of body weight per day showed that at the equivalent of puberty for the pups (50 days old), about 25% of their mammary ducts had precancerous lesions, some three to four times higher than unexposed controls [115]. The study is cited as evidence for the hypothesis that environmental exposure to bisphenol A as a fetus can cause breast cancer in adult women [116].

An expert panel of 12 scientists found that there is "some concern that exposure to the chemical bisphenol A in uterus causes neural and behavioral effects," according to the draft report prepared by the National Toxicology Program (NTP) Center for the Evaluation of Risks to Human Reproduction. For the general adult population, the expert panel found a negligible concern for adverse reproductive effects following exposures [117]. A study of cross-sectional data from the 2003-2004 U.S. National Health and Nutritional Examination Survey demonstrated positive and statistically significant correlations between the concentration of bisphenol A in the urine and self-reported histories of cardiovascular disease and diabetes [118].

An analysis of the literature published on low-dose leaching of bisphenol A effects by Vom Saal et al found a suggestive correlation between the source of funding and the conclusion drawn. Industry funded studies tend to find no significant effects while government funded studies tend to find significant effects [119].

As a result of all these studies, there has been a significant push by the polymer industry to look for alternatives to polycarbonates that are BPA free and also have physical and mechanical properties to them. Polymers such as Polyethylene terephthalate (PET) and polypropylene ethylene (PPE) do not contain BPA can be used for bottle applications but lack the toughness necessary for durable goods and higher-end packaging material. Eastman Chemical Company has recently introduced a new trademarked polymer – Tritan ™ in an attempt to match mechanical properties of BPA-PC [120].

With the aim of improving upon the mechanical properties of PET, Eastman developed a series of polyesters that substitute 1,4-cyclohexanedimethanol (CHDM) for part of the ethyl glycol used to make PET. Depending on the proportion of CHDM to ethylene glycol, the copolymers have various degrees of chemical resistance, toughness and stiffness. However, these copolymers have poor temperature resistance. Eastman subsequently replaced ethylene glycol with another diol that could boost the temperature performance of polyesters: 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD). This monomer, CHDM and dimethyl terephthalate (DMT) are copolymerized to create Tritan.

The company has tested Tritan for various mechanical properties in comparison with other polymers mainly polycarbonates [121]. Table 29 summarizes the comparison of the mechanical properties of Tritan with polycarbonates.

Table 29. Mechanical properties of Tritan and Polycarbonate

Property	**Tritan ™ TX 1000**	**PC (Range)**
Density (g/cm^3)	1.18	1.20 – 1.22
Youngs Modulus (GPa)	1.551	2 – 2.4
Tensile strength (MPa)	42 – 53	55 – 75
Compressive strength (MPa)	-	> 80
Elongation at break	210 %	80 – 150 %
Water adsorption over 24 hr	-	0.1 %
Glass transition temperature	105 °C	150 °C

There is no peer reviewed source of information on the endocrine disruption potential of any of the monomers used to manufacture Tritan. The only report available is published by Eastman Company based on the testing done using Quantitative Structure Activity Relationship (QSAR) analysis by Dr. William Welsh at the Robert Wood Johnson Medical School, Piscataway, NJ [122]. Additional and more definitive studies were conducted at the Wil Research Laboratories, LLC at Ashland, OH to assess the potential for chemicals to be endocrine disrupting chemicals (EDC) using laboratory animals. These studies concluded that none of the raw materials used in the manufacture of Tritan are responsible for endocrine disruption. However, the environmental impacts of the life cycle phases in the production of Tritan have not been previously studied.

Whereas, life cycle assessments (LCA) for biobased polymers are plentiful [123-126], there have been few studies specifically focused on the environmental impact of polycarbonates. Vercalsteren studied the existing systems for drinking cups at public events in order to gain an insight into the current environmental impacts of various types of polymers [127]. Based on the eco-efficiency assessment it was shown that in the base case for small events, the PC cup system showed a significantly favorable environmental score compared to the polypropylene, one way polyethylene & one way polylactic acid coated cardboard cup system [128]. Due to the absence of literature on the overall environmental impact of polycarbonates and Tritan, this research study aims to perform an extensive LCA for these two products.

6.1 INTRODUCTION TO LIFE CYCLE ANALYSIS

Life Cycle Analysis, also known as ‘life cycle assessment’, ‘ecobalance’, and ‘cradle-to-grave analysis’ is the investigation and evaluation of the environmental impacts of a given product or service caused or necessitated by its existence. The goal of LCA is to compare the full range of environmental and social damages assignable to products and services, to be able to choose the least burdensome one. At present, it is a way to account for the effects of the cascade of technologies responsible for goods and services. It is limited to that, though, because the similar cascade of impacts from the commerce responsible for goods and services is unaccountable because what people do with money is unrecorded. As a consequence LCA succeeds in accurately measuring the impacts of the technology used for delivering products, but not the whole impact of making the economic choice of using it.

The term ‘life cycle’ refers to the notion that a fair, holistic assessment requires the assessment of raw material production, manufacture, distribution, use and disposal including all intervening transportation steps necessary or caused by the product's existence. The sum of all those steps or phases is the life cycle of the product. The concept can also be used to optimize the environmental performance of a single product or to optimize the environmental performance of a company.

The common categories in which the environmental impacts are evaluated are global warming (greenhouse gases), acidification, smog, ozone depletion, eutrophication, eco-toxicological and human-toxicological pollutants, habitat destruction, desertification, land use as well as depletion of minerals and fossil fuels.

The procedures of LCA are part of the ISO 14000 environmental management standards: in ISO 14040:2006 [129] and 14044:2006 [130]. ISO 14044 replaced earlier versions of ISO

14041 to ISO 14043. According to the ISO 14040 and 14044 standards, a LCA is carried out in four distinct phases [131]. These phases are often interdependent in a way that the results of one phase will determine how other phases are completed. The interaction between these phases is shown in Figure 46.

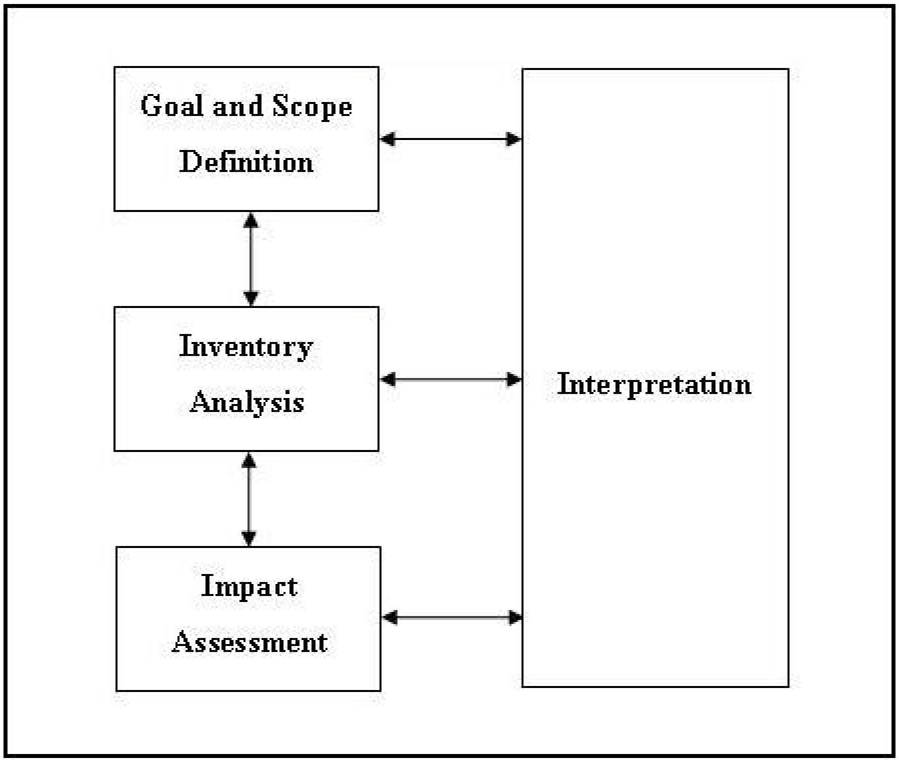


Figure 46. Illustration of phases of LCA

6.1.1 Goal and scope

In the first phase, the LCA-practitioner formulates and specifies the goal and scope of study in relation to the intended application. LCA relates environmental impact to a product or rather to the function of a product system. Hence, it is vital to express the function in quantitative terms as a functional unit. The object of study is described in terms of a functional unit. Apart from describing the functional unit, the goal and scope should address the overall approach used to establish the system boundaries. The system boundary determines which unit processes are included in the LCA and must reflect the goal of the study. In recent years, two additional approaches to system delimitation have emerged. These are often referred to as ‘consequential’ modeling and ‘attributional’ modeling. Finally the goal and scope phase includes a description of the method applied for assessing potential environmental impacts and which impact categories are included.

6.1.2 Life cycle inventory

This second phase 'Inventory' involves data collection and modeling of the product system, as well as description and verification of data. This encompasses all data related to environmental (e.g., CO_2) and technical (e.g., intermediate chemicals) quantities for all relevant unit processes within the system boundaries that compose the product system. Examples of inputs and outputs quantities include inputs of materials, energy, chemicals and outputs of air emissions, water emissions or solid waste. Other types of exchanges or interventions such as radiation or land use can also be included.

Usually LCA inventory and modeling are developed and conducted using dedicated software packages. Depending on the software package used, it is possible to model life cycle costing and life cycle social impacts in parallel with environmental life cycle. The data must be related to the functional unit defined in the goal and scope definition. Data can be presented in tables and some interpretations can be made already at this stage. The results of the inventory is an LCI which provides information about all inputs and outputs in the form of elementary flow to and from the environment from all the unit processes involved in the study.

6.1.3 Life cycle impact assessment

The third phase 'Life Cycle Impact Assessment' is aimed at evaluating the contribution to impact categories such as global warming, acidification etc. The first step is termed characterization. Here, impact potentials are calculated based on the LCI results. The next steps are normalization and weighting, but these are both voluntary according the ISO standard. Normalization provides a basis for comparing different environmental impact categories (all impacts get the same unit). Weighting assigns a weighting factor to each impact category depending on the relative importance. The weighting step is not always necessary to create a so called “single indicator”.

6.1.4 Interpretation

Life cycle interpretation is a systematic technique to identify, quantify, check and evaluate information from the results of the LCI and the LCIA, and communicate them effectively. It includes an analysis of the major contributions, sensitivity analysis and uncertainty analysis. This stage concludes whether the ambitions from the goal and scope can be met. More importantly: what can be learned from the LCA? All conclusions are drafted during this phase. Sometimes an independent critical review is necessary, especially when comparisons are made that are used in the public domain. ISO has defined the following two objectives of life cycle interpretation:

1. Analyze results, reach conclusions, explain limitations, and provide recommendations based on the findings of the preceding phases of the LCA, and to report the results of the life cycle interpretation in a transparent manner.
2. Provide a readily understandable, complete, and consistent presentation of the results of an LCA study, in accordance with the goal and scope of the study.

6.2 LIFE CYCLE ASSESSMENT OF POLYCARBONATE AND TRITAN

Given the issues surrounding BPA-PC and endocrine disruption as discussed in section 2.0, and that Tritan is proposed as its replacement, this study presents the first comprehensive life cycle assessment of Tritan and compares it with the environmental impacts of polycarbonate manufactured via the Melt process.

6.2.1 Goal and Scope

The goal of this LCA is to compare the environmental impacts associated with the manufacture of specified quantity of the polymers (polycarbonate & Tritan) required for fulfilling the functions described by the functional unit. This comparison would be used to determine the environmentally preferable choice between a product made from PC and from Tritan.

Polycarbonates are used in a variety of application. The functional unit for this study is based on two of its most important application; sheets for outdoor shelter use and water bottles. The functional unit for the outdoor shelter use is the quantity of polymer required to make a sheet of 1m x 1m x 0.005 m dimension. Based on the density of PC and Tritan, this corresponds to 6 kg of polycarbonate and 5.9 kg of Tritan. The functional unit for making water bottles would be the quantity of polymer required to make a bottle with a 24 oz capacity. This quantity is obtained by calculating an average mass of polymer used in the various bottles available in the market. The products and their specifications considered are detailed in Table 30. Based on this data, the functional unit is 81.36 g for polycarbonate and 120.40 g for Tritan if an average value for mass of polymer per ml capacity is used. However, this parameter is lower for bottles with higher capacity as shown in Figure 47. The functional unit is 87.72 g for polycarbonate and 119.25 g for Tritan if it calculated based on the trend seen in Figure 47.

Table 30. Product specifications of PC and Tritan based water bottles in the market

Product	**Material**	**Capacity (ml)**	**Weight of bottle (g)**
Nalgene	Tritan	1000	159.72
Camelbak	Tritan	750	122.94
Nalgene	Tritan	650	93.26
Nalgene	Tritan	355	75.08
Bluewave	PC	1890	171.03
Blue Q	PC	1000	106.58
Pro Team	PC	710	99.99
Lock & Lock	PC	500	60.32
Mighty	Polyethylene	650	71.20
Extreme	Aluminum	621	81.00

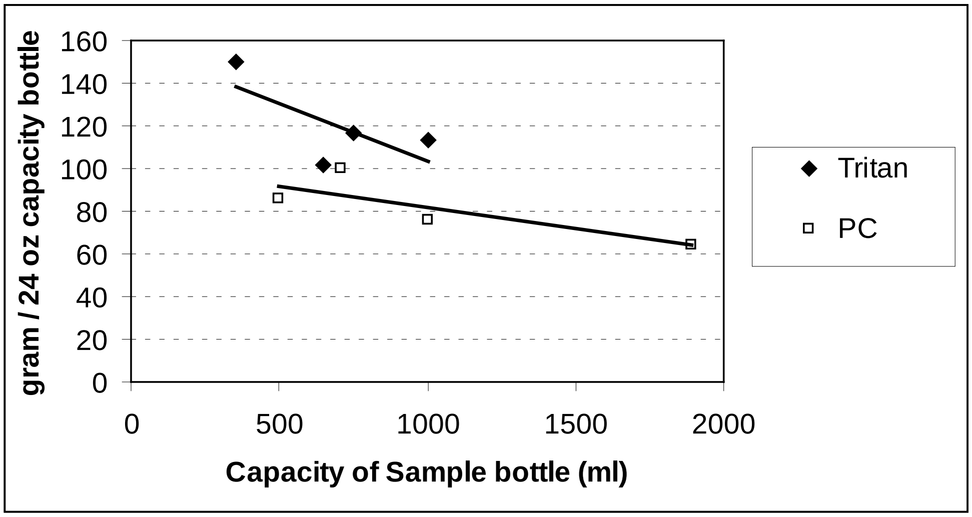


Figure 47. Mass of polymer vs, capacity of bottle

System boundary defines the scope of the LCA study specifying the processes included. The system boundary for manufacture of Tritan covers extraction and purification of organic raw material from crude oil, its transportation to the manufacturing site, production of the three main monomers – 2,2,4,4-tetramethyl-1,4-cyclobutane diol (TMCD), dimethyl terephthalate (DMT), 1,4-cyclohexane dimethanol (CHDM) and their further processing to manufacture Tritan. The system boundary will also include the extraction and purification of metals & supports that are being used as catalyst in the various stages of Tritan manufacture. Figure 48 shows the major categories that have been included in the analysis. The production of TMCD, DMT and CHDM is analyzed in detail in 6.2.2.1.

The system boundary for polycarbonates covers extraction and purification of organic raw material from crude oil, its transportation to the manufacturing site, the production of the two main monomers – BPA and diphenyl carbonate (DPC), and their subsequent processing by melt process to manufacture polycarbonates. To date, only two commercial production methods have been demonstrated to produce high quality resin and remain economically viable. These processes are the two-phase interfacial (phosgene) and the melt transesterification (DPC) process. Brunelle et al gives a more in-depth review of these two processes [132]. The production of polycarbonate is analyzed in detail in 6.2.2.2. Since, most of the major polycarbonate manufacturing companies have started using the melt process; it has been selected as the route for manufacture of PC for comparison with Tritan.

