

**Modeling of the phase behavior of light (C<sub>2</sub> & C<sub>3</sub>) olefins in liquid phase epoxidation systems and experimental determination of gas/liquid mass transfer coefficients**

By

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in partial fulfillment of the requirements for the degree of  
Masters of Science

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Date Thesis Defended

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## **ABSTRACT**

Conventional technologies for the selective epoxidation of olefins such as ethylene and propylene to form their corresponding epoxides are either non selective and/or produce much waste. A novel biphasic process for the epoxidation of olefins has been developed by the researchers at Center for Environmentally Beneficial Catalysis (CEBC), employing environmentally benign substances (catalyst methyltrioxorhenium, oxidant aqueous H<sub>2</sub>O<sub>2</sub>) dissolved in a suitable solvent (determined to be methanol). HYSYS® software was used to study the phase behavior and generate quantitative data on the solubility of gaseous olefins in the liquid phase which aided in the optimization of the reaction conditions. A detailed stirred tank reactor model was developed to estimate the gas/liquid mass transfer coefficient which was determined to be 0.14 sec<sup>-1</sup> at 1000 rpm which ensured operation outside the diffusion limited region. Inerts such as N<sub>2</sub> and CO<sub>2</sub> can be used to mitigate the flammability envelope of these highly flammable gases.

## Table of Contents

Abstract	ii
Table of Contents	iii
List of Figures	viii
List of Tables	xi
Acknowledgements	xii
Chapter 1 Introduction	1
1.1 Chlorohydrin Process	4
1.1.1 Chlorohydrin Process using Lime	4
1.1.2 Chlorohydrin Process using Cell Liquor	5
1.2 Hydroperoxidation Process	7
1.2.1 Propylene Oxide/ <i>t</i> -butyl alcohol by hydroperoxidation using <i>t</i> -butyl hydroperoxide	7
1.2.2 Propylene Oxide/Styrene by hydroperoxidation using ethyl benzyl hydroperoxide	10
1.2.3 Propylene oxide by hydroperoxidation using cumene hydroperoxide	14
1.3 Development of the New Process	16
1.3.1 The CEBC Process	17
1.4 Conventional Processes for the manufacture of Ethylene Oxide	20
1.4.1 Ethylene Oxide by Chlorohydrination	22
1.4.2 Vapor Phase Oxidation of Ethylene	24

1.5 Thesis Objectives	26
1.6 Application of the principles of Green Chemistry and Engineering	27
1.7 Potential Significance/Impact	28
Chapter 2 Vapor Liquid Equilibria of Mixtures involving Propylene, Propylene Oxide, Water, Methanol and Nitrogen	
2.1 Introduction	32
2.2 Activity Model	33
2.3 Universal Quasi Chemical Theory (UNIQUAC Model)	35
2.4 Interaction Parameters	38
2.4.1 Universal Quasi Chemical Functional Activity Coefficients (UNIFAC) model	38
2.5 Peng Robinson Equation of State	41
2.6 VLE Modeling using HYSYS® simulator	43
2.7 Results and Discussion	44
2.7.1 Binary System	44
2.7.1.1 Propylene (1) and Methanol (2)	44
2.7.1.2 Propylene (1) and Nitrogen (2)	46
2.7.1.3 Propylene (1) and Water (2)	47
2.7.1.4 Propylene Oxide (1) and Propylene (2)	49
2.7.1.5 Propylene Oxide (1) and Methanol (2)	50
2.7.2 Multi-component System	51

2.7.2.1 Propylene (1), Methanol (2) and Nitrogen (3)	52
2.7.2.2 Propylene (1), Water (2) and Nitrogen (3)	53
2.7.2.3 Propylene (1), Methanol (2) and Water (3)	54
2.8 Summary	55
Nomeclature	56
Chapter 3 ReactIR Measurement of the Mass Transfer Coefficient for Propylene	
Transport into the Liquid Phase	
3.1 Introduction	60
3.2 Mass Transfer Studies	60
3.3 Experimental Procedure	62
3.4 Mathematical Model to Estimate Mass Transfer Coefficient from Constant Pressure Propylene Uptake Data in a Stirred Vessel	62
3.5 Summary	68
Nomeclature	68
Chapter 4 Liquid Phase Epoxidation of Ethylene and Investigation into the phase behavior of its components	
4.1 Introduction	71
4.2 Liquid Phase Epoxidation of Ethylene	73
4.3 Results and Discussions	76
4.3.1 Ethylene (1) and Alcohols (2)	76

4.3.2 Ethylene (1) and Carbon dioxide (2)	81
4.3.3 Ethylene (1) and Water (2)	82
4.3.4 Ethylene Oxide (1) and Alcohols (2)	83
4.3.5 Carbon dioxide (1) and Methanol (2)	87
4.3.6 Ethylene Oxide (1) and Ethylene (2)	88
4.3.7 Ethylene Oxide (1) and Carbon dioxide (2)	89
4.3.8 Ethylene Oxide (1) and Water (2)	90
4.4 Summary	91

## Chapter 5 Investigation of Flammability Envelope of the components in the

Epoxidation system in presence of inerts such as CO<sub>2</sub> and N<sub>2</sub>

5.1 Introduction	95
5.1.1 Inert Gases to reduce Flammability Envelope	97
5.2 Computational methods to estimate flammability Envelopes	98
5.3 Methodology	99
5.3.1 Gibbs Free Energy Minimization-HYSYS	99
5.3.2 Computational Procedure for the Model	100
5.4 Results and Discussions	102
5.4.1 Propylene and Propylene Oxide	103
5.4.2 Ethylene and Ethylene Oxide	105
5.5 Summary	107

Chapter 6 Conclusions & Recommendations	
6.1 Conclusions	109
6.2 Recommendations	110
Appendix A	112
Appendix B	114
Appendix C	116



## **List of Figures**

Figure 1.1: Consumption of propylene oxide by various end users in the year 2005	2
Figure 1.2: Organization of the Oxidation test bed	17
Figure 1.3: Schematic of Pressure Intensified Propylene Epoxidation Process	18
Figure 2.1: Vapor-Liquid of propylene (1) and methanol (2) at 25°C	45
Figure 2.2: Vapor-Liquid Equilibrium of propylene (1) and nitrogen (2) at 22.5 °C	47
Figure 2.3: Solubility of propylene (1) in water (2) at 22.5 °C	49
Figure 2.4: Vapor-Liquid of propylene oxide (1) and propylene (2) at 25 °C	50
Figure 2.5a &b: Vapor-Liquid of propylene oxide (1) and methanol (2) in (a) isobaric conditions (b) isothermal conditions	52
Figure 2.6: Solubility of propylene in methanol under varying nitrogen pressure	52
Figure 2.7: Solubility of propylene in water under varying nitrogen pressure	53
Figure 2.8: Solubility of propylene in methanol and water at 25 °C	56
Figure 3.1: Schematic of the experimental setup	61
Figure 3.2: Effect of agitation on propylene dissolution into the liquid phase for a reactor pressure of 3.1 bars and 25 °C	63
Figure 3.3: Plot of pressure profile of propylene reservoir with varying agitation speed to check for linearity	65
Figure 3.4: Comparison of the Mass Transfer Coefficient estimated by the empirical equation and that obtained from experiments in a 50 ml	67

## Parr reactor

Figure 4.1: World Consumption trends of ethylene oxide	72
Figure 4.2: Schematic of the biphasic process for ethylene epoxidation	73
Figure 4.3: Effect of temperature and pressure on the yield of Ethylene Oxide	75
Figure 4.4a: Vapor Liquid Equilibrium of ethylene-methanol and ethylene isopropanol at 25 °C	77
Figure 4.4b: Vapor-Liquid equilibrium of ethylene-ethanol at 10 °C	78
Figure 4.4c: Vapor-Liquid equilibrium of ethylene-n-propanol at 10 °C	78
Figure 4.4d: Vapor-Liquid equilibrium of ethylene-isopropanol at 10 °C	79
Figure 4.4e: Vapor-Liquid equilibrium of ethylene-methanol at 40 °C	79
Figure 4.5: Dew and Bubble Point curve of ethylene (1) and carbon dioxide (2)	82
Figure 4.6: Solubility of ethylene (1) in water (2) at 35 °C	83
Figure 4.7a: Vapor-Liquid equilibrium of ethylene oxide and methanol at -10°C, 0°C, 10 °C, 25 °C	84
Figure 4.7b: Vapor-Liquid equilibrium of ethylene oxide and ethanol at -10°C, 0°C, 10°C, 25°C	84
Figure 4.7c: Vapor-Liquid equilibrium of ethylene oxide and n-propanol at -10°C, 0°C, 10°C, 25°C	85
Figure 4.7d: Vapor-Liquid equilibrium of ethylene oxide and isopropanol at -10°C, 0°C, 10°C, 25°C	85
Figure 4.7e: Vapor-Liquid equilibrium of ethylene oxide and n-butanol at -10°C, 0°C, 10°C, 25°C	86

Figure 4.7f: Vapor-Liquid equilibrium of ethylene oxide and isobutanol at -10°C, 0°C, 10°C, 25°C	86
Figure 4.8: Vapor-Liquid equilibrium of methanol and carbon dioxide at -10°C, 0°C, 10°C, 25°C	88
Figure 4.9: Vapor-Liquid equilibrium of ethylene-ethylene oxide at 25°C	89
Figure 4.10: Vapor-Liquid equilibrium of ethylene oxide (1) and carbon dioxide (2)	90
Figure 4.11a: Vapor-Liquid equilibrium of ethylene oxide (1) and water (2) at 25 °C	91
Figure 4.11b: Vapor-Liquid equilibrium of ethylene oxide (1) and water (2) at 40 °C	91
Figure 5.1: Flammability envelope of methane in presence of various inerts	97
Figure 5.2: Gibbs Reactor for estimation of flammability envelope	100
Figure 5.3: Flammability envelope for propane at 1 atm and 25 °C	102
Figure 5.4: Flammability envelope for methane at 1 atm and 25 °C	102
Figure 5.5: Flammability envelope of acetic acid (a) Effect of pressure (b) Effect of temperature	103
Figure 5.6: Flammability envelope of propylene at 1 atm and 25 °C	104
Figure 5.7: Flammability Envelope of propylene oxide at 1 atm and 25 °C	104
Figure 5.8: Flammability envelope of ethylene at 1 atm and 25°C	106
Figure 5.9: Flammability envelope of ethylene oxide at 1 atm and 25 °C	106

## **List of Tables**

Table 1.1: World Consumption trends of propylene oxide	1
Table 1.2: Propylene Oxide uses and their applications	2
Table 1.3: Propylene Oxide producers, process route and their plant capacities as of year 2007	3
Table 1.4: Comparison of propylene oxide manufacturing using lime and cell liquor chlorohydrin processes	8
Table 1.5: Comparison of propylene oxide/tert-butyl alcohol process practiced by Huntsman ICI and Lyondellbasell	10
Table 1.6: Comparison of the propylene oxide/styrene monomer process Practiced by Lyondellbasell and Shell Industries	13
Table 1.7: Ethylene Oxide producers as plants as of year 2008	21
Table 1.8: Ethylene Oxide uses and their application	22
Table 2.1: Binary Interaction Parameters of Propylene and Methanol at 25 °C	45
Table 2.2: Binary Interaction Parameters used in the model	52
Table 3.1: Values of Parameters based on vessel geometry of Parr Reactor	68
Table 4.1: Binary Interaction coefficients of ethylene with various alcohols	80
Table 4.2: Binary Interaction parameters for various ethylene oxide and alcohol systems	87

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## Chapter 1

### 1 Introduction

Propylene Oxide (PO) is an important chemical intermediate for a broad spectrum of consumer products and the major producers are Lyondellbasell, Dow Chemicals, Shell Chemicals, and Huntsman ICI. Propylene oxide is mostly converted into glycols, polyols and glycol ethers; these products find application in a variety of areas as shown in Table 1.1. Figure 1.1 shows the breakdown of propylene oxide consumption based on the product and its end use in major application areas. There has been a steady rise in the demand of PO, and the global market is expected to grow at a rate of approximately 4.7 % per annum [1]. Recent trends are shown in Table 1.1.

**Table 1.1:** World Consumption Trends of Propylene Oxide [2]

Year	Capacity (million tonnes/year)
1995	4.41
2000	5.70
2003	6.1
2005	6.95

Based on year 2000 data, the United States consumption of propylene oxide is the highest in the world at 41.7% followed by Europe at 36.7% and Asia at 15.2% at the end of year 2000.<sup>[2]</sup> The market for propylene oxide is expected to grow in Asia due to its growing population and improving standard of living. The cost of the product in mid 2000 was approximately 40 cents/lb and the current market price

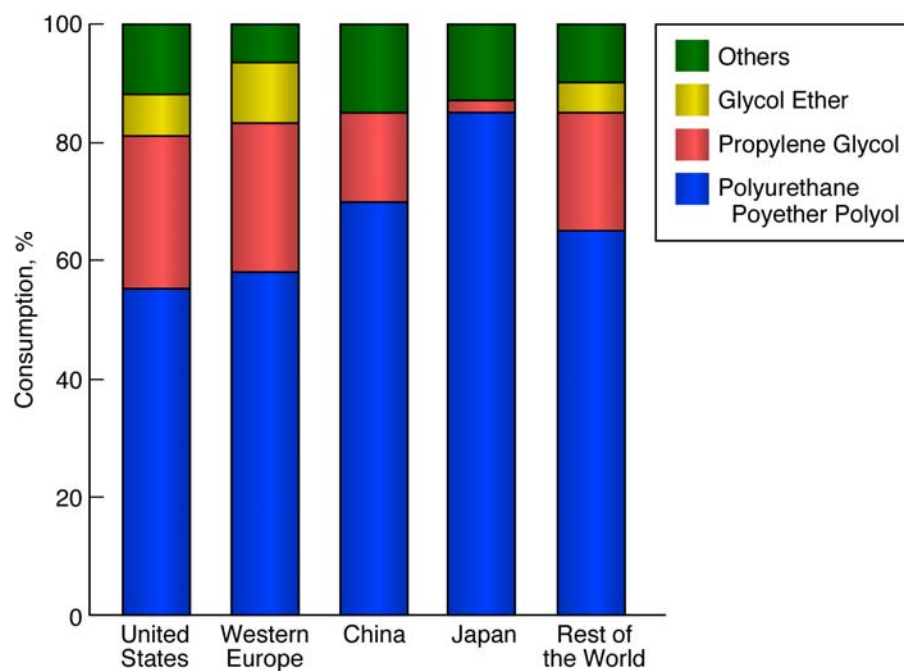
being 60 cents/lb.<sup>[3]</sup> The following table contains the list of derivatives of propylene oxide and their applications.