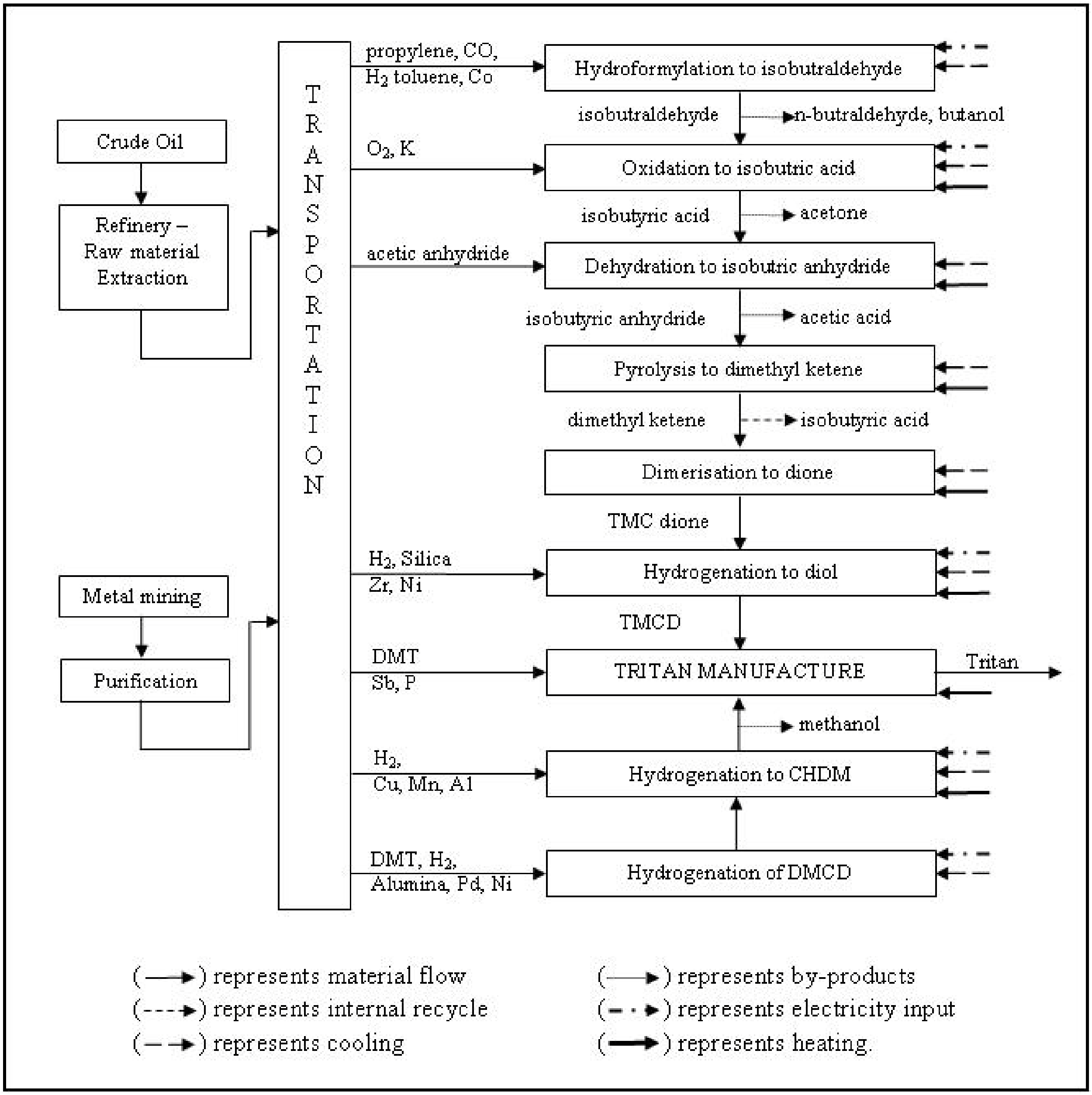


Figure 48. System boundary for LCA of Tritan

6.2.2 Life cycle inventory

LCA is a powerful tool to study the broad environmental impacts of polymers, however many challenges exist due to the emerging nature of products like Tritan. LCA relies on information about resource use, emissions and impacts throughout the life cycle. For emerging products such data is difficult to find in traditional LCA databases. Inventory data on fine and specialty chemicals is difficult to find even for mature products. In this study, we have tried to overcome this issue by developing a new inventory for the material and energy used on site for the synthesis of the monomers used in the production of polycarbonate and Tritan.

6.2.2.1 Life cycle inventory for Tritan

The inventory data for Tritan is developed from the patent data for the production of Tritan and its raw materials. The emissions and downstream treatment is hard to estimate or model and hence have been accounted only for those products that are currently present in the LCA databases. The energy requirement in the manufacture of Tritan has been estimated by designing a model plant in ASPEN Plus (process simulator) operating at conditions specified in the patents.

As described in section 6.0, the three main monomers that are copolymerized to create Tritan are dimethyl terephthalate (DMT), 1,4-cyclohexanedimethanol (CHDM) and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD). The three monomers are added in a molar ratio of 5:4:2 respective, where CHDM is added in 33.33 % excess. Figure 49 shows the synthesis route for making Tritan as described by Eastman Company [133] and figure 50 shows the synthesis route for manufacture of the three main raw materials for manufacture of Tritan.

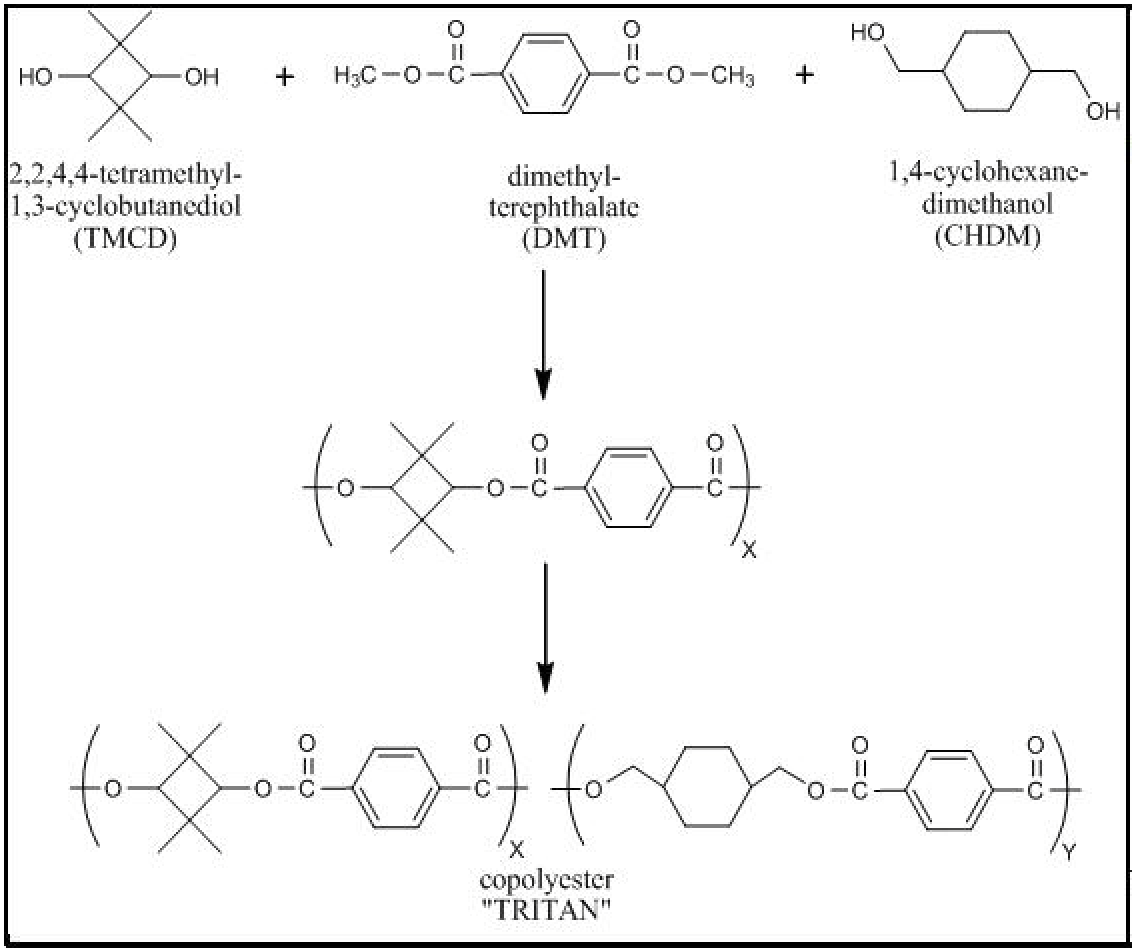


Figure 49. Process chemistry for synthesis of Tritan

The manufacture of TMCD is 6 step process starting from propylene. The hydroformylation of propylene using a ruthenium carbonyl or cobalt carbonyl catalyst gives isobutyraldehyde which is formed as the by-product from the oxo synthesis of propylene to n-butyraldehyde. The kinetics of this reaction have been studied in detail by Yang et al & Gholap et al [134-137]. Isobutyraldehyde then undergoes liquid phase oxidation in presence of an alkaline metal containing compound to form isobutyric acid [138, 139]. Isobutyric anhydride is then manufactured by reaction of isobutyric acid with acetic anhydride. Acetic acid is distilled out as it is being formed in the reaction mixture [140]. Pyrolysis of isobutyric anhydride to dimethylketene (DMK) and isobutyric acid is conducted at 300 °C to 600 °C under reduced pressure of 20 to 500 torr. The resulting mixture is rapidly cooled to condense the isobutyric acid and the unreacted isobutyric anhydride [141]. The highly volatile dimethylketene vapor is sent to an adsorption zone where it is dissolved in an inert solvent comprising liquid (melted) 2,2,4,4-tetramethylcyclobutane-1,3-dione (TMC dione). All the dimethylketene adsorbed by the dione is dimerized to the dione. Finally, TMCD is synthesized by hydrogenation of 2,2,4,4-tetramethylcyclobutane-1,3-dione in the presence of a promoted copper, cobalt or nickel-based catalyst [142-146].

Manufacture of DMT is a two step process starting from p-xylene. Terephthalic acid is produced by oxidation of p-xylene by oxygen in air. The oxidation is conducted using acetic acid as solvent and a catalyst composed of cobalt and manganese salts, using a bromide promoter [147, 148]. The terephthalic acid is then esterified with methanol to for DMT.

Manufacture of CHDM is a two-step process involving hydrogenation of DMT to dimethyl-1,4-cyclohexane dicarboxylate (DMCD) and then further hydrogenation to CHDM in presence of a Raney metal catalyst [149-151].

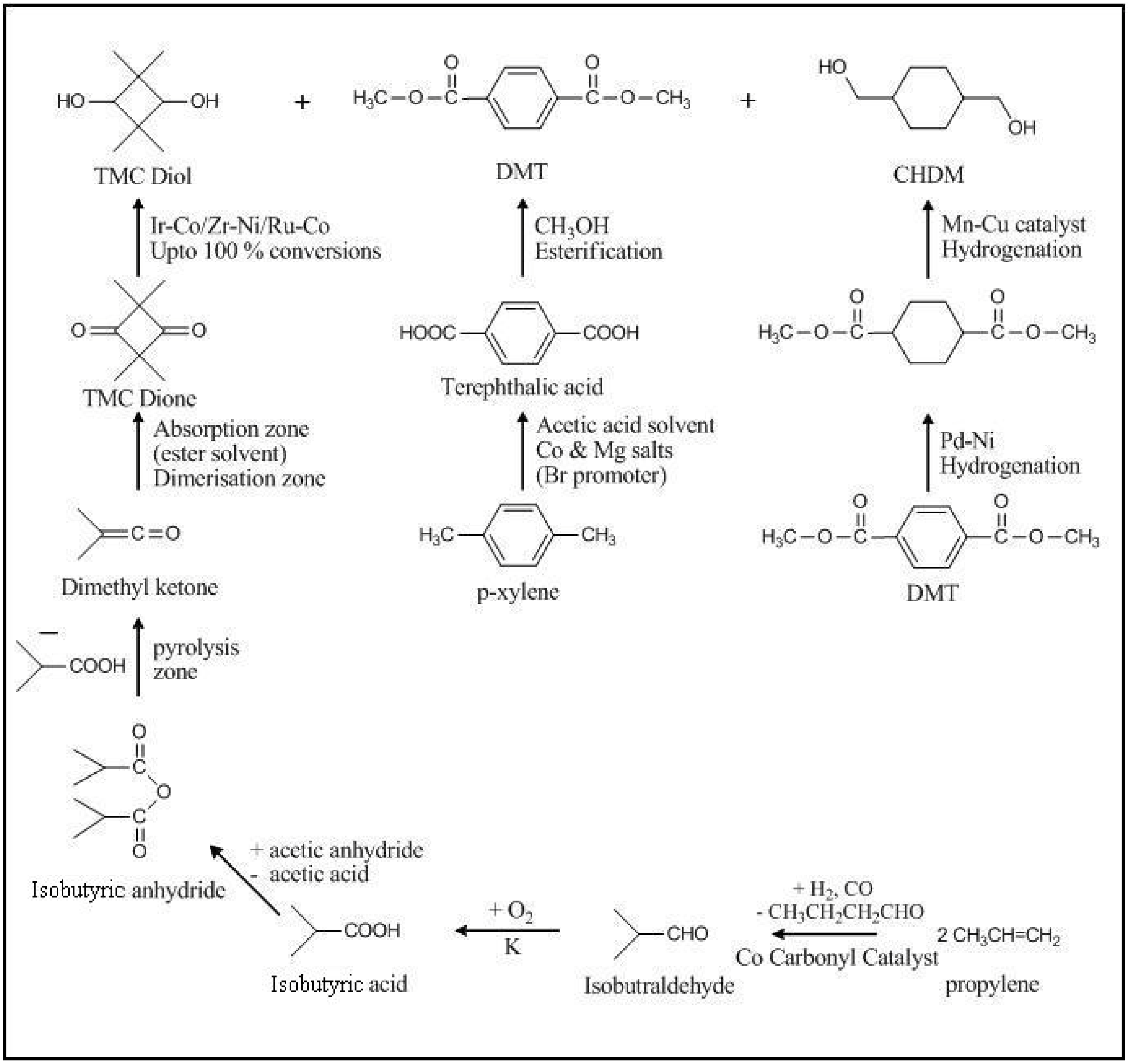


Figure 50. Process chemistry for synthesis of monomers used in the manufacture of Tritan

In most of the reaction steps, 100 % conversion and selectivity cannot be achieved and hence there is a significant amount of unreacted material that would be present in the product stream. Depending on how this unreacted raw material is dealt with, the environmental impacts would vary. Hence, we have considered two sets of inventory scenario in this study. In the first scenario, none of the raw material that is recovered after product separation is recycled back to the process. In the second scenario, 100% of unreacted material that can be recovered is sent back as a recycle stream.

The conversion, selectivity and reaction conditions used for developing the material and energy requirement inventory for both these scenarios are shown in Table 31 for TMCD synthesis & Table 32 for CHDM & Tritan synthesis. These tables also include the information about the different databases used to characterize the inventory components. The inventory for DMT is based on the amount used as specified in patented literature [133] and is directly obtained using the ETH-ESU 96 database in SimaPro.

The energy requirement varies in both the recycling scenarios; the first with no internal recycle and second with complete internal recycle. Therefore, the inventory for the energy requirement is calculated separately for both these scenarios using Aspen Plus. In order to develop the inventory a simulated plant is designed for the manufacture of Tritan starting from propylene for the synthesis of TMCD and DMT for the synthesis of CHDM. The simulated plant was designed for the reaction conditions, conversion and selectivity detailed in Table 31 & 32 for the various steps involved. Figures 51, 52 & 53 show the process flow diagram for the scenario with 100 % recycle of the unreacted raw material that could be separated. For the no internal recycle scenario, the unreacted raw material streams were discarded and not recycled back. The raw material and energy requirement inventory for the different manufacturing steps is given in Table 33.

Table 31. Conversion, selectivity & reaction conditions in synthesis of TMCD

	Product	**Selectivity (%)**	**Conversion (%)**	**Pressure (atm)**	**Temperature (°C)**	**Database / Reference**
Step 1: Hydroformylation of propylene to isobutyraldehyde	Isobutyraldehyde	47.5	100	9.87	150	SimaPro - ETH - ESU 96 & Ecoinvent, [134, 135, 137]
	n-butyraldehyde	47.5				
	Butanol	5				
Step 2: Oxidation to isobutyric acid	Isobutyric acid	93.4	96.6	4.84	60	SimaPro - ETH - ESU 96 & Ecoinvent, [139]
	Acetone	5.49				
Step 3: Dehydration to isobutyric anhydride	Isobutyric anhydride	100	92.4	0.526	118	SimaPro Ecoinvent, [140]
Step 4: Pyrolysis to dimethyl ketene	Dimethyl ketene	100	54	0.162	495	[141]
Step 5: Dimerization to form TMC dione	TMC dione	100	100	1	117	[141]
Step 6: Hydrogenation to diol	TMCD	100	97.8	32	160	SimaPro - ETH - ESU 96 & Ecoinvent, [142]

Table 32. Conversion, selectivity & reaction conditions in synthesis of CHDM & Tritan

	Product	**Selectivity (%)**	**Conversion (%)**	**Pressure (atm)**	**Temperature (°C)**	**Database / Reference**
Step 1: Hydrogenation of DMT to DMCD	DMCD	100	97.58	125.1	180	SimaPro ETH-ESU 96, [150]
Step 2: Hydrogenation of DMCD to CHDM	CHDM	99.92	99.46	62.05	220	SimaPro ETH-ESU 96, [150]
DMT	-	-	-	-	-	SimaPro ETH-ESU 96, [133]
Synthesis of Tritan	Tritan	100	91	0.95	238	SimaPro Ecoinvent, [133]

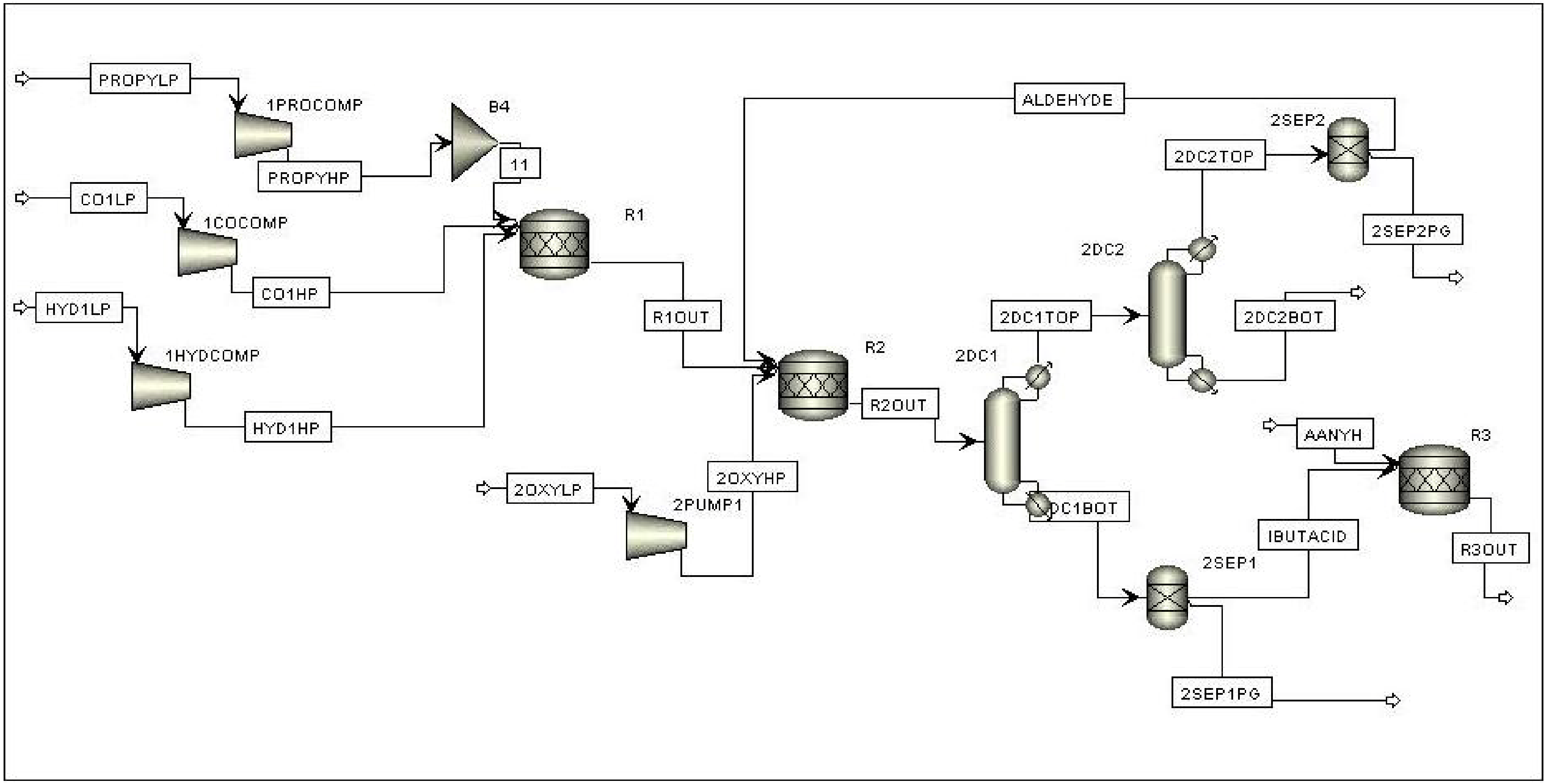


Figure 51. Process flow diagram for steps 1 to 3 in the synthesis of TMCD

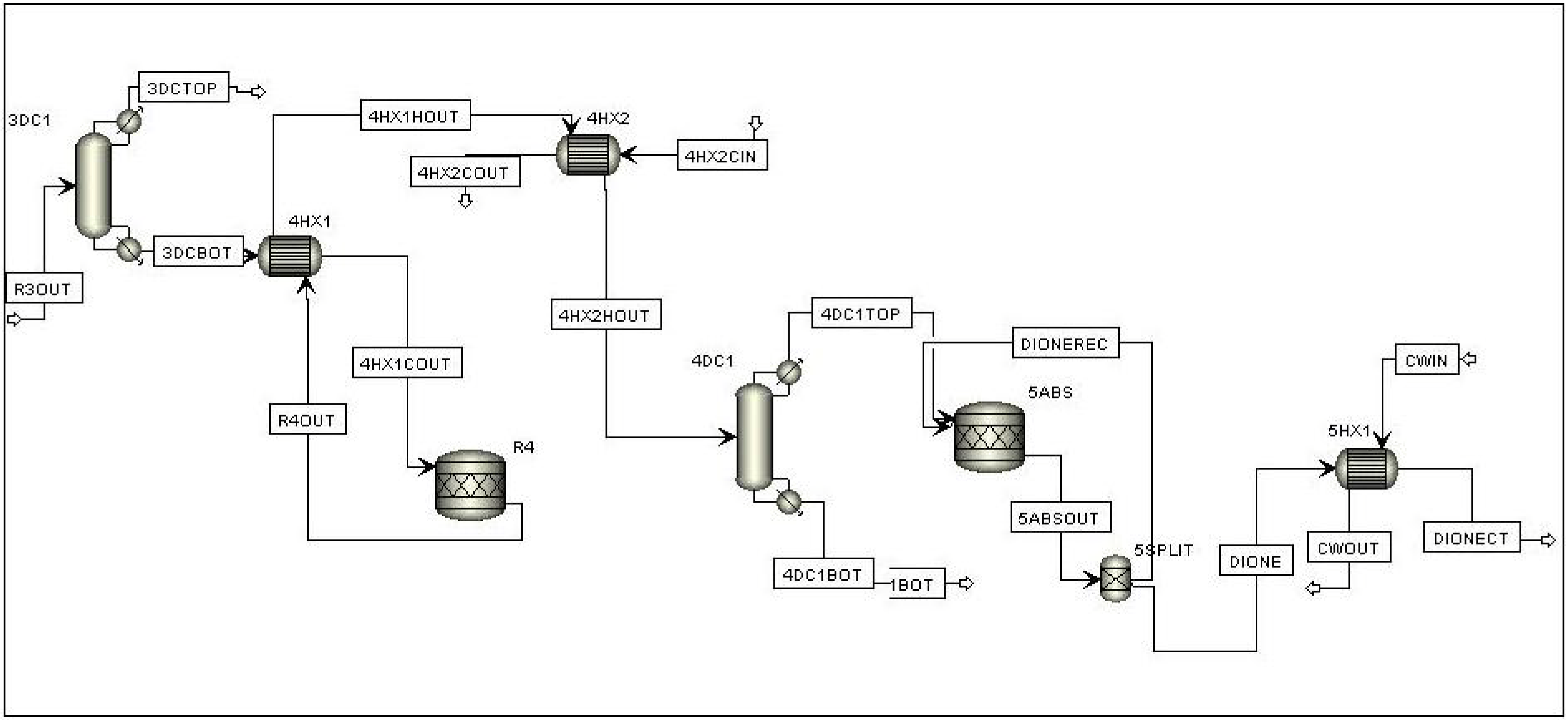


Figure 52. Process flow diagram for steps 4 & 5 in the synthesis of TMCD

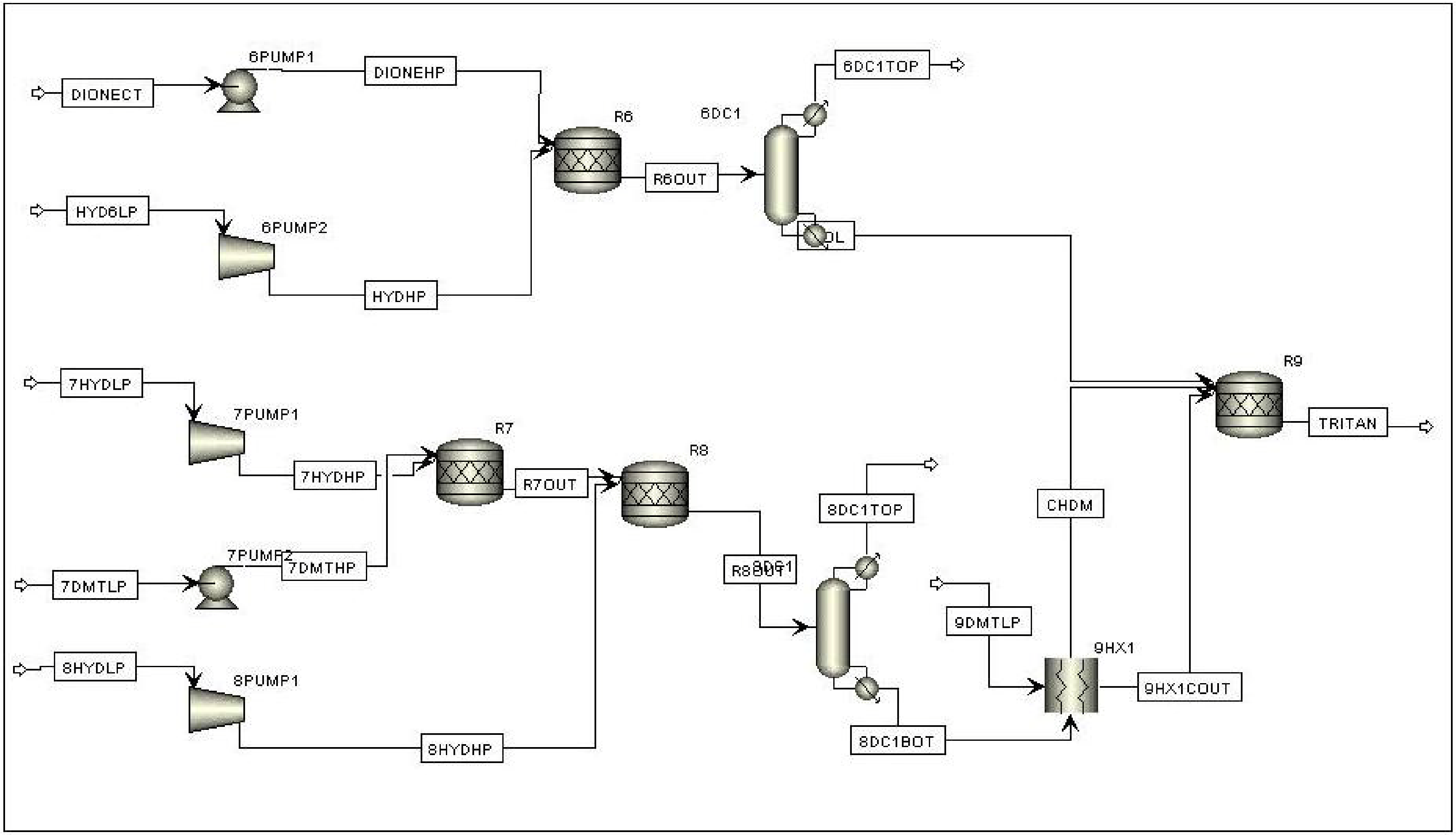


Figure 53. Process flow diagram for step 6 in the synthesis of TMCD, steps 1 & 2 in the synthesis of CHDM and synthesis of Tritan

Data from Table 31 & 32 and results from the process simulations are used to develop the inventory for the steps involved in the manufacture of Tritan (Table 33). Since detailed information on the life of catalysts is not available for these processes, it is assumed that the catalyst deactivation period is 3 months & the quantity of catalyst used is accordingly allocated.

Table 33. Life cycle inventory for steps involved in the manufacture of Tritan

	Component	**No Recycle**	**100 % Recycle**
		Material (kg/hr) & Energy (kW.hr)	
Step 1 (TMCD): Hydroformylation of propylene to isobutyraldehyde			
Raw Material	Propylene	7.7916	1.7379
	Hydrogen	0.3927	0.0874
	Oxygen	5.1864	1.1568
	Cobalt	1.07E-05	2.39E-06
Product	Isobutyraldehyde	6.3419	1.4145
By Product	n-butyraldehyde	6.3419	1.4145
	Butanol	0.6862	0.1343
Energy	Electricity	1.6284	0.3726
	Cooling	8.6396	1.8368
Step 2 (TMCD): Oxidation of isobutyraldehyde to isobutyric acid			
Raw Material	Isobutyraldehyde	6.3419	1.4145
	Oxygen	1.3593	0.2832
	Potassium	0.00063	1.39E-04
Product	Isobutyric acid	6.9981	1.5411

Table 33 (continued).

By-product	Acetone	0.2709	0.0597
	Peroxide	0.0483	0.0106
	Isopropyl alcohol	0.0198	0.0044
	Unreacted isobutyraldehyde	0.2156	-
Energy	Electricity	0.1022	0.0211
	Cooling	7.5619	1.9987
	Heating	2.0474	0.5575
Step 3 (TMCD): Dehydration of isobutyric acid to isobutyric anhydride			
Raw Material	Isobutyric acid	6.8981	1.5411
	Acetic anhydride	4.9958	1.8232
Product	Isobutyric anhydride	5.6916	2.7923
By-product	Unreacted isobutyric acid	0.5222	-
	Unreacted acetic anhydride	1.3021	-
	Acetic acid	4.3452	2.1162
Energy	Cooling	1.0863	5.1593
	Heating	2.5412	5.4604
Step 4 & 5 (TMCD): Pyrolysis of isobutyric anhydride to dimethyl ketene & its dimerisation to TMC dione			
Raw Material	Isobutyric anhydride	5.6916	2.7923
Product	TMC dione	1.3613	1.2234
By-product	Isobutyric acid	1.7118	-
	Unreacted anhydride	2.6182	-

Table 33 (continued).

Energy	Cooling	0.3869	5.7413
	Heating	1.0640	6.2535
Step 6 (TMCD): Hydrogenation of TMC dione to TMCD			
Raw Material	TMC dione	1.3613	1.2234
	Hydrogen	0.0384	0.0352
	Zirconium	1.89E-06	1.73E-06
	Nickel	3.91E-05	3.58E-05
	Silica	6.3E-05	5.78E-05
Product	TMCD	1.3634	1.2557
By-product	Unreacted TMC dione	0.0308	-
Energy	Electricity	0.1125	0.3357
	Cooling	0.7748	2.3959
	Heating	0.1709	0.4318
Step 1 (CHDM): Hydrogenation of DMT to DMCD			
Raw material	DMT	3.7863	2.6151
	Hydrogen	0.1153	0.0796
	Palladium	1.75E-05	1.21E-05
	Nickel	3.51E-08	2.42E-08
	Alumina	0.000175	1.21E-04
Product	DMCD	3.8096	2.6313
By-product	Unreacted DMT	0.0916	-

Table 33 (continued).