**Table 1.2:** Propylene Oxide Uses and their applications. <sup>[2, 4]</sup>

<b>Product</b>	<b>Percentage</b>	<b>Industrial Uses</b>
Urethane Polyether Polyols	60	Sports gear, flooring, shoe soles, plastics, rigid and soft foams
Propylene Glycol	19	Preservatives, antifreeze, solvent in paints and plastics, nail polish, fire fighting
Dipropylene Glycol	6	Plasticizers, unsaturated polyester resins, cosmetics, polyurethane polyols
Glycol Ethers	5	Solvents for resins, lacquers, paints
Miscellaneous	8	

Figure 1.1 shows the breakdown of propylene oxide consumption based on products and their end uses in the major consuming regions.

There are two major routes for the manufacture of propylene oxide; the chlorohydrin process mainly used by Dow Chemicals and the hydroperoxidation process used by Lyondellbasell, Shell and Huntsman ICI. The global production capacities of propylene oxide via these routes are provided in the table 1.3. The various processes based on these general routes and the associated chemical stoichiometries are discussed in the following sections.



**Figure 1.1:** Consumption of Propylene Oxide by various end uses in the year 2005<sup>[1]</sup>.



**Table 1.3:** Propylene Oxide producers, process route and their plant capacities as of year 2007.

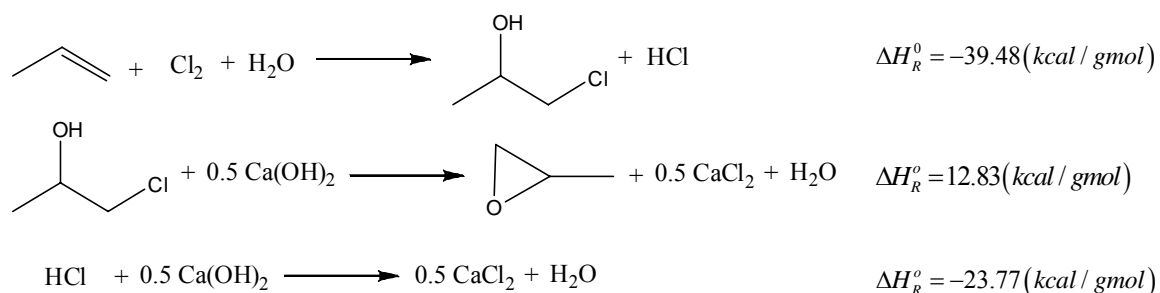
<b>Plant</b>	<b>PO Capacity (tons/year)</b>	<b>Process</b>
<b>Dow Chemical Company [2]</b>		
Freeport, Texas	680,000	Chlorohydrin Process
Plaquemine, Louisiana	331,000	Chlorohydrin Process
Stade, Germany	550,000	Propylene Oxide/Styrene Monomer
<b>Lyondellbasell Industries [1, 5]</b>		
Bayport, Texas	565,000	Propylene Oxide/t-Butyl Alcohol
Channelview, Texas	560,000	Propylene Oxide/Styrene Monomer
Rotterdam, Botlek, Netherlands	245,000	Propylene Oxide/ t-Butyl Alcohol
Fossumer, France	220,000	Propylene Oxide/t-Butyl Alcohol
<b>Shell Chemicals [6]</b>		
Jurong Island, Singapore	160,000	Propylene Oxide/Styrene Monomer
Moerdijk, Netherlands	210,000	Propylene Oxide/Styrene Monomer
CSPCL, Nanhai Petrochemical Complex	250,000	Propylene Oxide/Styrene Monomer
Ellba, Netherlands	250,000	Propylene Oxide/Styrene Monomer
<b>Huntsman ICI [1]</b>		
Port Neeches, Texas	238,000	Propylene Oxide/t-Butyl Alcohol
<b>Repsol Quimica [1]</b>		
Puerto Ilano, Spain	60,000	Propylene Oxide/Styrene Monomer
Tarragona, Spain	150,000	
<b>Sumitomo Chemicals [1]</b>		
Japan	200,000	Cumene Hydroperoxide Route
<b>SK Everttek [1]</b>		
Ulsan, South Korea	190,000	Propylene Oxide/Styrene Monomer

### 1.1 Chlorohydrin Process

This process for the production of propylene oxide has been practiced since 1910. It is a mature technology and there have been several improvements to the process. Two variations of this process that are currently in practice used slaked lime or cell liquor for treating propylene chlorohydrin, respectively.

### 1.1.1 Chlorohydrin Process using Lime [7, 8]

The conventional chlorohydrin process starts with the production of propylene chlorohydrin (PCH) by reacting propylene with chlorine in excess water at 49 °C and 1.17 bars to achieve 97% and nearly 100% propylene and chlorine conversions respectively, with selectivities of 93.6% to propylene chlorohydrin (PCH), 4.3% to propylene dichloride (PDC) and 2.1% to dichloroisopropyl ether (DCIPE). The PCH is treated with calcium hydroxide to form propylene oxide and calcium chloride. The process conditions are moderate temperature and pressure conditions of 92 °C, 1.51 bars with 95% selectivity towards PO. The process is linked to a chlorine/caustic plant and the consumption of chlorine is 1.35-1.5 units per unit of propylene oxide. The major drawbacks of this process include a large waste aqueous stream containing organic matter and 5-6 wt% calcium chlorides. The volume of salts generated is 40 times the amount of product formed in the reaction.

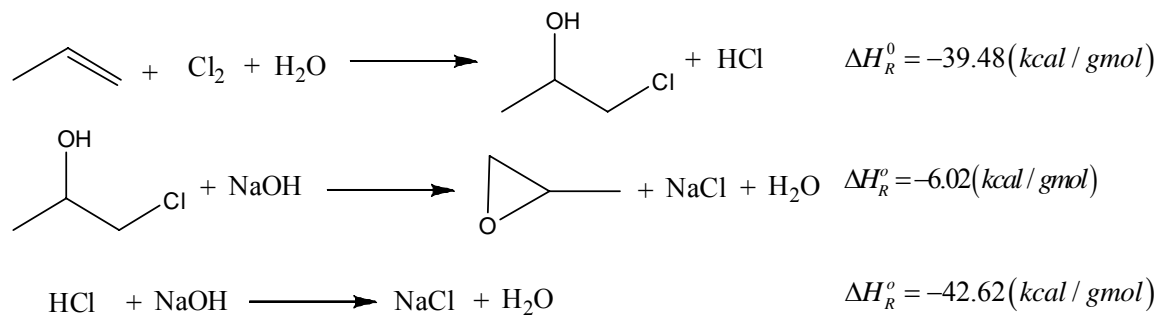


Scheme 1: Propylene Chlorohydrination

### 1.1.2 Chlorohydrin Process using Cell Liquor

This process has certain advantages over the conventional process. Cell liquor from the chlorine or caustic plant is used in place of lime to give propylene oxide and sodium chloride. This eliminates the calcium hydroxide section in the conventional

PO plant and the cell liquor evaporation step in the chlorine or caustic plants. The process conditions are similar to those of the conventional process in the chlorohydrination process at 40 °C and 4.13 bars. The selectivities attained in the chlorohydrination step (based on propylene converted) are 95 mol% propylene chlorohydrin, 3.7 mol% propylene dichloride and 1.3 mol% dichloroisopropyl ether (DCIPE) [8].