Energy	Electricity	0.6041	0.4172
	Cooling	1.2078	0.8342
Step 2 (CHDM): Hydrogenation of DMCD to CHDM			
Raw material	DMCD	3.8096	2.6313
	Hydrogen	0.1528	0.1055
	Copper	7.25E-06	5.01E-06
	Manganese	1.09E-06	7.55E-07
	Aluminum	3.6E-06	2.49E-06
Product	CHDM	2.7268	1.8834
By-product	Methanol	1.2116	0.8351
	Unreacted DMCD	0.0236	-
Energy	Electricity	0.5722	0.3952
	Cooling	1.1120	0.7681
	Heating	0.3177	0.2194
Manufacture of Tritan			
Raw material	TMCD	1.3634	1.2557
	DMT	4.498	4.2274
	CHDM	2.7268	1.8834
	Tin	0.0017	0.00147
	Phosphorus	0.00026	0.00022
Product	Tritan	5.9	5.9

Table 33 (continued).

By-product	Methanol	1.3783	1.3783
	Unreacted TMCD	0.11227	-
	Unreacted DMT	0.4131	-
	Unreacted CHDM	0.8658	-
Energy	Cooling	-	0.3282
	Heating	0.0916	0.8967

6.2.2.2 Life cycle inventory for polycarbonate

To date, the two-phase interfacial (phosgene) and the melt transesterification (DPC) process are the only two commercial production processes that have been demonstrated to produce high quality resin and remain economically viable. Brunelle et al gives an in-depth review of these two processes [132] and the general scheme for both these processes is shown in Figure 54. Since most of the major polycarbonate manufacturing companies have started using the melt process, it has been selected for comparison with Tritan.

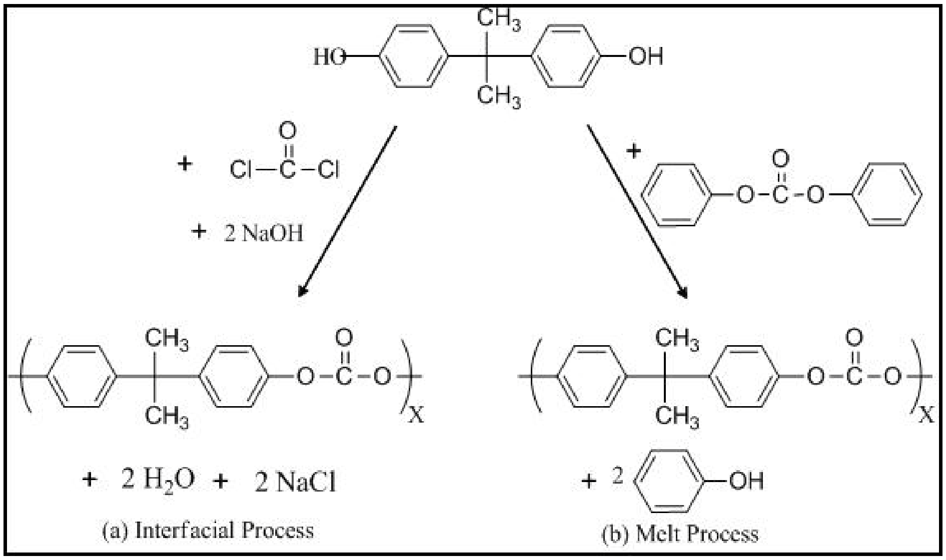
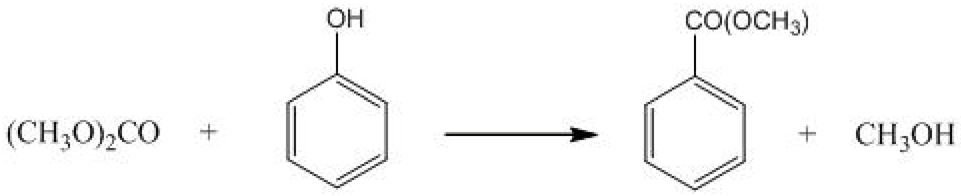
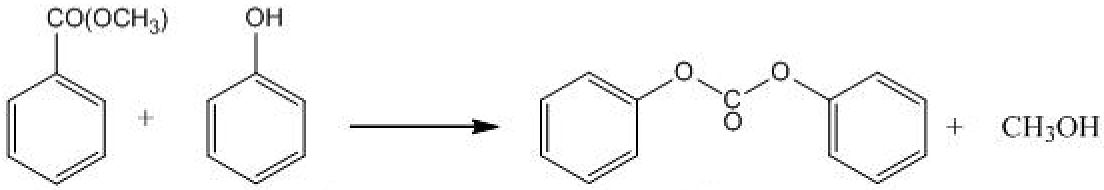


Figure 54. Process chemistry for synthesis of polycarbonate via interfacial & melt process

The melt process involves base-catalyzed condensation polymerization of DPC with BPA. The reaction is run at sufficiently high temperature (150 – 350 °C) such that the starting monomer, oligomers and the final polymer remain molten throughout the course of the reaction. The reactor pressure is staged throughout the course of the reaction to allow the efficient removal of phenol with pressure ranging from 150-200 torr initially to 0.1-1 torr in the later stages of the conversion. Using this method the PC resin is prepared without any additional solvent, drying step or phosgene [152]. The phenol obtained as the by product reacts with dimethyl carbonate (DMC) to recover the diphenyl carbonate (DPC) which is recycled to the PC manufacturing unit. The synthesis of DPC from DMC and phenol takes place through the formation of methyl phenyl carbonate (MPC) and can be catalyzed either by homogeneous or heterogeneous catalysts. The reaction of DMC to DPC is a two-step reaction. The first step is the transesterification of DMC with phenol to the intermediate MPC and methanol (see equation 6.1). The second step involves transesterification of MPC with phenol (see equation 6.2) [153].



(6.1)



(6.2)

The methanol obtained as the by-product reacts with carbon monoxide and oxygen in the DMC manufacturing unit (see equation 6.3) [154].

$$2\,CH_3OH + CO + 0.5\,O_2 \longrightarrow (CH_3O)_2CO + H_2O \tag{6.3}$$

In order to develop the inventory for PC, a simple plant was designed using Aspen Plus for the manufacture of polycarbonate from bisphenol-A and DPC. The recycling units for DPC and DMC were also included. The simulated plant was designed at the reaction conditions, conversion and selectivity detailed in Table 34 for the various steps involved. Figure shows the process flow diagram for the manufacture of PC and Figure 56 shows the process flow diagram for 100% recycle of the unreacted raw material that could be separated. The energy requirement in the manufacture of polycarbonates is estimated from the simulated process operating at conditions specified in the patents. The raw material and the energy consumption inventory for the different manufacturing steps is given in Table 34.

Data from Table 34 and results from the process simulations are used to develop the inventory for the steps involved in the manufacture of polycarbonate (Table 35). Since detailed information on the life of catalysts used is not available for these processes, it is assumed that the catalyst deactivation period is 3 months & the quantity of catalyst used is accordingly allocated.

Table 34. Conversion, selectivity & reaction conditions for steps in synthesis of polycarbonate, DPC & DMC

	Product	**Selectivity (%)**	**Conversion (%)**	**Pressure (atm)**	**Temperature (°C)**	**Database / Reference**
Polycarbonate manufacture	Polycarbonate (phenol – byproduct)	100	100	0.02	240	SimaPro Ecoinvent, [132, 155, 156]
DPC manufacture	DPC (MeOH – byproduct)	95	16	14.61	180	SimaPro ETH-ESU 96, [153, 157-159]
DMC manufacture	DMC (water – by product)	100	32.5	24.17	120	SimaPro Ecoinvent, ETH-ESU 96, [154, 160]

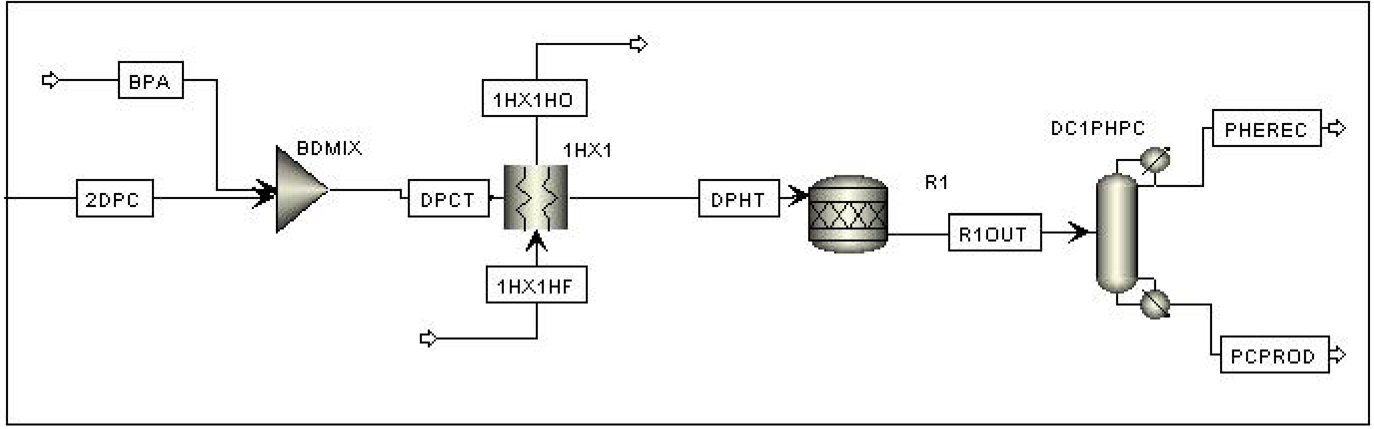


Figure 55. Process flow diagram for manufacture of polycarbonate

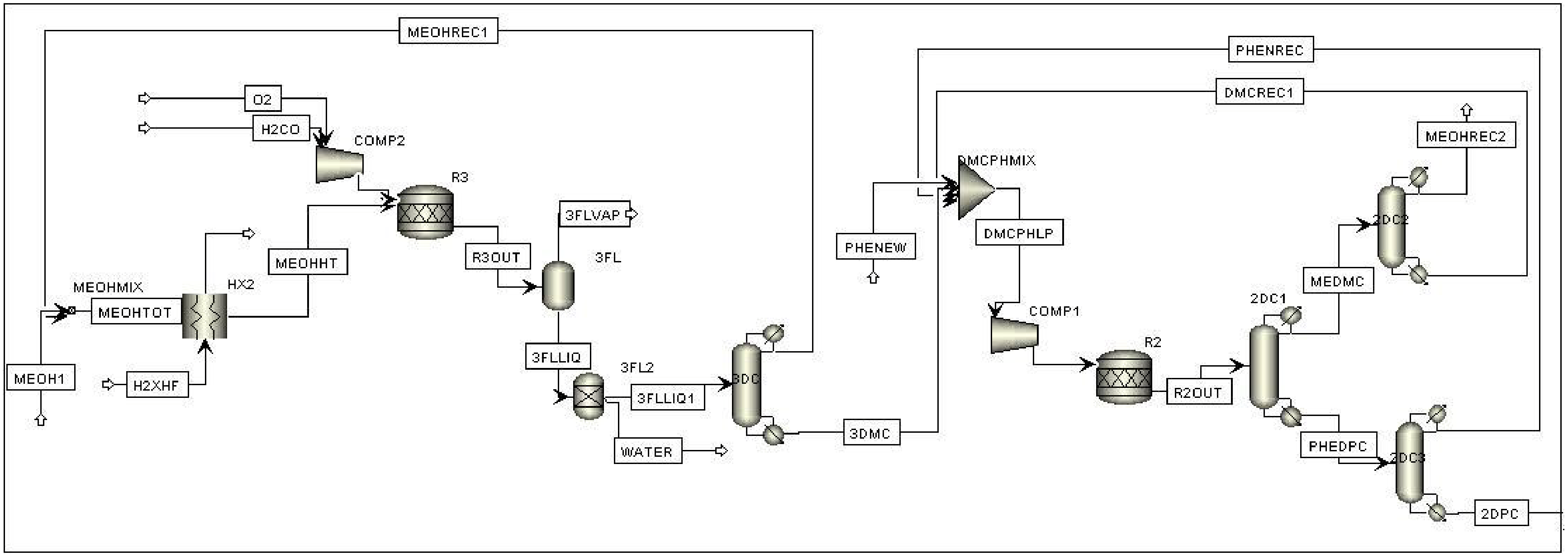


Figure 56. Process flow diagram for manufacture of DPC and DMC

Table 35. Life cycle inventory for manufacture of polycarbonate

	Component	**Material (kg/hr) / Energy (kW.hr)**
Raw Material	Bisphenol-A	4.3238
	Phenol	0.0778
	Methanol	0.1408
	Oxygen	0.3178
	Carbon monoxide	0.5466
	NaOH (PC catalyst)	5.04E-07
	Tin (DPC catalyst)	7.71E-05
	Copper (DMC catalyst)	1.63E-04
Product	Polycarbonate	4.4896
By-product	Water	0.3948
Energy	Electricity	0.8250
	Cooling	16.7306
	Heating	15.2006

6.2.3 Allocation

Allocation is an important aspect in the goal & scope definition as well as in the inventory. Many processes result in several products. Therefore the environmental burdens from the process must be split on the different output products. It is agreed that allocation should be made as logical as possible, there is controversy as to what is the most logical allocation as it would vary depending on the case being considered. A sensitivity analysis is performed to study the effect of mass, price and 100% allocation to the primary product on the environmental impacts. Table 36 shows the allocation percentages for various stages in the manufacture of Tritan.

Table 36. Allocation percentages for different stages of Tritan manufacture

Process	Product & By products	Allocation Percent		
		Mass	Economic Value (EV)	No Allocation
Hydroformylation to isobutyraldehyde	Isobutyraldehyde n-butryraldehyde Butanol	47.73 47.73 4.54	51.50 43.13 5.38	100 - -
Oxidation to isobutyric acid	Isobutyric acid Acetone	96.27 3.73	98.43 1.57	100 -
Dehydration to isobutyric anhydride	Isobutyric anhydride Acetic acid	56.89 43.11	65.82 34.18	100 -
Pyrolysis to DMK & its absorption to TMC dione	TMC Dione Isobutyric acid	44.3 55.7	100* -	100 -
Hydrogenation to CHDM	CHDM Methanol	69.28 30.72	92.27 7.73	100 -
Polymerization of DMT, TMCD & CHDM to Tritan	Tritan Methanol	80.87 19.13	97.45 2.54	100 -

*Allocation only used in the ‘No internal recycle’ scenario because isobutyric acid is recycled in the ‘Full internal recycle’ scenario.

The price allocation is based on the contribution of the value of a component (Mass x Price) to the value of all the components involved in the product stream. The environmental impacts using the “Mass Allocation” and “Economic Value Allocation” are compared for the scenario with full internal recycle for Tritan.

In case of polycarbonates manufacture, water is formed as a by-product. The mass allocation used in the LCI for PC’s is 92.47% for PC and 7.53% for water. Since, water produced as an industrial by-product would have negligible economic value, the economic value allocation for PC is 100%.

6.2.4 Life cycle impact assessment

A life cycle assessment using SimaPro 7 software is conducted to compare the environmental impacts of polycarbonates and Tritan. SimaPro is a tool which uses industry & research data to quantify the environmental impacts of a product or process. It contains inventory databases that include material & energy use and emission for many materials, fuels and processes. TRACI 2 v3.01 which is an impact assessment method built into SimaPro is employed for the LCA without adaptation [161]. It is a midpoint assessment tool developed by the US Environmental Protection Agency (EPA) which assesses the inventories and groups them into environmental impact categories.

6.3 RESULTS AND DISCUSSIONS

The environmental impacts that are studied using the TRACI impact assessment tool are Global warming potential (GWP), Acidification (ACID), Carcinogens (CAR), Non-carcinogens (NCAR), Respiratory effects (RESP), Eutrophication (EUTR), Ozone Depletion (OZDP), Ecotoxicity (ECO) and Smog potential (SMOG). The different scenarios that were studied in the manufacture of polycarbonates and Tritan are discussed in the following sections.

6.3.1 Effect of recycling strategy on environmental impacts of Tritan

The two scenarios that are analyzed for the manufacture of Tritan are – "No recycle" and "Complete internal recycle". In the "no recycle" scenario, none of the raw material that is recovered after product separation is recycled back to the process. In the second scenario, 100% of unreacted material that can be recovered is sent back as a recycle stream. The inventory used for analysis is discussed in section 6.2.2.1 and the results are shown in Figure 57.

As a result of recycling the potentially separable unreacted chemicals and by-products, the overall material requirement for the production of the Tritan reduces. There is also a reduction in the energy requirement for the primary manufacturing units because of the reduced material that needs to be processed as a result of the recycle. However, there is also an increase in the amount of energy required in the separation units to separate these recyclable products from the by-product streams. The combined effect of all these factors is expressed in Figure 57 where 10 to 20% reduction in the impacts is observed in most categories studied. Since the most effective recycling likely to be employed in industrial practice, the "complete internal recycle" scenario is used for further analysis.