Scheme 2: Saponification of PCH

The cell liquor produced in the membrane process is dilute enough to be used in the saponification as compared to the concentrated caustic produced in the mercury process that tends to transform propylene oxide to propylene glycol. The propylene chlorohydrin is reacted with caustic and forms propylene oxide and sodium chloride. The process conditions for this step are a temperature of 85 °C and a pressure of 4.4 bars and the conversion and selectivity towards PO are 99.9% and 95%.

The advantage of using the conventional chlorohydrin process is that it produces commercial grade caustic soda. Further, the chlorine content in the waste stream is less in the conventional chlorohydrin process by approximately 50% but requires an additional step for the treatment of the solids in the waste stream. The cost

of the PO product is higher in the cell liquor process but less waste is generated compared to the conventional chlorohydrin process (Table 1.4). The main advantage is that the cell liquor process requires 10% less capital investment. The major producer of propylene oxide using the chlorohydrin route is Dow Chemicals. A large amount of waste is generated during the manufacture of propylene oxide using this technology. The inherent disadvantage of chlorohydrin routes is the requirement for large amount of chlorine (mercury process) and caustic (membrane process) that increases the cost of production.

**Table 1.4:** Comparison of propylene oxide manufacturing using the lime and cell liquor chlorohydrin processes. [9-11]

Aspects	Lime	Cell Liquor
<b>Chlorohydrination</b>		
Temperature (°C)	49	40
Pressure (bar)	1.17	4.3
Conversion (Propylene %)	97	97
Selectivity		
Propylene Chlorohydrin (mol %)	93.6	95
Propylene Dichloride (mol %)	4.3	3.7
Dichloro Isopropyl Ether (mol %)	2.1	1.3
<b>Saponification</b>		
Temperature (°C)	92	85
Pressure (bar)	1.51	4.4815
Conversion (Propylene %)	99.9	99.9
Selectivity		
Propylene Oxide (mol %)	95	95
Propylene Glycol (Mol %)	5	5
Lime Added	13% excess	1% excess alkali
Product Value (cents/lb)	45.05	50.61

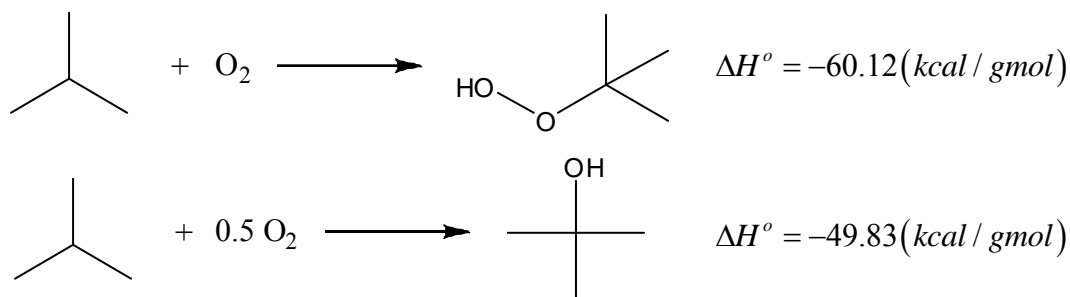
## 1.2 Hydroperoxidation Process

The manufacture of propylene oxide by hydroperoxidation is a widely adopted route and is a newer technology. Shell Chemicals, Lyondellbasell and Huntsman ICI are the leaders of this technology. There are two routes for hydroperoxidation based on the feed and the byproducts that are produced with propylene oxide.

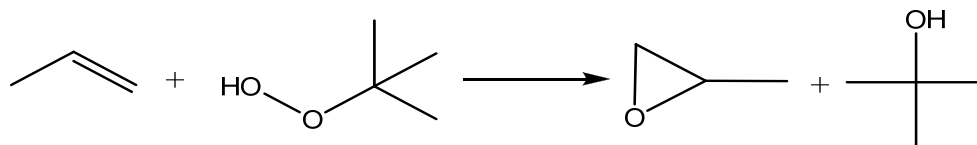
### 1.2.1 Propylene Oxide/*t*-Butyl Alcohol by Hydroperoxidation using *t*-Butyl Hydroperoxide

This process may be integrated with an existing methyl *t*-butyl ether (MTBE) unit. The feed isobutane is subjected to non-catalytic liquid phase oxidation using hydrogen peroxide at 110-150 °C and 20.6-55.1 bars for durations from 4 to 10 hours

to yield tertiary butyl hydrogen peroxide (TBHP) and tertiary butyl alcohol (TBA). Oxygen or air can be used as an oxidant with air being preferred due to its lower cost and ready availability. The oxygen concentration is kept around 5 mol% to 12 mol% for safety reasons. The conversion of isobutane is 10-25%, the selectivities to TBHP and TBA being 60-70 mol% and 30-40 mol%, respectively. The preferred solvents for this process are TBHP and TBA as other solvents could cause separation issues. The byproducts of this reaction are acids, aldehydes, ketones and other alcohols [12, 13].



Scheme 3: Isobutane Oxidation



Scheme 4: Epoxidation of Propylene

Propylene is subjected to catalytic epoxidation in TBHP solvent to form propylene oxide and TBA. Molybdenum is used as a catalyst; the operating conditions are 80-130 °C and 17.23-68.94 bars for a duration of 3 hours. The decomposition of TBHP is a major side reaction at higher temperatures with a poor selectivity to propylene oxide. This problem is abated by either having a high concentration of propylene or alternatively using of an alkaline earth metal such as

barium oxide that stabilizes the hydroperoxide and prevents radical chain decomposition. The conversion of TBHP is 98% with PO selectivity being 98.4 mol% [14, 15].

Table 1.5 gives a comparison of the hydroperoxidation processes adopted by Huntsman ICI and Lyondellbasell for producing PO.

**Table 1.5:** Comparison of propylene oxide/*t*-butyl alcohol process practiced by Huntsman ICI and Lyondellbasell [14-19]