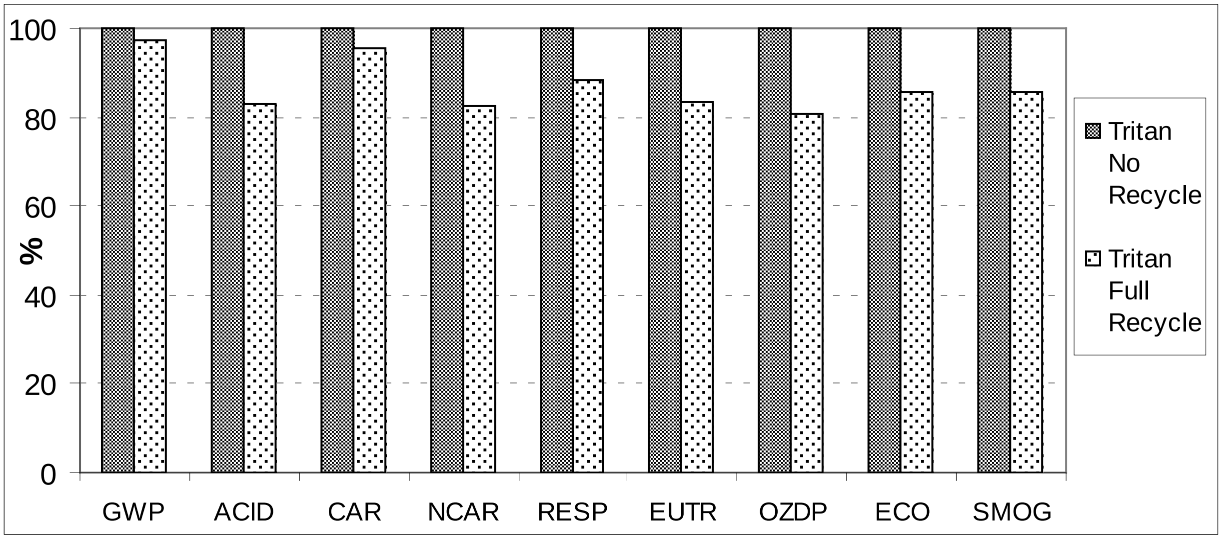


Figure 57. Comparison of environmental impacts for Tritan with "No recycle" and "Full internal recycle"

6.3.2 Effect on allocation on environmental impacts of Tritan

The process of manufacture of Tritan via the route described in section 6.2.2.1 involves a significant amount of n-butyraldehyde, acetic acid and methanol formed as by-products over the entire synthesis process. Table 37 shows the distribution of raw material input that is converted to final products & by-products in the manufacture of Tritan and polycarbonates. Since, Tritan accounts for only 48.55% of the raw material consumed, it is extremely important to assign an appropriate allocation strategy to study the environmental impacts of Tritan. As discussed in section 6.2.3, the three different allocation strategies studied are mass allocation, economic value allocation and 100% allocation to primary product. The LCI for the "Full internal recycle" was used for this analysis. The comparative impacts for these strategies are shown in Figure 58.

Table 37. Product distribution for Tritan and polycarbonate

Tritan			**Polycarbonates**		
	kg	**%**		**kg**	**%**
Total Raw Material	12.151		**Total Raw Material**	6.673	
Product - Tritan	5.9	48.55	**Product** - PC	6.0	89.91
By-products			**By-products**		
Methanol	2.230	18.35	Water	0.489	7.32
Acetic acid	2.116	17.41	Material lost as impurity in product	0.184	2.77
n-butyraldehyde	1.415	9.34			
Others + Material lost as impurity in product	0.491	4.04			

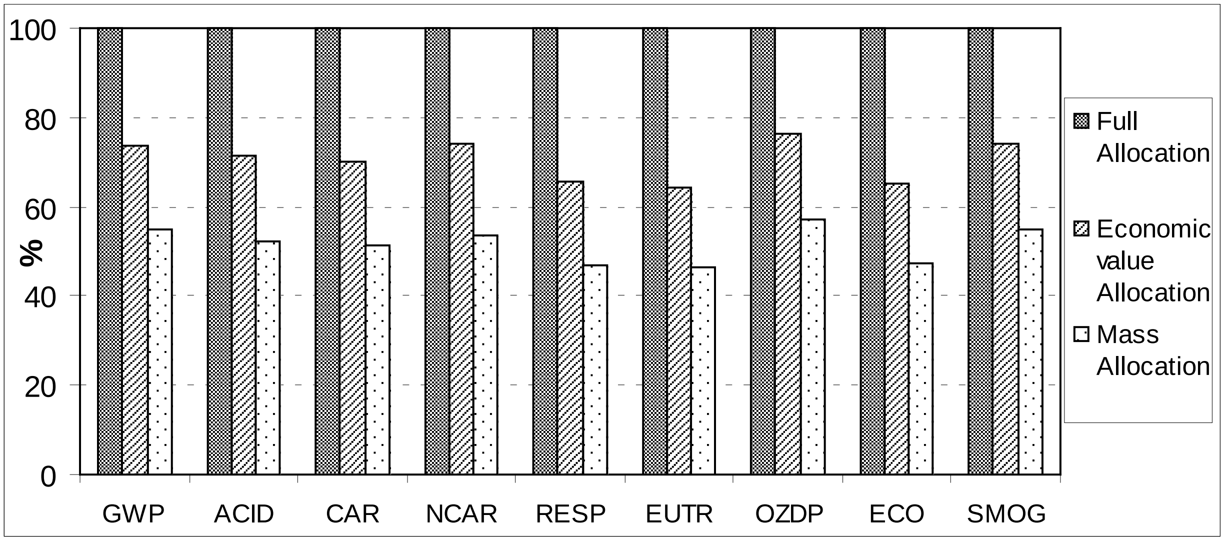


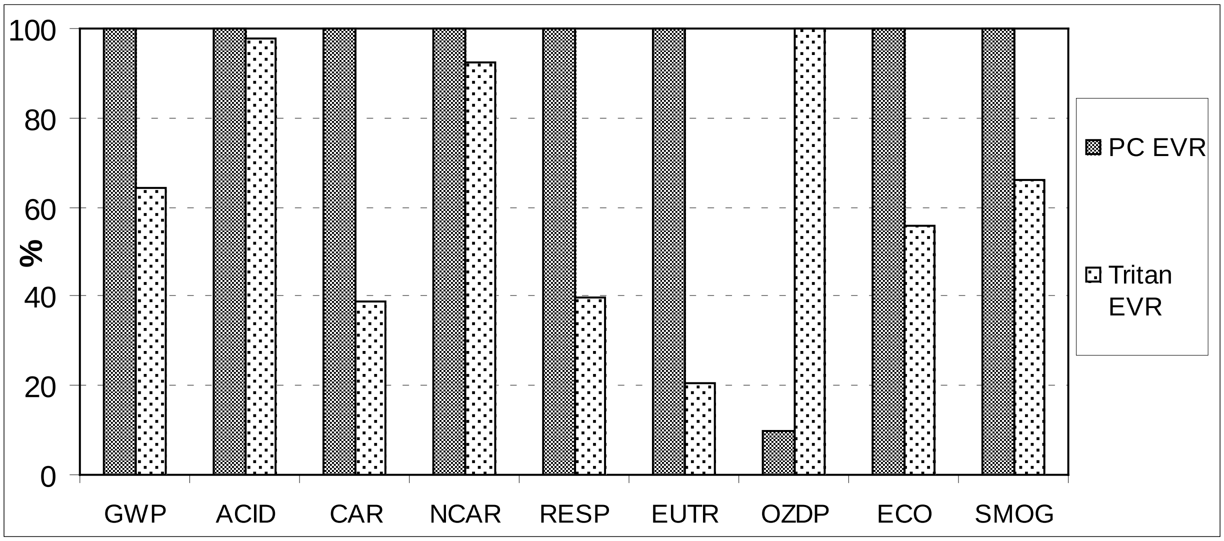
Figure 58. Effect of different allocation strategies on environmental impacts of Tritan

As expected, the environmental impact for the case where 100% allocation is given to the primary product is the highest compared to cases with economic value and mass allocation. Methanol, acetic acid and n-butyraldehyde which are the main by-products in the process of manufacture of Tritan are also important building blocks in the chemical industry. Therefore, it would be most appropriate to consider the economic value allocation in the analysis of environmental impacts of Tritan and its comparison with polycarbonate.

Since, polycarbonates have only water as the by-product, the environmental impacts using mass allocation is 92.46% of the impacts observed with economic value allocation (100% allocation to PC). The economic value allocation would be more appropriate for polycarbonates too and is considered for further analysis.

6.3.3 Comparison of environmental impacts of Tritan and polycarbonate

The comparative results of environmental impacts of Tritan and polycarbonate in different categories are shown in Figure 59. The impacts are based on the LCI developed using the complete internal recycle scenario and the economic value allocation. Tritan has significantly lower impact than polycarbonates in the global warming potential, carcinogens, respiratory effects, eutrophication, ecotoxicity and smog categories. Tritan has marginally lower impacts than PC in the acidification and non-carcinogen category. PC has lower impact than Tritan only in the ozone depletion category. DMT used for manufacturing Tritan and also for manufacturing its monomer CHDM is the major contributor in this category.



(EVR – Economic value allocation & full internal recycle)

Figure 59. Comparison of environmental impacts of PC & Tritan (1m x 1m x 0.005m sheet)

Figure 60 shows the comparison of the absolute impacts in various categories for both allocation methods for Tritan and polycarbonates. The y-axis represents the impacts in terms of the kg CO_2 equivalent for global warming, H^+ mole equivalent for acidification, kg benzene equivalent for carcinogens, kg toluene equivalent for non-carcinogens, kg particulate matter < 2.5 micrometer for respiratory effects, kg Nitrogen equivalent for eutrophication, kg CFC-11 equivalent for ozone depletion, kg 2,4-D (2,4-dichlorophenoxy acetic acid) equivalent for ecotoxicity and kg NO_x equivalent for the smog category. There is no reference that suggests a way to compare between the different impact categories. For e.g. one cannot conclude that the impact of global warming potential (38.5 kg CO_2 equivalent) for polycarbonates is more than the impact of ecotoxicity (23 kg 2,4-D equivalent) since both have been evaluated using different reference substances and quantify the impact in different categories.

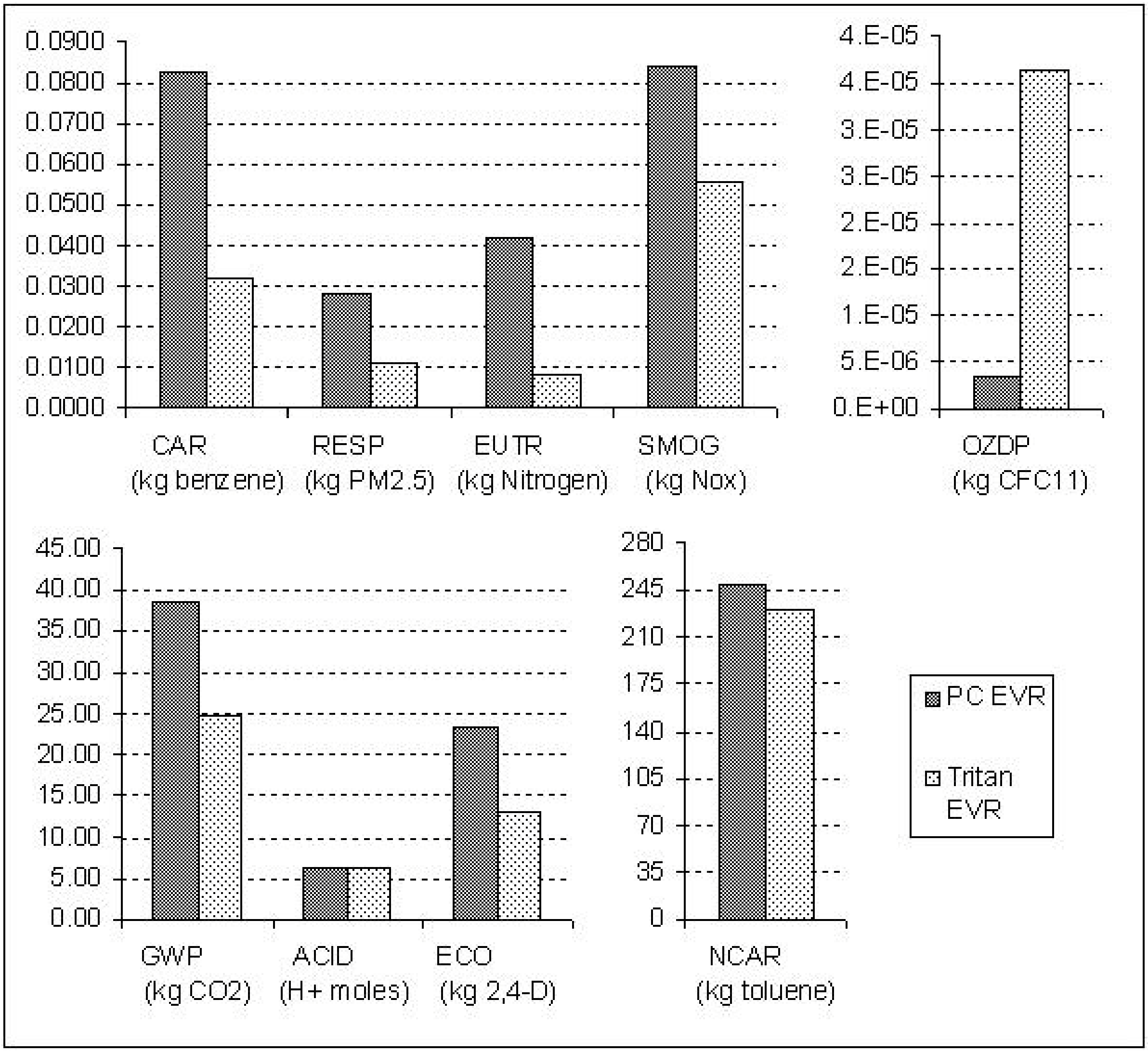


Figure 60. Absolute environmental impacts of polycarbonate and Tritan

Use of mass allocation to account for the by-products results in about 7.5 % reductions in the impacts of PC and about 25 – 29 % reductions in the impacts for Tritan. As a result, if mass allocation is used in the impact assessment, the comparison between PC and Tritan would shift more in favor of Tritan compared to the results in Figure 59 & 60.

6.3.4 Effect of functional units on environmental impacts of PC & Tritan

The environmental impacts shown in Figure 58 & 59 are based on a functional unit of a 1m x 1m x 0.005m sheet of the polymer, which corresponds to 6 kg of PC and 5.9 kg of Tritan. However, if a 24 oz bottle is considered as the functional unit, then the corresponding weight of PC is 87.72 gm and that of Tritan is 119.25 gm (as per the analysis in section 6.2.1 using the best case scenario for Tritan). This would result in a significantly different comparison as the amount of Tritan required increases by about 38 %. The results of this comparison are shown in Figure 61.