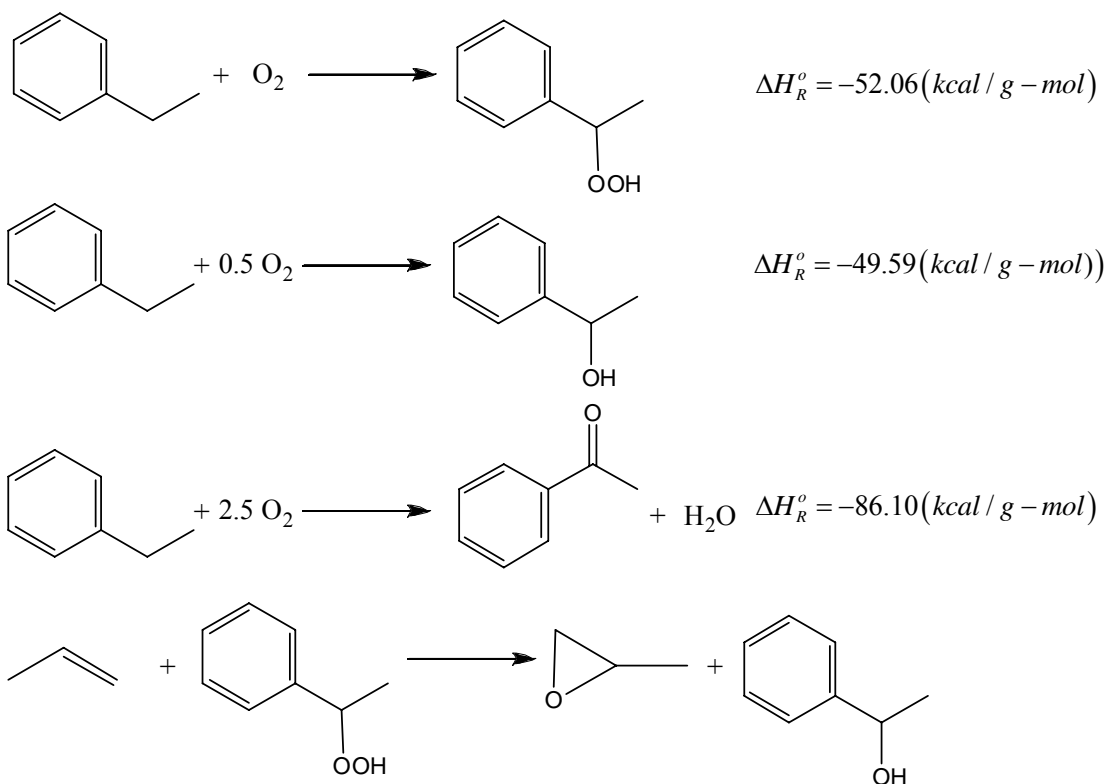
<b>Aspect</b>	<b>Lyondellbasell</b>	<b>Huntsman ICI</b>
<b>Product Ratio (PO/TBA)</b>	1:2.3	1:2.7
	<b>Isobutane Oxidation</b>	
Temperature (°C)	137	134
Pressure (bar)	31.0	21.1
Conversion (Isobutane %)	36.9	46
Selectivity TBHP (mol %)	53.4	48
TBA (mol %)	40.2	47
Residence Time (hours)	10	8.5
	<b>Propylene Epoxidation</b>	
Temperature (°C)	121	110 and 135
Pressure (bars)	35.508	35.508
Catalyst	Molybdenum Solution	11% Molybdenum as Ammonium Heptamolybdate/ethylene Glycol/Water
Conversion (%)	98	98.4
Selectivity (PO mol %)	98.4	98.3
<b>Capital Investment</b>	More Capital Intensive	Less Capital Intensive (due to smaller size of reactors and refrigeration system)
<b>Propylene Oxide Purification</b>	TBA/Water as an extractive distillation agent	Acetone/Water agent for separation of methanol an additional column required
<b>Product Cost (cents/lb)</b>	48.78	44.94

### **1.2.2 Propylene Oxide/Styrene by Hydroperoxidation using Ethyl benzene Hydroperoxide**

This process co produces propylene oxide and styrene monomer. The first step in this process is the exothermic non-catalytic liquid phase oxidation of ethylbenzene (EB) in hydrogen peroxide at a temperature of 130-160 °C, pressure 1.72-14.8 bars for 3-7 hours to give ethylbenzene hydrogen peroxide (EBHP), methyl benzyl alcohol (MBA), acetophenone (ACP) and additional byproducts like acids, ketones, aldehydes. This oxidation involves a free radical mechanism, and either air or oxygen is used for the oxidation. The EB conversion is in the range of 5-20 mol% with a selectivity of 65-85 mol % to EBHP, 5-20 mol % to ACP, and 5-10 mol % to MBA. The conversion of ethylbenzene is kept low as the higher conversions lead to lower selectivities towards EBHP [16].

In the presence of a suitable catalyst, propylene epoxidizes to form propylene oxide and methyl benzyl alcohol in EBHP. The byproducts include acetophenone, phenols, and aldehydes as shown in the scheme 5.





Scheme 6: Ethylbenzene Oxidation & Propylene Epoxidation

The selectivity to propylene oxide is lower in this process compared to the TBHP process as the ethylbenzene is less stable than isobutane. Treating the EBHP with titanium catalyst improves the yield of PO and reduces the deactivation of catalyst. The MBA is dehydrated in the vapor phase at 180-280 °C in the presence of titanium dioxide to form styrene. The acetophenone can be hydrogenated to MBA with or without the presence of solvents such as ethylbenzene which can be further processed to styrene. This process is usually carried at H<sub>2</sub>: ACP mol ratio of 2:1 to 8:1 at 90-115 °C and about 82.7 bars pressure in presence of a copper-chromium catalyst, with copper dispersed in a zinc oxide matrix. The major side reaction of this step is the excessive hydrogenation of ACP to ethylbenzene. This process conditions

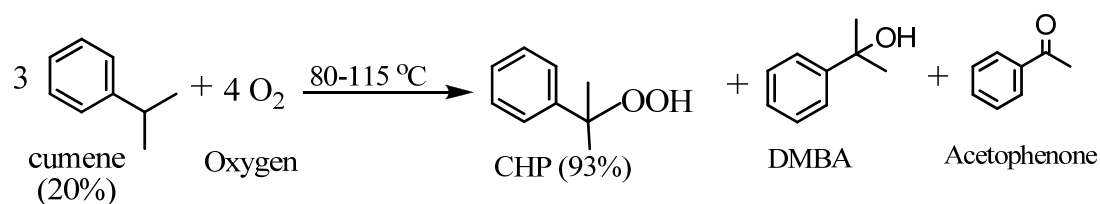
PO/SM route practiced by Shell Chemicals and Lyondellbasell for the manufacture of PO as shown in Table 1.6 [17-19].

**Table 1.6:** Comparison of the propylene oxide/styrene monomer process practiced by Lyondellbasell and Shell Industries [12, 20-25].

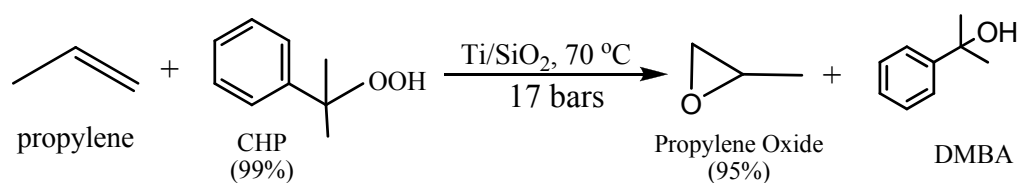
<b>Aspects</b>	<b>Lyondellbasell</b>	<b>Shell Chemicals</b>
<b>Product Ratio (PO/SM)</b>	1:2.25	1:2.20
	<b>Ethylbenzene Oxidation</b>	
Temperature (°C)	141	155
Pressure (bars)	3.44	3.44
Conversion (EB %)	7.2	8.4
Selectivity (mol %)		
EBHP	85.8	80
MBA	4.4	6
ACP	7.7	11.6
<b>Residence Time (hours)</b>	4	4
	<b>Propylene Epoxidation</b>	
Temperature (°C)	115	100
Pressure (bars)	21.7	29.59
Catalyst	6% Molybdenum Solution	Ti Catalyst on Silica Support
Feed		
Propylene/ EBHP	7.2:1	16.7:1
Percentage EBHP in EB	17	19.6
Residence Time (hours)	1.25	
Conversion (EBHP)	99.5	99
Selectivity		
Propylene Oxide (mol %)	86	98.9
Acetophenone (mol %)	4.4	
Catalyst Recovery	Required	Not Required
	<b>Styrene Production</b>	
Temperature (°C)	230	270
Pressure (bars)	5.8	20
Catalyst	p-Toluene sulfonic acid	Alumina
Conversion (MBA)	95	93
Selectivity (Styrene mol %)	98.6	98.7
Product Cost (cents/lb)	45.74	45.78