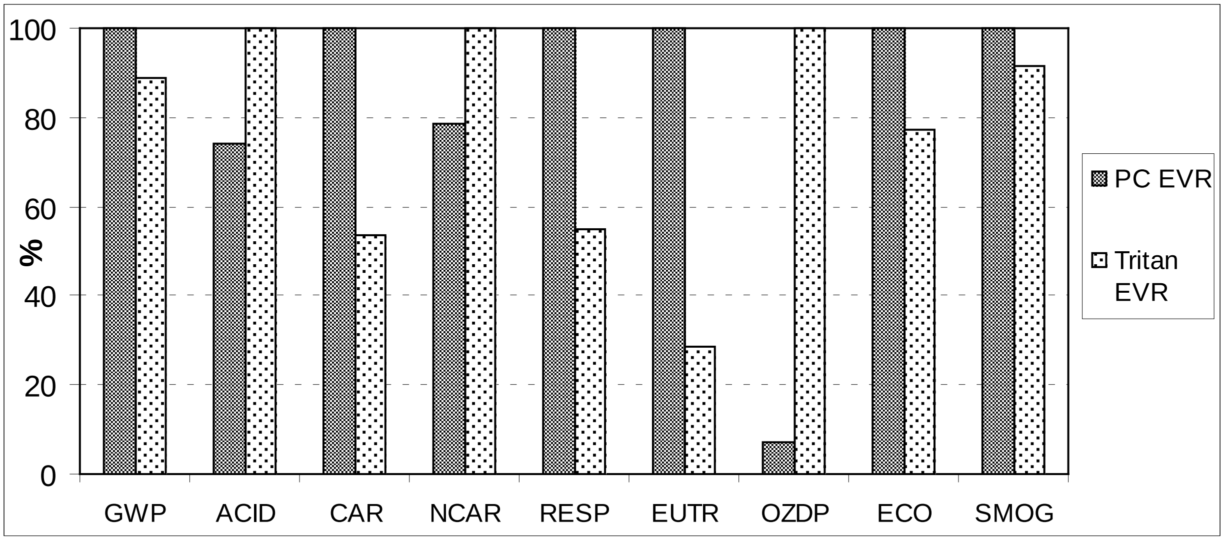


Figure 61. Comparison of environmental impacts of PC & Tritan (24 oz bottle)

For this functional unit, PC has significantly higher environmental impact than Tritan in the carcinogens, respiratory effects, eutrophication and ecotoxicity category. Their impacts are similar in the global warming and smog category and Tritan has significantly higher impacts in the acidification, non-carcinogens and ozone depletion category. Based on these results, it is important that the companies manufacturing bottles made from Tritan need to look into their design models to make sure that the bottles are not overdesigned and additional material is not consumed. If the design is appropriate, then Tritan does not seem to have a significant advantage over the use of PC in the bottle manufacturing sectors as far as the environmental impacts are concerned.

6.3.5 Contribution of components of Tritan to its environmental impacts

Dimethyl terephthalate, 1,4-cyclohexane dimethanol and 2,2,4,4-tetramethyl cyclobutanediol are the three main components that are involved in Tritan manufacturing. Figure 62 shows the contribution of each of these components to the total environmental impact of Tritan compared to their contribution by weight %.

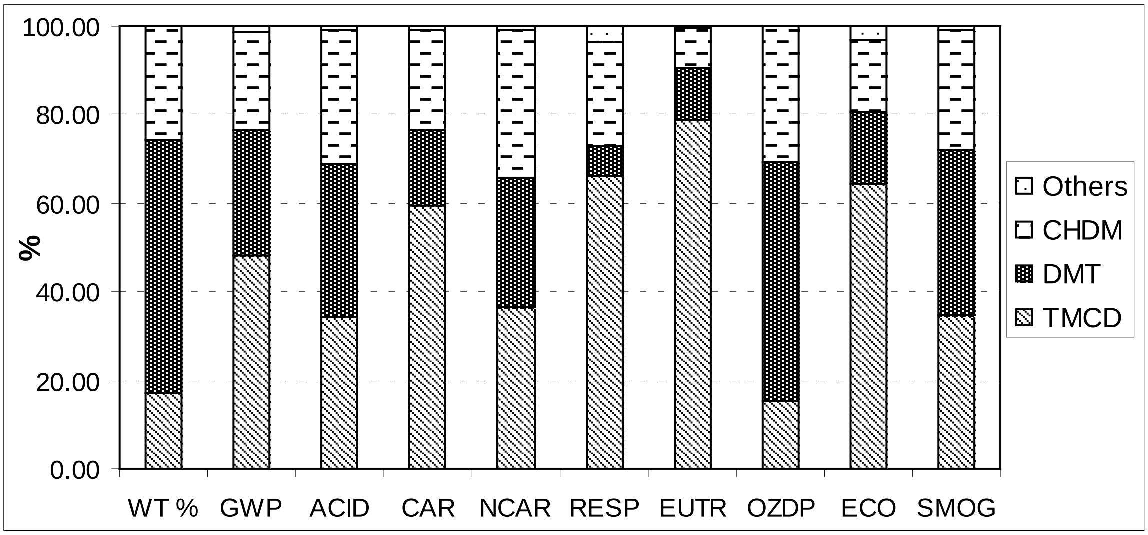


Figure 62. Contribution of CHDM, DMT & TMCD to the environmental impact of Tritan

For Tritan, the weight percent contribution of CHDM, DMT & TMCD, & is 25.57, 57.39 & 17.04 % respectively. However, as seen in Figure 61, in most impact categories the contribution is skewed more towards TMCD. TMCD contributes more than 35 % of the total impact in all the categories except ozone depletion. The contribution is more than 55 % in the carcinogens, respiratory effects, eutrophication and ecotoxicity categories. This skewed behavior is because of material and energy consumed at each step in the manufacture of TMCD which as discussed in section 6.2.2.1 is a 6 step process.

Within TMCD, the significant contribution is from acetic anhydride, propylene, carbon monoxide and the energy consumed. Within CHDM, the significant contribution is from the dimethyl terephthalate, palladium (catalyst) and the energy consumed. Within DMT, the significant contribution is from the p-xylene and energy consumed in its manufacturing process.

6.3.6 Contribution of components of PC to its environmental impacts

Phenol and acetone used in the manufacture of bisphenol-A and methanol, carbon monoxide and oxygen used in the manufacture of DMC are the major raw materials used in the synthesis of PC. Figure 63 shows the contribution of each of these components to the total environmental impact of PC. Phenol, acetone, carbon monoxide and the energy consumed in the manufacturing process have significant contribution to the overall environmental impact of PC's. Rest of the raw materials are included in the "others" category.

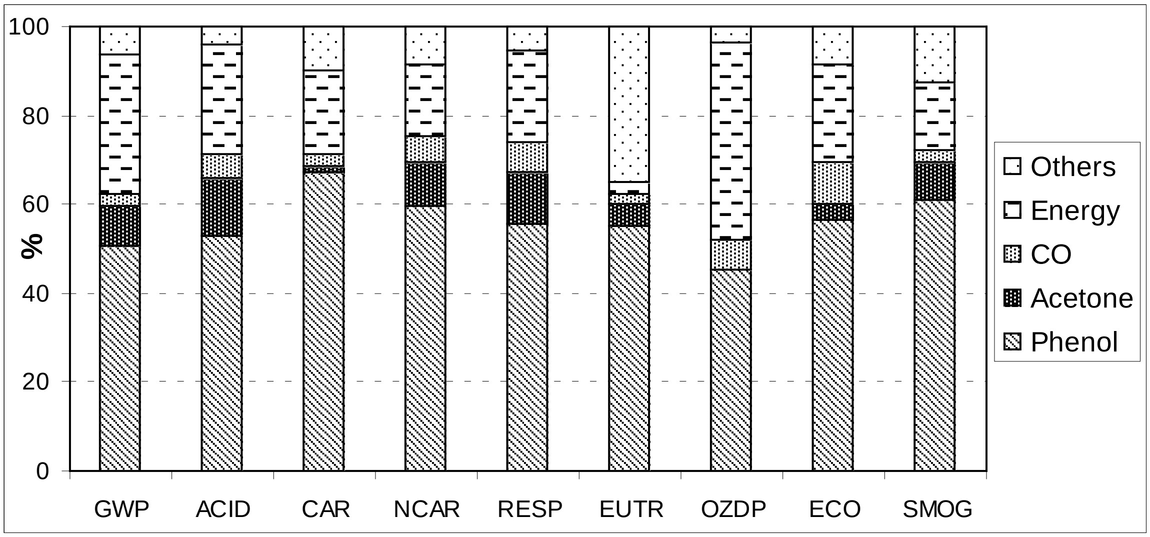


Figure 63. Contribution of phenol, acetone, carbon monoxide and energy to the environmental impact of PC

6.4 COMPARISON OF ENVIRONMENTAL IMPACT OF PC (MELT PROCESS) WITH THAT OF PC (INTERFACIAL PROCESS) DATABASES IN SIMAPRO

The environmental impacts based on the LCI developed for the Melt process as described in section 6.2.2.2 is compared with the environmental impacts of PC using the various databases available in the SimaPro library. The databases compared are – PC ETH U (ETH-ESU 96 Unit processes), PC I (IDEMAT 2001), Polycarbonate E (Industry data 2.0), Polycarbonate, at plant/RER U (Ecoinvent Unit processes). The LCI for these databases is based on the Interfacial process for manufacture of PC. Figure 64 shows the comparison of the environmental impacts of PC using the 5 different LCI databases.

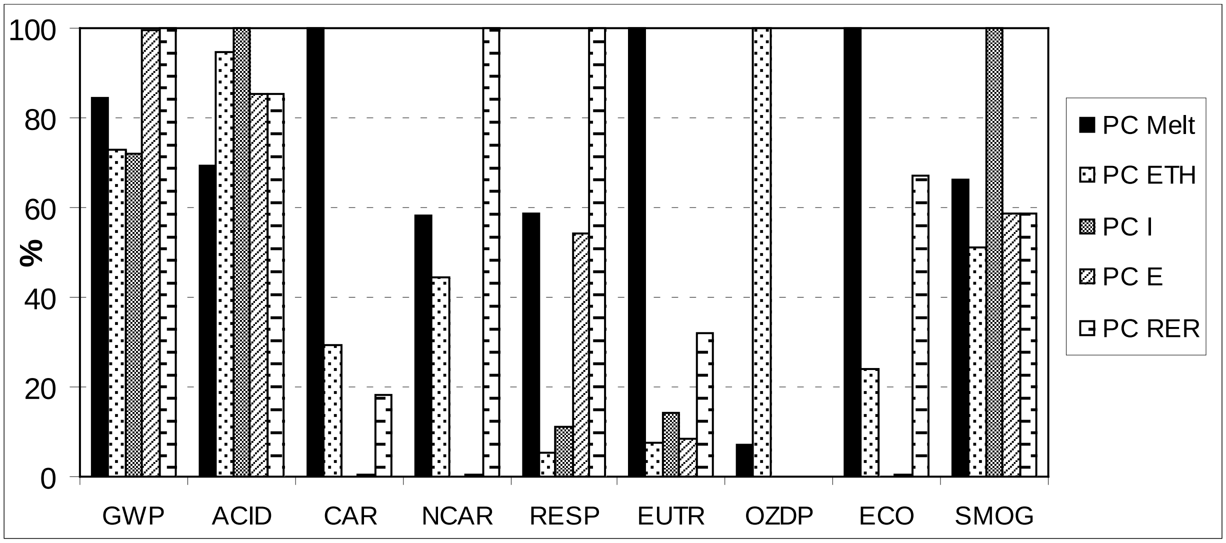


Figure 64. Comparison of environmental impact of PC using different databases

There is a vast discrepancy between the environmental impacts due the different databases considered for PC manufactured by the Interfacial process. This can be attributed to the difference in the manner in which the recovery of solvent (dichloromethane) and hydrogen chloride formed as the by-product might be accounted for. Because of the large discrepancy in the LCI databases available for the Interfacial process, the comparison between the two manufacturing process (Melt and Interfacial) cannot be conducted with any significant certainty.

6.5 SUMMARY

Based on the life cycle analysis comparison performed between polycarbonate and Tritan, it can be concluded that Tritan has a significantly lower impact than polycarbonate in most of the impact categories studied for a functional unit of a sheet of polymer. However, the impact due to Tritan increases by about 38 % when a bottle with a 24 oz capacity is considered as the functional unit. In this case, the overall environmental impacts of these two polymers are comparable.

The environmental impacts of Tritan are strongly dependent on the type of allocation technique used in the impact assessment stage. When no allocation method is used, the impacts are about 40 % higher compared to the economic value allocation. Mass allocation gives about 25 % lower impacts compared to the economic value allocation. In case of polycarbonates, the environmental impacts due to mass allocation are about 7.5 % lower than those due to economic value allocation. Since, methanol, acetic acid and n-butyraldehyde formed as by-products during the process of manufacture of Tritan are important building blocks in the chemicals industry, the economic value allocation was considered to be the most appropriate choice for impact assessment.

The analysis of the two extreme scenarios for the treatment of unreacted raw material showed that by recycling 100% of the separable unreacted raw material, the environmental impacts reduced by about 10 to 20 % in the different categories compared to the scenario with no recycle at all. Since, the most efficient scenario is likely to be used during industrial production; the “complete recycle” scenario was used for the analysis of Tritan.

The contribution of the major components (CHDM, TMCD & DMT) in the manufacture of Tritan to the total environmental impact showed that in most categories the contribution due to TMCD was much higher compared to its weight contribution. This can be attributed to the mass as well as energy consumed in all the 6 stages in the manufacture of TMCD. In case of polycarbonate, the major contributor to the environmental impact was the phenol that is used in the manufacture of BPA and DPC which are the two main monomers used in the manufacture of polycarbonate.

It is important to point out that this study has not taken into consideration the endocrine disruption potential of polycarbonates, which has been the primary reason to look for BPA-free alternatives for polycarbonates. This is due to the lack of inventory data on the quantitative impacts of PC and Tritan on endocrine disruption. Thus, on the basis of this present study, the introduction of Tritan is certainly a right step in the direction towards BPA free polymers. Improvements to make the process for manufacture of TMCD & CHDM more efficient would certainly help in reducing the impacts in most of the categories. A more extensive LCA taking into account other factors such as cost, performance and end-of-life issues specific to polymers needs to be considered to evaluate the final economic and environmental performance of Tritan and polycarbonates.

7.0 FUTURE WORK

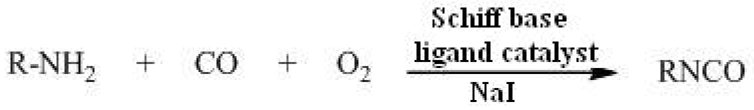
This dissertation study described a novel process for the manufacture isocyanates from a primary amine, carbon dioxide and an electrophilic dehydrating agent in the presence of an apolar, aprotic solvent at extremely low temperatures. The novel process was compared with the conventional phosgenation route for manufacture of isocyanate by performing a quantitative analysis based on the raw material and the energy requirement of the two processes using Aspen Plus process simulator. Based on the results of these process simulations, it was concluded that at the present state of development of the novel route, it requires significantly more amount of raw material and energy compared to the phosgene route. However, the analysis identified the hot-spots for higher raw material and energy consumption in the novel process developed. The process that contributes significantly to the high energy requirement for the non-phosgene route is the separation of the acetone from the product stream and the separation of trifluoroacetic acid and its recovery to trifluoroacetic anhydride. Based on this study, some of the potential areas where future work can be targeted to make the process more efficient would be as follows,

1. Exploration of polar aprotic solvents such as acetone, which would have a high solubility for carbon dioxide, extremely low freezing temperatures for higher conversion to isocyanate and boiling point higher than the isocyanate for lower energy requirement for separation by distillation.

2. Molecular design of new anhydrides which have strong electron withdrawing groups (for high pKa value of the acid) and can also be efficiently recovered from their corresponding acid. This would reduce the energy associated with the anhydride recovery unit.
3. Development of an effective technique to recover the amine and acid from the salt formed as the byproduct. The recycling of these raw materials would reduce the overall material requirement for the process.

This research study demonstrated the importance of the application of chemical engineering fundamentals to chemistry in the development of a new process. The simultaneous validation of the effectiveness of a newly developed process at an industrial level is equally important, because what might seem to be the best option at a lab-scale might not necessarily be the most efficient option at the industrial scale. A set of guidelines can be developed which can be followed by researchers working on developing new processes to simultaneously evaluate the performance of their process on an industrial scale.

Amongst the various non-phosgene routes that have been discussed in Section 2.2 for the manufacture of isocyanates, oxidative carbonylation of amine to isocyanate (Section 2.2.3) appeared to be a promising alternative to the phosgenation route as it gave satisfactory yields of isocyanate (69.8% yield for TDI) at moderate operating conditions [33].



$$\text{R-NH}_2 \quad + \quad \text{CO} \quad + \quad \text{O}_2 \quad \xrightarrow[\text{NaI}]{\substack{\text{Schiff base} \\ \text{ligand catalyst}}} \quad \text{RNCO}$$

However, the energy required for the separation of the large amount of solvents used in this process and the stability and regenerative ability of the catalysts needs to be studied before this route can be claimed as an effective alternative to the phosgenation route for manufacture of isocyanates. Therefore, an analysis similar to Section 5.0 should be performed to compare the effectiveness of this route on an industrial level and use the results to make the process more efficient. Also, isocyanates are known to spontaneously react with alcohols. Hence, the reaction of isocyanate formed as the product with 2,2,2-trifluoroethanol used as the solvent needs to be investigated.

In the second part of this dissertation study, a life cycle analysis was performed to compare the environmental impacts of polycarbonate and Tritan. It was concluded that in most of the scenarios studied, Tritan had lower or similar environmental impacts as that of polycarbonates and should be the choice of preference because of it being bisphenol-A free. In future, an extensive LCA taking into account other factors such as cost, performance and end-of-life issues specific to polymers can be studied to evaluate the final economic and environmental performance of Tritan and polycarbonates. As an extension to this research, Tritan can be compared to other bisphenol-A free polymers such as polyethylene terephthalate (PET) and polypropylene ethylene (PPE) for their environmental impacts.

APPENDIX A

ANALYTICAL TECHNIQUES

Fourier Transform Infra-red (FTIR) Spectroscopy & Gas Chromatography are the two main analytical techniques used in this study. The following sections explain the aspects of these techniques relevant to this study.

A.1 FOURIER TRANSFORM INFRA-RED (FTIR) SPECTROSCOPY

A Research Series FTIR (Model: RS 2) is used to qualitatively identify the presence of various functional groups in the experimental samples. Zubrick gives the detailed procedure to be followed for the IR spectroscopic analysis of the different solid and liquid reaction samples [162]. These procedures are discussed in detail in Section 4.3.5. The peaks monitored that are of significance to this research project are the isocyanate (-NCO) peak at 2276 cm^{-1}, amide (-NHCO-) peak in the 1709 cm^{-1} range, salt of acid and amine peak in the 1660 – 1685 cm^{-1} range, acid (-COOH) peak at 1873 cm^{-1} and anhydride (-CO-O-OC-) peak at 1783 cm^{-1} [163]. The IR spectra of the amide formed as a result of reaction between trifluoroacetic acid and n-butyl isocyanate in acetone and the salt of trifluoroacetic acid and n-butylamine is shown in Figure 65 and 66 respectively.

For a quantitative analysis of the components present in the experimental sample, the method of comparing peak ratios is used [164]. The IR peak at 2929 cm^{-1} (-CH stretching) is considered to be the standard peak to which all the other peaks are compared in order to get a better quantitative feel for the concentrations of the components present in the sample.

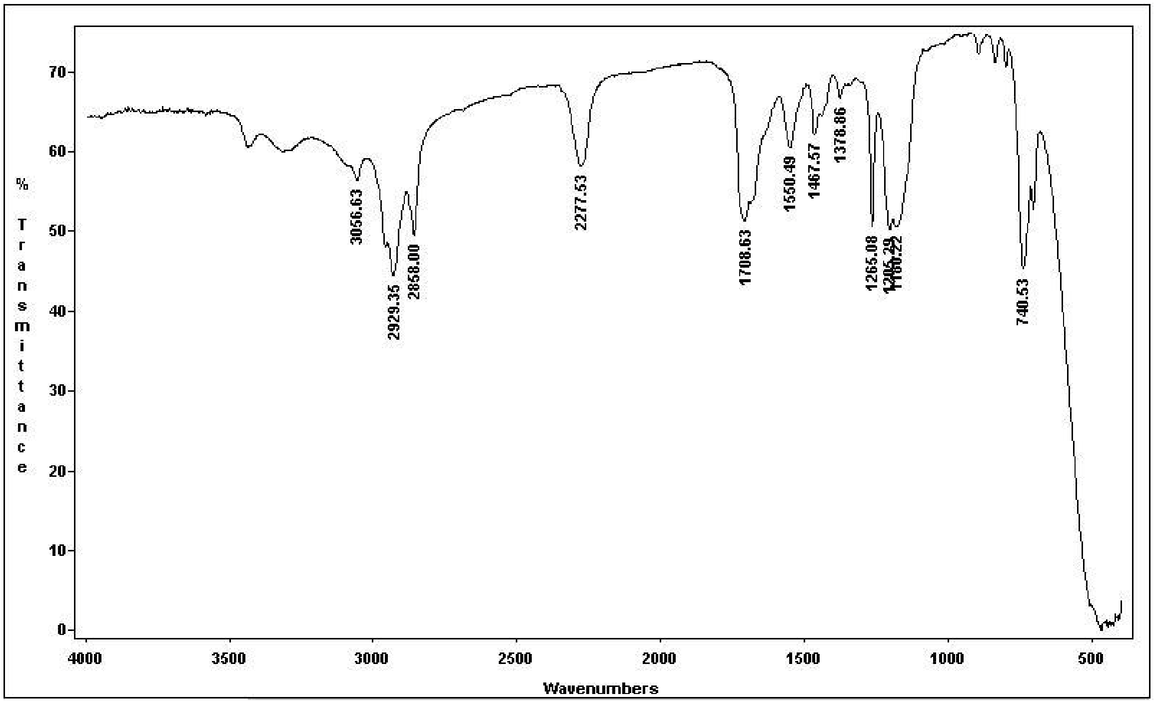


Figure 65. IR spectra of amide formed by reaction of n-butyl isocyanate & TFA

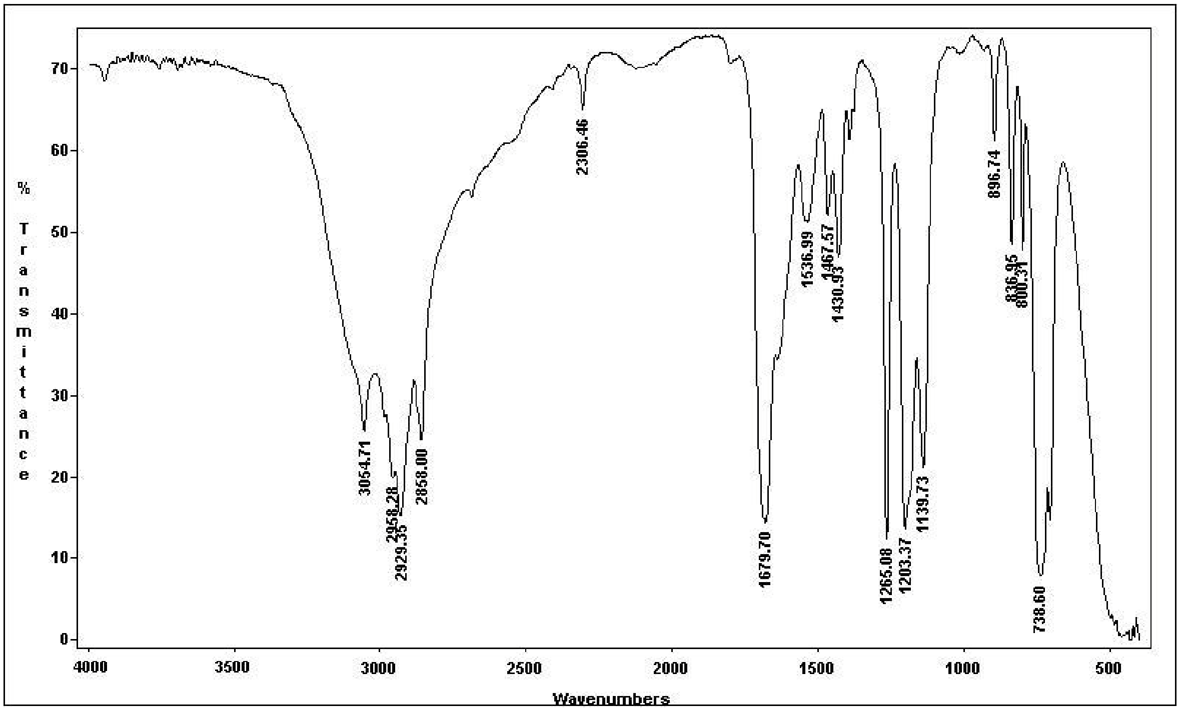


Figure 66. IR spectra of salt of n-butylamine and trifluoroacetic acid

A.2 GAS CHROMATOGRAPHY

An HP 5890A gas chromatograph (GC) is used to analyze the isocyanate formed. This GC is equipped with a Flame Ionization Detector (FID), using a DB-1 capillary column (30m×0.253mm×0.50μm). The column is kept at 100°C for 4 minutes (with helium used as the carrier gas) and then programmed to 210°C at the rate of 15°C/min and then held for another 5 minutes. The injector is held at 100°C and the detector held at 140°C. The GC conditions used for detection of butyl isocyanate have been described in Table 5.

At those conditions, a calibration chart (as shown in Figure 3) was generated which was used for quantitative analysis of butyl isocyanate present in a given sample.

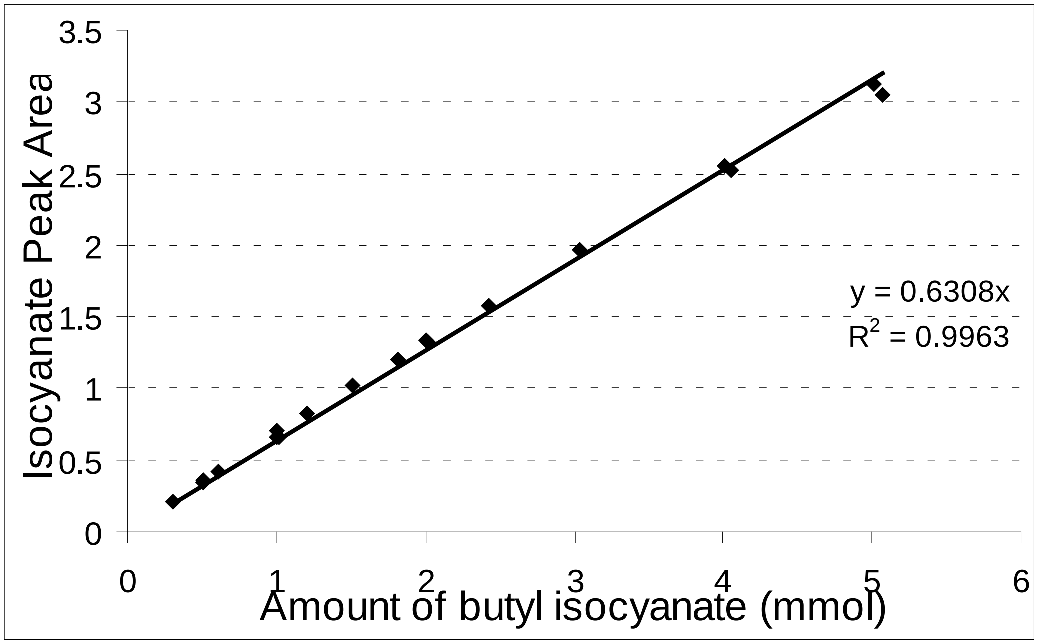


Figure 67. GC calibration chart for butyl isocyanate

Table 38. GC conditions for the detection of butyl isocyanate

Item	Detection of butyl isocyanate
Detector	FID
Column	DB-1 capillary column (30m×0.253mm×0.50μm)
Injection amount, μL	0.5
Carrier gas	He
Carrier gas flowrate, (pressure); ml/min (psi)	35.5 (50)
H_2 flowrate, (pressure); ml/min (psi)	34.5 (33)
Air flowrate, (pressure); ml/min, (psi)	415 (70)
Total flowrate, ml/min	485
Injection temperature, °C	100

Table 38 (continued).

Detector temperature, °C	140
Oven temperature, °C	100
Initial time, min	4
Rate, °C/min	15
Final temperature, °C	5
Final time, min	5

The response factors can change for different concentrations. That is why you need to make a calibration curve. If the curve is linear then you can use the average of the response factors to calculate the concentration. As seen from the chart, the response factor (RFa) for the analyte i.e. butyl isocyanate will be the slope of the straight line due to the linear nature of the calibration chart. Therefore,

$$\mathrm{RFa} = \frac{\text{Analyte peak area}}{\text{Analyte mass}} = 0.6308$$

A.3 PROCEDURE TO OBTAIN IR SPECTRA FOR A LIQUID SAMPLE

The following procedure is applied to obtain IR spectra for a liquid sample [162].

1. Make sure the sample is dry. This is because the sample is put between two sodium chloride plates which are water soluble.
2. Put 1-2 drops of the sample on one plate, then cover it with another plate. The sample should be spread out to cover the entire plate.

3. Place the sandwich in the IR salt plate holder and cover it with a hold-down plate.
4. Slide the holder and plate into the bracket on the instrument in the sample beam
5. Run the spectrum
6. Take the salt cells out of the instrument and clean them. It is often sufficient to clean it with a little acetone followed by drying.

APPENDIX B

STREAM TABLES (PHOSGENATION ROUTE)

B.1 ISOCYANATE MANUFACTURING UNIT

	PHFEED	**NH2FEED**	**DCBFEED**	**PHREC1**	**DCBREC3**
Temp, K	298.15	298.15	298.15	283.92	379.75
Pressure (atm)	1	1	1	1.5	1
Vapor fraction	1	0	0	0.0018	0
Total flow, kg/hr	37.69	250	5.65	725.96	1885.87
Butylamine		250.00			
Butyl isocyanate				0.31	0.31
Phosgene	37.69			723.07	1.49E-12
HCl				2.52	
Dichlorobenzene			5.65		1878.67
Butyl formamide					6.89
Carbon monoxide				0.07	

ISOCYANATE MANUFACTURING UNIT – cont.

	PHHIP	NH2HIP	DCBHIP	PHHIPT	DCBNHHIP	R1OUT	DCBREC2	R2INHT	R2OUT
Temp, K	288.95	298.49	379.90	363.15	363.15	363.15	451.84	418.15	418.15
Pressure (atm)	1.500	3.041	3.041	1.500	3.041	3.041	1.000	3.041	3.041
Vapor fraction	0.0415	0.0000	0.0000	1.0000	0.0000	0.3412	0.1439	0.4967	0.4963
Total flow, kg/hr	763.65	250	1891.52	763.65	2141.52	2905.17	1885.87	2905.17	2905.76
Mass Flow, kg/hr									
Butylamine		250.00			250.00	21.25		21.25	
Butyl isocyanate	0.31		0.31	0.31	0.31	310.67	0.31	310.67	310.67
Phosgene	760.75		1.49E-12	760.75	1.49E-12	451.38	1.49E-12	451.38	422.64
HCl	2.52			2.52		230.59		230.59	251.78
Dichlorobenzene			1884.32		1884.32	1884.32	1878.67	1884.32	1884.32
Butyl formamide			6.89		6.89	6.89	6.89	6.89	36.28
Carbon monoxide	0.07			0.07		0.07		0.07	0.07

B.2 DISTILLATION COLUMNS

	R2OUT	PHHCLLP	ISODCH	HCLVAP	PHREC	ISODC	DCBH1	ISOPURE
Temperature K	418.15	248.18	418.25	202.97	292.21	387.78	452.25	294.26
Pressure atm	3.041	0.5	0.8	2	2	1	1	1
Vapor Frac	0.4963	1	0	0.9000	0	0	0	0
Mass Flow kg/hr	2905.76	674.37	2231.39	253.55	420.83	312.36	1919.03	312.36
Mass Flow kg/hr								
Butyl isocyanate	310.67	0.31	310.36	0.00	0.31	310.05	0.31	310.05
Phosgene	422.64	422.22	0.42	4.22	418.00	0.42	1.5E-12	0.42
HCl	251.78	251.78	2.07E-05	249.26	2.52	2.1E-05	3.2E-23	2.07E-05
DCB	1884.32		1884.32			1.88	1882.43	1.88
Butyl formamide	36.28		36.28			0.0001	36.28	0.0001
CO	0.067	0.067	9.31E-14	0.067	1.04E-08			

DISTILLATION COLUMNS – cont.