### 1.2.3 Propylene Oxide by Hydroperoxidation using Cumene Hydroperoxide:

This is the latest technological development in the hydroperoxide route for the manufacture of propylene oxide. The first step of this process, cumene oxidation, is well studied in the work related to phenol production. In the PO production process, an exothermic liquid phase oxidation of cumene yields three major products: cumene hydroperoxide (CHP), dimethyl benzyl alcohol (DMBA), and acetophenone (ACP). This reaction is kinetically controlled and temperature is therefore a major controlling factor. This non-catalytic reaction is carried out at 80-115 °C. A conversion of 20% cumene is obtained with the following selectivities: CHP: 93 mol %, DMBA 5.9 mol % and ACP 0.9 mol %. [26]



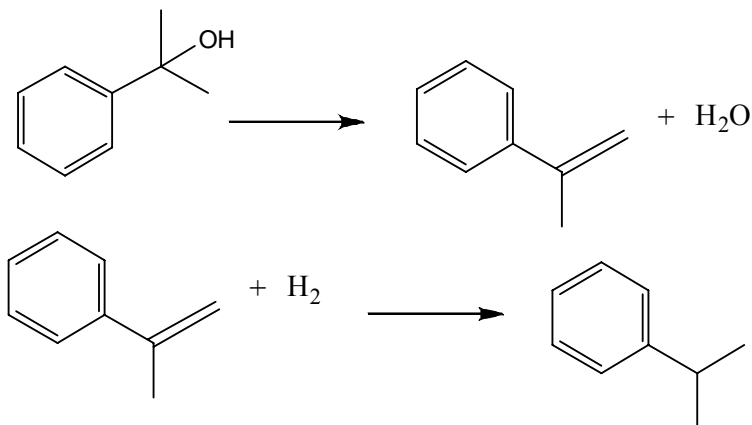
Scheme 6: Cumene Oxidation



Scheme 7: Propylene oxidation with cumene hydroperoxide

In the presence of titanium silicate catalyst propylene reacts with CHP at a temperature of 60 °C and a pressure of 17.2 bars to form propylene oxide and DMBA with a conversion of 99% based on CHP and a selectivity of 95 mol% towards PO as shown in scheme 7. The DMBA formed in this step during cumene oxidation is

subjected to catalytic dehydration at 80 °C using supported Pd/C catalyst to form  $\alpha$ -methyl styrene (AMS), which is then hydrogenated to form cumene. The conversion for both the dehydration and hydrogenation steps is greater than 99% with a selectivity of 97.3 mol % towards cumene as shown in scheme 8 [27, 28].



Scheme 8: Dehydration and Dehydrogenation of DMBA

### Summary of drawbacks/challenges associated with conventional PO technologies

Commercial technologies currently practiced by the industry are energy intensive in nature. Chlorohydrin process generates a large excess of aqueous waste per mole of propylene oxide produced. The hydroperoxide routes have a low product to byproduct ratio (or a high E-factor). Hence, the profitability of the plant also depends on the demand and the value of the byproduct. A recent legislation in the US bans the use of methyl tertiary-butyl ether (MTBE) as an additive in gasoline to increase the octane number. This has significantly affected the economics of PO/TBA technology as the *t*-Butyl alcohol market has been adversely affected. Styrene is mostly consumed in the manufacture of plastic and rubber products. The growth of this product is at a slow rate of approximately 3.4 %. These drawbacks have resulted

in continued research to develop a commercial process that uses environmentally benign substances and is less energy intensive and has a higher selectivity towards propylene oxide. Minimizing waste in the propylene oxide manufacturing process has been an important industry objective for long time.

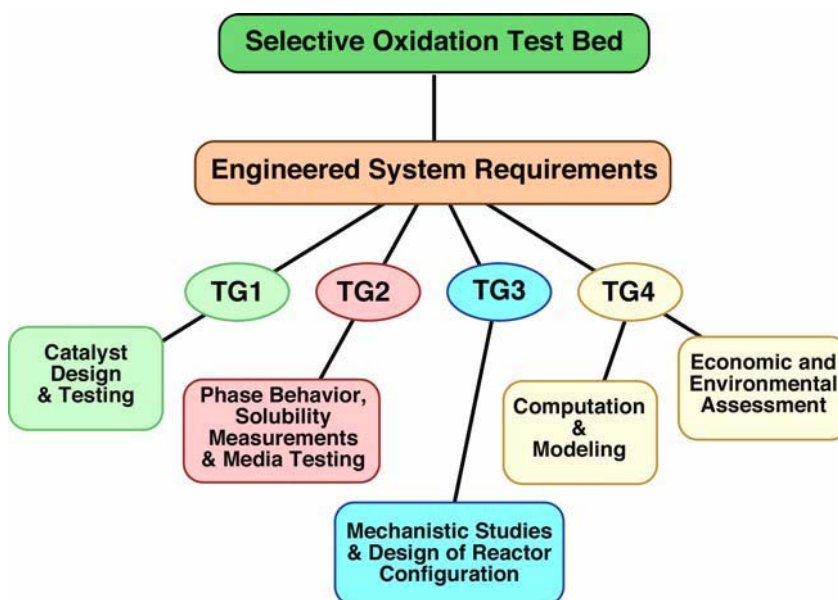
Dow Chemicals, BASF catalysts and Solvay have developed an alternative route for the manufacture of propylene oxide using hydrogen peroxide known as the HPPO process. The heterogeneous catalyst TS-1 is used in methanol solvent. This process has a good yield with high E-factor and requires less capital investment compared to the other processes. A new plant to produce PO will begin commercial production by 2009. Solvay/BASF/Dow will build a 230,000 metric tonnes hydrogen peroxide plant that will be the source of oxidant for the propylene epoxidation plant. The economics of the hydroperoxidation route are controlled by the cost of hydrogen peroxide [2].

### **1.3: Development of New Process**

An ongoing research program at the Center for Environmentally Beneficial Catalysis (CEBC) at the University of Kansas (KU) is developing a new process for the manufacture of propylene oxide. The NSF center at KU is a multidisciplinary research organization where engineers and chemists collaborate to develop state of the art technologies that adhere to the principles of green chemistry and engineering.

The work is reported as a part of the oxidation test bed at the Center for Environmentally Beneficial Catalysis (CEBC). The general organization of the test

bed is given in Figure 1.2. The thrust groups house the various areas of expertise required to develop and engineer innovative new process technologies. As a result of collaboration between engineers and chemists within CEBC, a new process concept was demonstrated and is being developed for possible commercialization.