	DCB1	**DCBH2**	**DCB2**	**HEAVIES**	**DCBREC1**
Temperature K	451.87	454.04	452.00	472.97	451.91
Pressure atm	1	1	1	1	1
Vapor Frac	1	0	0	0	0.8000
Mass Flow kg/hr	1509.89	409.14	375.99	33.15	1885.87
Mass Flow kg/hr					
Butyl isocyanate	0.31	4.73E-06	4.73E-06	1.94E-16	0.31
Phosgene	6.94E-18	1.49E-12	1.49E-12	3.72E-33	1.49E-12
Dichlorobenzene	1505.95	376.49	372.72	3.76	1878.67
Butyl formamide	3.63	32.65	3.27	29.39	6.89

B.3 CHLORINE RECOVERY UNIT – (FROM HYDROCHLORIC ACID)

	HCL-VAP	HCL-PURE	PHO-SABS	WAT-IN	WAT-HT	WAT-LT	GAS-OUT	HCL-22	HCL-17	H2	CL2-IN
Temp, K	203.00	203.00	203.00	298.15	352.73	338.15		243.15	353.15	353.15	353.15
Pressure (atm)	2	2	2	1	1	1	2	2	1	1	1
Vapor Fraction	0.9017	1	0	0	0.1614	0.1201		0	0.1681	0.5867	1
Total flow, kg/hr	253.48	249.26	4.22	121.72	4894.97	4894.97	0.00	5144.22	4773.25	128.32	242.37
Mass Flow, kg/hr											
Phosgene	4.22		4.22								
HCl	249.26	249.26			847.35	847.35		1096.61	847.35		
Water				121.72	4047.62	4047.62		4047.62	3925.90	121.43	
Hydrogen										6.89	
Chlorine											242.37

B.4 CHLORINE RECOVERY UNIT – (FROM ANHYDROUS HYDROGEN CHLORIDE)

	HCLVAP	**HCLPURE**	**PHOSABS**	**O2IN**	**CL2IN**	**H2O**	**HCLREC**
Temp, K	203	203	203	298.15	353.15	353.15	353.15
Pressure (atm)	2	2	2	1	1	1	1
Vapor Frac	0.9017	1	0	1	1	0	1
Total flow, kg/hr	253.48	249.26	4.22	54.69	242.37	61.58	0.00
Mass Flow, kg/hr							
Phosgene	4.22		4.22				
HCl	249.26	249.26					
Water						61.58	
Chlorine					242.37		
Oxygen				54.69			0.001

B.5 PHOSGENE MANUFACTURING UNIT

	CO-IN	CL2-IN	CL2CO-LT	PHR1-IN	PHR1-OUT	PHR2-IN	PHR2-OUT	PHCO2-PH	CO-OUT	PH-REC2
Temp, K	298.15	353.15	327.00	378.15	443.09	373.15	373.15	273.15	273.15	273.15
Pressure atm	1	1	1	1	1	1	1	1	1.5	1.5
Vapor Frac	1	1	1	1	1	1	1	0.2432	1	0
Mass Flow kg/hr	101.91	242.37	344.28	344.28	344.28	344.28	344.28	344.28	28.84	315.44
Mass Flow kg/hr										
Phosgene					335.60	335.60	337.15	337.15	22.29	314.86
Chlorine		242.37	242.37	242.37	1.80	1.80	0.69	0.69	0.18	0.51
CO	101.91		101.91	101.91	6.88	6.88	6.44	6.44	6.37	0.07

APPENDIX C

STREAM TABLES (NON-PHOSGENE ROUTE)

C.1 ISOCYANATE MANUFACTURING UNIT

	NH2-FEED	NH2-ACET	ACET1	DI-ACET	TFAA-FEED	TFAA-REC	TFAA-ACET
Temp, °C	25.00	-29.77	-47.90	-61.28	25.00	-20.33	-16.30
Pressure (bar)	1.013	1.013	1.013	1	1.013	1	1
TFA acid		0.18		0.72			0.18
TFA anhydride					51.37	347.76	399.13
Butylamine	138.89	138.89					
Butyl isocyanate		0.24		0.96			0.24
Carbon Dioxide		81.77		645.90			81.77
Aceton		296.48	17.98	1206.76			296.48
Butyl formamide		1.1E-07		4.4E-07			1.1E-07
Methanol		0.38		1.51			0.38
Acetic acid		0.02		0.06			0.02
Acetic anhydride		0.00		0.00			0.00

ISOCYANATE MANUFACTURIN UNIT – cont.

	R1ZIOUT	RMAINOUT	SALT	PRODMIX
Temp, °C	-78	-78	-78	-78
Pressure (bar)	1.0133	1	1	1
Vapor fraction	0	0.0237	0	0.0246
Total flow, kg/hr	2373.87	3152.06	62.13	3089.93
Mass Flow, kg/hr				
TFA acid	0.90	294.62		294.62
TFA anhydride		93.93		93.93
Butylamine	8.33	8.33		8.33
Butyl isocyanate	1.20	145.50		145.50
Carbon dioxide	663.72	745.49		745.49
Acetone	1503.23	1799.71		1799.71
Zwitterion	131.38			
Carbamate	63.13			
Salt		62.13	62.13	
Butyl formamide	5.5E-07	6.6E-07		6.6E-07
Methanol	1.88	2.26		2.26
Acetic acid	0.08	0.10		0.10
Acetic anhydride	0.01	0.01		0.01

ISOCYANATE MANUFACTURIN UNIT – cont.

	PVPF3	**PVPTOT**	**ABSOUT**	**NOTFA**	**PVPTFA**
Temp, °C	25	25	-78	-78	-78
Pressure (bar)	1	1	1	1	1
Vapor fraction	0	0	0.0012	0.0285	0
Total flow, kg/hr	276.00	276.00	3363.80	2794.42	569.38
Mass Flow, kg/hr					
TFA anhydride			93.65	93.65	
Butyl isocyanate			144.05	144.05	
Carbon dioxide			745.49	745.49	
Acetone			1799.71	1799.71	
Butyl formamide			11.52	11.52	
PVP	275.85	275.85			
PVP-TFA			569.38		569.38
Acetic acid	0.15	0.15			
Acetic anhydride	0.00	0.00			

C.2 DRY ICE MANUFACTURING UNIT

	CO2REC	CO2	ACECO21	CO2REC1	COMP1OUT
Temp, °C	-20.33	-47.9	-47.9	-47.9	-20
Pressure (bar)	1	1	1	1	20.265
Vapor fraction	0.3248	1	0	1	0
Total flow, kg/hr	2532.11	519.52	2012.59	255.49	255.49
Mass Flow, kg/hr					
TFA acid	1.08	0.00	1.08	1.9E-04	1.9E-04
Butyl isocyanate	1.44	5.0E-05	1.44	2.5E-05	2.5E-05
Carbon dioxide	745.49	517.28	228.21	254.40	254.40
Acetone	1781.73	2.23	1779.50	1.10	1.10
Methanol	2.26	1.5E-03	2.26	7.5E-04	7.5E-04
Acetic acid	0.10	1.7E-06	0.10	8.3E-07	8.3E-07
Acetic anhydride	6.0E-03	2.6E-08	6.0E-03	1.3E-08	1.3E-08

DRY ICE MANUFACTURING UNIT – Cont.

	CO2-FEED	**CO2-HIGHP**	**DRYICE**	**ACET3R**	**ACET1R**	**ACET2R**
Temp, °C	25	-28.9	-87.82	-47.9	-47.9	-47.9
Pressure (bar)	1.013	14.824	1.013	1	1	1
Vapor fraction	1	0	0.3116	0.1430	0.1430	0.1430
Total flow, kg/hr	63.95	63.95	319.45	379.06	1518.50	379.06
Mass Flow, kg/hr						
TFA acid			1.9E-04	0.18	0.72	0.18
Butyl isocyanate			2.5E-05	0.24	0.96	0.24
Carbon dioxide	63.95	63.95	318.35	81.77	327.56	81.77
Acetone			1.10	296.48	1187.68	296.48
Methanol			7.5E-04	0.38	1.51	0.38
Acetic acid			8.3E-07	0.02	0.06	0.02
Acetic anhydride			1.3E-08	1.0E-03	4.0E-03	1.0E-03

C.3 DISTILLATION COLUMNS

	FL1-TOP	FL1-BOT1	ACET-REC	ISO-AMIDE	ISO	AMIDE
Temp, °C	-50.00	-50.00	-50.33	97.47	95.28	198.08
Pressure (bar)	1	1	1	1	1	1
Vapor fraction	1	0	0	0	0	0
Total flow, kg/hr	586.58	2207.84	2035.73	172.11	160.46	11.66
Mass Flow, kg/hr						
TFA anhydride	93.65	6.7E-06				
Butyl isocyanate	0.00	144.05	1.44	142.61	142.47	0.14
Carbon dioxide	491.17	254.31	254.31	1.3E-08	1.3E-08	1.5E-22
Acetone	1.75	1797.96	1779.98	17.98	17.98	6.4E-06
Butyl formamide	6.6E-07	11.52	0.00	11.52	0.01	11.51

C.4 TRIFLUOROACETIC AANHYDRIDE RECOVERY UNIT

	METFEED	METRECH	METTOT	PVPTFA	NOPVP	PVPF3	METTFA	METREC1
Temp, °C	63.70	63.71	25.22	-78.00	25.00	25.00	58.64	63.71
Pressure (bar)	1	1	1	1	1	1	1	1
Vapor fraction	0	0	0	0	0	0	0	0
Total flow, kg/hr	5.30	956.45	961.75	39861.36	39567.98	1255.13	600.00	655.13
Mass Flow, kg/hr								
TFA acid		0.34	0.34			293.87	293.52	0.35
PVP				39291.94	39567.79			
PVP-TFA				569.38				
Methanol	5.30	955.96	961.26			961.26	306.48	654.79
Acetic acid		0.145	0.145		0.145			
Acetic anhydride		0.004	0.004		0.004			

TRIFLUOROACETIC ANHYDRIDE RECOVERY UNIT – Cont.

	AAFEED	**CAAOUT**	**CTFAOUT**	**TFAARECO**	**TFAAFL**	**METAA**	**AACID**	**METREC2**
Temperature °C	25	60	60	60	10	10	113.25	63.73
Pressure bar	1	1	1	1	1	1	1	1
Vapor Frac	0	0	1	0.2938	1	0	0	0
Mass Flow kg/hr	131.40	131.40	600.00	731.40	257.56	457.32	155.99	301.33
Mass Flow kg/hr								
TFA acid			293.52	17.61	1.08			
TFA anhydride				254.11	254.11			
Methanol			306.48	306.48	2.26	304.22	3.04	301.18
Acetic acid				145.31	0.10	145.22	145.07	0.15
Acetic anhydride	131.40	131.40		7.89	0.01	7.88	7.88	0.00

C.5 ACETIC ANHYDRIDE RECOVERY UNIT

	ACIDCOLD	**AAR2IN**	**AAPYRO**	**CH4**	**AIR**	**TOSTACK**	**ACIDHOT**	**KETENE**
Temperature °C	386.15	386.15	386.15	298.15	298.15	412.32	973.15	973.15
Pressure bar	1	1	1	1	1	1	1	0.3533
Vapor Fraction	0	0	0	1	1	1	1	1
Mass Flow kg/hr	152.53	24.22	128.31	4.83	131.85	136.67	128.31	128.31
Acetic acid	142.24	22.59	119.65				119.65	48.53
Acetic anhydride	10.29	1.63	8.65				8.65	8.65
Methane				4.83				
Oxygen					30.71	11.45		
Nitrogen					101.14	101.14		
Ketene						0.00	0.00	49.79
Water						10.84	0.00	21.34
Carbon Dioxide						13.24		

ACETIC ACID RECOVERY UNIT – Cont.

	KET-ETH	ETHYL-ACE	WATER	EA-ACID	KET-VAP	NH3	R2-OUT	KET	FL-BOT	EA	A-ANHY
Temp, °C	920.02	298	278	278	278	298	323.15	281.2	281.15	284.6	409.05
Pressure (bar)	1	1	1	1	1	1	0.0987	0.1	0.1	1	1
Vapor fraction	1	0	0	0	1	1	0.1455	1	0	0	0
Total flow, kg/hr	137.12	8.81	19.90	70.97	46.25	1.70	143.15	2.35	140.80	11.94	128.86
Mass Flow, kg/hr											
Acetic acid	48.53		3.5E-03	48.34	0.19		10.34	0.04	10.30	2.48	7.81
Acetic anhydride	8.65		2.9E-08	8.63	0.02		121.79	0.18	121.61	0.61	121.00
Ketene	49.79		3.9E-04	4.53	45.26		0.50	0.43	0.08	0.08	3.9E-11
Water	21.34		19.89	1.31	0.13						
Ethyl acetate	8.81	8.81	2.5E-08	8.16	0.65		8.81	0.34	8.47	8.43	0.04
Ammonia						1.70	1.70	1.36	0.34	0.34	1.8E-10

	CO2-REC	**CO2**	**ACE-CO21**	**CO20 REC1**	**COMP1-OUT**	**CO2-FEED**	**DRY-ICE**	**ACET-3R**	**ACET-1R**	**ACET-2R**
Temp, °C	-20.33	-47.9	-47.9	-47.9	-20	25	-87.82	-47.9	-47.9	-47.9
Pressure (bar)	1	1	1	1	20.265	1.013	1.013	1	1	1
Vapor fraction	0.3248	1	0	1	0	1	0.3116	0.1430	0.1430	0.1430
Total flow, kg/hr	2532.11	519.52	2012.59	255.49	255.49	63.95	319.45	379.06	1518.50	379.06
Mass Flow, kg/hr										
TFA acid	1.08	0.00	1.08	1.9E-04	1.9E-04		1.9E-04	0.18	0.72	0.18
Butyl isocyanate	1.44	5.0E-05	1.44	2.5E-05	2.5E-05		2.5E-05	0.24	0.96	0.24
Carbon dioxide	745.49	517.28	228.21	254.40	254.40	63.95	318.35	81.77	327.56	81.77
Acetone	1781.73	2.23	1779.50	1.10	1.10		1.10	296.48	1187.68	296.48
Methanol	2.26	1.5E-03	2.26	7.5E-04	7.5E-04		7.5E-04	0.38	1.51	0.38
Acetic acid	0.10	1.7E-06	0.10	8.3E-07	8.3E-07		8.3E-07	0.02	0.06	0.02
Acetic anhydride	6.0E-03	2.6E-08	6.0E-03	1.3E-08	1.3E-08		1.3E-08	1.0E-03	4.0E-03	1.0E-03

APPENDIX D

ENERGY REQUIREMENTS FOR ISOCYANATE MANUFACTURE

D.1 PHOSGENATION ROUTE

The energy requirements given below are for an isocyanate manufacturing rate of 312.36 kg/hr.

Isocyanate Manufacturing Unit			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
PHCOMP	0.33	-	-
NH2PUMP	0.07	-	-
CBPUMP	0.30	-	-
PHHX	-	59.47	-
DCHX	-	-	67.39
R2HX	-	-	-
R1	-	11.90	-
R2	-	15.66	-

Distillation Columns			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
PRIDC	-	50.31	0.40
PHHCLDC	-	29.16	2.54
ISODC	-	103.52	84.72
DCBDC1	-	220.96	112.17
DCBDC2	-	75.49	75.37
HXPI	-	-	15.36

Chlorine Recovery Unit (HCl acid)			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
ELECTRO1	363.55	-	-
HCLABS	-	-	97.15
WTHX	-	-	198.79

Chlorine Recovery Unit (anhydrous HCl)			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
ELECTRO1	309.02	-	-

Phosgene Manufacturing Unit			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
PHR1	-	98.26	-
PHR2	-	-	12.32
PHFLSH	-	2.76	-
PHX1	-	3.21	-
PHX2	-	-	4.48
PHX3	-	-	38.29

The total energy requirement for each section, for an isocyanate manufacturing rate of 312.36 kg/hr is given below.

	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
Isocyanate Manufacturing Unit	0.70	87.03	67.39
Distillation Columns	0.00	479.44	290.56
Chlorine Recovery Unit (HCl acid)	363.55	-	295.94
Chlorine Recovery Unit (anhydrous HCl)	309.02	-	-
Phosgene Manufacturing Unit	-	104.234	55.09842

D.2 NON-PHOSGENE ROUTE

The energy requirements given below are for an isocyanate manufacturing rate of 144.46 kg/hr.

Isocyanate Manufacturing Unit			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
R1Z1	-	-	64.63
RMAIN	-	-	40.88
FILTER1	-	-	0.08
TFAABS	-	-	14.31
FILTER2	-	-	2.37

Distillation Columns			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
FLASH1	-	91.48	-
DCISOACE	-	361.87	349.83
DCISOAMI	-	20.17	19.62

TFAA Recovery Unit			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
STRIPPER	-	4.85	-
FILTER3	-	-	7.29
DCMETTFA	-	167.58	130.89
HXTF	-	-	119.10
TFAARECO	-	32.53	-
TFAAFL	-	-	9.90
DCMETAA	-	151.97	127.39

Dry Ice Manufacturing Unit			
	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
CO2SEP	-	-	48.85
COMP1	14.71	-	35.60
COMP2	3.48	-	10.06

The total energy requirement for each section, for an adjusted isocyanate manufacturing rate of 312.36 kg/hr is given below.

	Energy Requirement (kW.hr)		
	Electricity	Heating	Cooling
Isocyanate Manufacturing Unit	-	-	264.41
Distillation Columns	-	1023.87	798.84
TFAA Recovery Unit	-	771.77	853.17
Dry Ice Manufacturing Unit	39.33	-	204.35

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