**Figure 1.2:** Organization of the Oxidation test bed

### 1.3.1 The CEBC Process

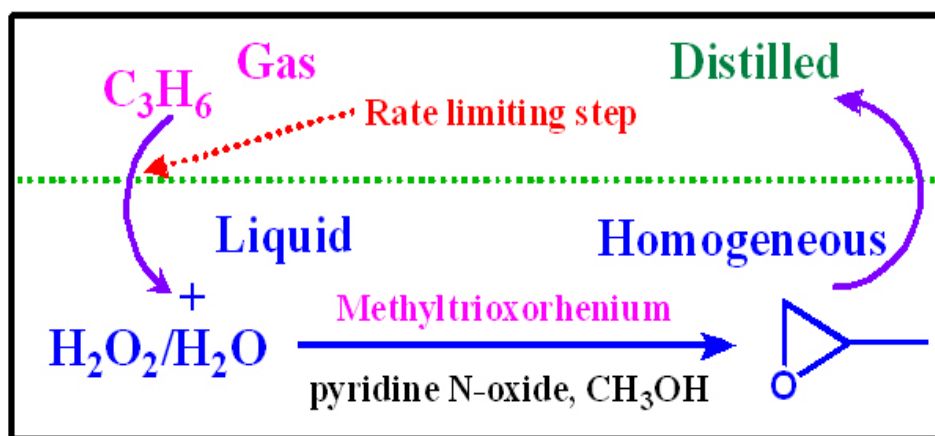
This novel biphasic process has been demonstrated for the synthesis of propylene oxide from propylene in the presence of the homogeneous catalyst methyl trioxorhenium, and co-solvent methanol. It is a gas-liquid reaction; propylene gas dissolves into the liquid phase containing the oxidant as shown in Figure 1.3.

The process is environmentally benign in nature and has mild operating conditions, temperature of 20-35 °C and pressure of 20 bars. A number of solvents

were found suitable and test runs were undertaken using methanol, isopropanol, *t*-butanol and acetonitrile. The systems formed homogeneous mixtures with the catalyst and oxidant in all cases. Methanol was chosen because it produced the highest cumulative propylene oxide yield. The economics of this process are affected by the cost of the catalyst methyl trioxorhenium and the oxidant hydrogen peroxide. The turnover number (TON) has to be very high to make the process economical. In presence of hydrogen peroxide, the catalyst formed two complexes, the monoperoxo complex and the diperoxo complex. Both complexes catalyze the epoxidation reaction. The key to high catalyst life is to retain the diperoxo species as the dominant species. Propylene Oxide undergoes ring opening in an acidic environment to form diols and strong bases that would destabilize the MTO catalyst and add to the complexity of maximizing MTO catalysis. Experiments were conducted with a variety of bases including pyridine, diphenylamine, pyridine N-oxide, and 2,4,6-tri(4-pyridyl)-1,3,5-triazine. Pyridine N-oxide is added to the liquid phase, to stabilize the system. The best bases were found to be Py, PyNO<sub>x</sub> the later is chosen as it is a very weak base, minimizing the threat of catalytic destruction. It is also found that PyNO accelerates the formation of MTO/H<sub>2</sub>O<sub>2</sub> adducts.

There have been numerous studies on selective epoxidation using H<sub>2</sub>O<sub>2</sub>. Beckman's group demonstrated the formation of percarbonate species in biphasic systems of sc-CO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and NaOH and reported a low conversion of 3% to propylene oxide [29]. Studies in these laboratories [30] showed the monophasic ternary systems, e.g., acetonitrile, CO<sub>2</sub> and water, give greatly improved conversions.

The use of CO<sub>2</sub> resulted in low yields in our process; this drawback was overcome by the innovative use of nitrogen instead of CO<sub>2</sub> to bring about pressure intensification to enhance propylene solubility in the liquid reaction phase thereby further overcoming the mass transfer limitations. The conversion of propylene was observed to be 99% with a propylene oxide yield greater than 98%.



**Figure 1.3:** Schematic of the Pressure Intensified Propylene Epoxidation Process

The literature reports that the catalyst is stable enough to be used for epoxidation reactions only with methyl compound. Successive batch reactions were carried out to study catalyst stability. There was no observed change in the pressure profiles of propylene going to the liquid phase showing high catalyst durability. The effect of temperature on catalyst life was studied by determining the propylene oxide yield at various temperatures. At higher temperature of 40 °C the yield decreased after the second batch cycle, suggesting deactivation. Water was also discovered to be one of the causes for catalyst deactivation. Replacing aqueous hydrogen peroxide with



urea hydrogen peroxide was found to increase the catalyst lifetime, but catalyst was eventually deactivated in both systems [31].

#### **1.4 Conventional Processes for the manufacture of Ethylene Oxide**

Ethylene Oxide was discovered in 1859 by A. Wurtz and its first commercial plant came into operation in 1925. The two routes that have been used in the production of ethylene oxide are the chlorohydrin process and the vapor phase oxidation of ethylene which was developed in 1931 by T. E. Lefort [32]. Union Carbide Chemicals was the first to manufacture EO commercially using either route. This business is now owned by Dow Chemicals. The list of the companies that produce ethylene oxide and the locations of the plants are given in Table 1.7. The uses of ethylene oxide and the applications are listed in Table 1.8.

**Table 1.7:** Ethylene Oxide producers and plants as of year 2008 [1-6].

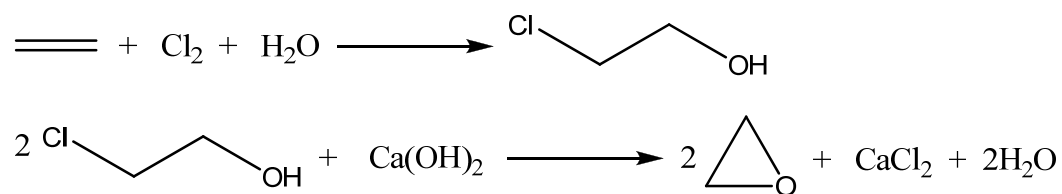
<b>Plant</b>	<b>Ethylene Oxide Capacity (tonnes/year)</b>
<b>BASF</b>	
Ludwigshafen, Germany	345,000
Antwerp, Belgium	500,000
Geismar, Louisiana	285,000
<b>Shell Chemicals</b>	
Geismar, Louisiana	415,000
Jurang Island, Singapore	110,000
Moerdijk, Netherlands	305,000
CPSCL, Nanhai Petrochemical Complex	320,000
Wilton, UK	
<b>Dow Chemicals</b>	
Seadrift, Texas	430,919
Plaquemine, Texas	273,066
St. Charles, Illinois	771,118
Terneuzen, Netherlands	163,295
Wilton, UK	317,519
<b>INEOS</b>	
Antwerp, Belgium	420,000
Lavera, France	220,000
Koln, Germany	280,000
<b>Reliance Petrochemicals Limited</b>	
Hazira, Gujarat	56,000
<b>Saudi Basic Industries Corporation</b>	
Middle East	718,500
<b>Eastman Chemicals</b>	
Longview, Texas	104,327
<b>Formosa Plastics</b>	
Point Comfort, Texas	249,479
<b>Old World Industries</b>	
Clear Lake, Texas	317,519
<b>Equistar</b>	
Bayport, Texas	340,199
<b>Sun Olin Chemicals Corporation</b>	
Claymont, Delaware	49,895
<b>Olin Corporation</b>	
Brandenburg, Kentucky	49,853

**Table 1.8:** Ethylene Oxide uses and their applications [1, 2, 32].

<b>Products</b>	<b>Application</b>
Ethylene Glycol	Polyester, Anti-freeze, Poly ethylene terephthalate (PET)
Poly(ethylene) glycol	Cosmetics, Pharmaceuticals, Paints, Lubricants
Ethylene Oxide Glycol	Brake Fluids, Detergents, Paints
Ethers	
Ethanolamines	Soap, Detergents, Natural Gas Purification
Ethoxylated Products	Biodegradable Detergents, Cleaning Agents, Emulsifiers, Dispersants

#### 1.4.1 Ethylene Oxide by Chlorohydrination

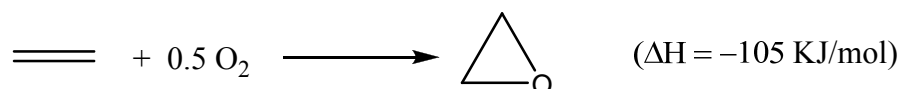
The Chlorohydrin process for the epoxidation of lower olefins is a two step process. This process was practiced in the U.S. in the mid 1950's but as of 1975 all the plants have adopted the economical vapor-phase oxidation process. In the chlorohydrin process, ethylene was reacted with aqueous chlorine to form ethylene chlorohydrin which was further converted into ethylene oxide by heating with lime water. The selectivity to ethylene oxide was 80% based on ethylene but a large amount chlorine is consumed which resulted in large aqueous waste stream making the process economically and environmentally unsustainable. The by products that accompanied with 100 kg of ethylene oxide were 10-15 kg 1, 2- dichloroethane, 7-9 kg 2, 2'- dichlorodiethyl ether and 300-350 kg calcium chloride. The main reason for the replacement of this process with the direct oxidation route was the large volume of chemical feedstock requirements, the enormous production of waste products and in particular, the cost of chlorine which was a major factor. The amount of waste generated in this process was high compared to the alternate route. The reactions that take place in this process are given below in scheme 9 [32, 33].



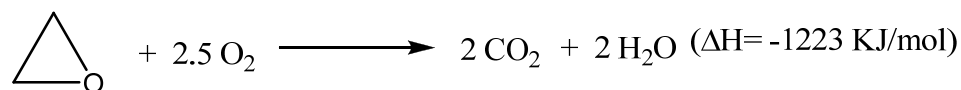
Scheme 9: Ethylene chlorohydration and saponification

### 1.4.2 Vapor Phase Oxidation of Ethylene

This process was originally developed in the 1930's and has undergone a lot of improvement over the course of time with numerous other industries adopting this technology over the chlorohydration technique. This was a result of the fundamental progress in the technology for catalyst manufacturing. The partial oxidation of ethylene to ethylene oxide (EO) is an exothermic reaction and is accompanied by two side reactions involving the complete combustion of feed ethylene and the product EO to produce carbon dioxide and water with the first combustion process generating 13 times the heat generated in the epoxidation reaction. Either air or oxygen can be used as oxidant for this process with a higher selectivity towards EO being achieved with oxygen [32, 34]. The total heat of the reaction is 357-546 KJ/mol of ethylene. The original process used silver catalyst dispersed on aluminum oxide support as the catalyst. The operating conditions of this process include a temperature of 260 °C and a moderate pressure of 30 bars [32].

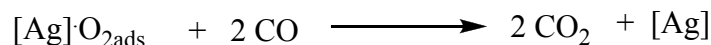
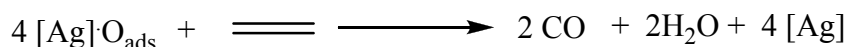
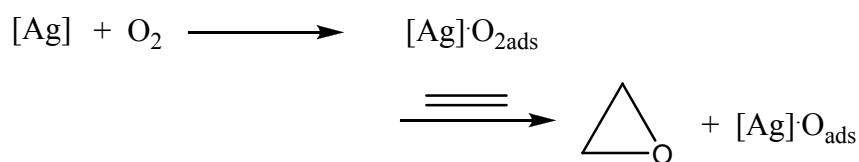


Scheme 10: Ethylene Oxidation



Scheme 11: Side Reactions accompanying the oxidation

The mechanism for the oxidation of ethylene involves the adsorption of oxygen molecule on the surface of the silver catalyst where it reacts with ethylene to form EO. The atomic oxygen remaining on the surface of catalyst is not capable of producing ethylene oxide and instead oxidizes ethylene or EO to form carbon monoxide and water. CO is further oxidized to CO<sub>2</sub>. The industrial catalyst contains 5-20 wt% silver and the activity and selectivity of the catalyst is primarily influenced by the active sites of the catalyst, the catalyst support and its physical properties [32]. The proposed mechanism of the reaction is given below. The flow sheet for the process using air and oxygen as oxidants is given in Appendix A.



[Ag]= Metal Surface

Scheme 11: Mechanism of oxidation

The vapor phase oxidation process has undergone many changes especially with respect to additives that aid in increasing selectivity. An EPA report reveals that 30% of the converted ethylene feed undergoes complete combustion [34]. Mitigating the secondary reaction is important in maintaining temperature and preventing thermal runaway reactions due to overheating of the reactor. Higher temperatures may result in burning of the catalyst destroying its active sites. Higher selectivity towards EO can be obtained by limiting the conversion of ethylene to less than 10%. The reaction is carried out in a tubular reactor but use of fluidized bed reactor results in a selectivity of 75% and space time yield of 600-700 EO (L catalyst)<sup>-1</sup> h<sup>-1</sup>. Air was originally used as an oxidant but since has been replaced by oxygen to minimize ethylene losses occurred due to the purging of the reactor stream to separate nitrogen at end of each pass. The second reason for choosing oxygen as the oxidant is the need for higher operating temperatures in the second reactor that lowered the selectivity towards ethylene oxide. The additional costs incurred due to the fractionation of air to obtain the oxygen were far less than those incurred due to loss of ethylene so all new plants use oxygen as the oxidant [32]. The other advantage is the reduction in the waste gases that were generated in the oxygen process which is only 2% of those resulting from the process using air. As there were no inert gases to discharge, carbon dioxide or methane was used as the inert medium in closed loop operations due to their high heat capacities which mitigate the thermal runaway reactions. In the oxygen process the waste gases were washed with potash solution rather than directly released into the atmosphere. The cost of ethylene which accounts for 70-80% of the

cost of ethylene oxide affects the economics of this process. In recent times there has been a renewed interest in improving the selectivity and conversion of the ethylene to EO process. Improvements in catalyst processing techniques have resulted in longer catalyst life and higher yields of ethylene oxide, leading to enhanced plant profitability.

Silver, due to its high selectivity was found to be the best catalyst for the oxidation process. Alkali metal salts (co-catalysts) were added as additives to the reaction mixture to increase the selectivity beyond 80%. In the case of rubidium and cesium additives the selectivity increased to 94% for fresh catalyst and is proven to remain in the mid 80's even after continuous operation for a month. There have been many improvements in the catalyst regeneration technique, the most commonly adopted step being the impregnation of cesium into the catalyst as a methanolic solution. In this way, the catalyst selectivity is reported to increased by 8% postponing an expensive catalyst change operation in the tube reactor.

### **1.5 Thesis Objectives**

The overall goal of this thesis is to investigate the phase behavior of propylene with liquid phase components in order to better understand the effect of N<sub>2</sub> and methanol in enhancing PO yield. A collateral goal is also to investigate whether the phase behavior of ethylene with liquid phase can be exploited to develop selective and inherently safe ethylene oxide manufacturing process and estimating the mass transfer coefficient of constant for the transport of propylene into the liquid phase.

Specific Objectives of this work are as follows:

- Model and validate (with published experimental data) the vapor-liquid equilibria (VLE) of propylene-nitrogen, propylene-methanol, propylene-water, propylene-methanol-water and propylene-methanol-nitrogen.
- Use of the phase equilibria data to design experiments for estimating the mass transfer coefficient for propylene transport into liquid phase in the ReactIR.
- Model and validate (with published experimental data) the vapor-liquid equilibria (VLE) displayed by ethylene/alcohol mixtures, ethylene oxide/alcohol mixture, ethylene/ethylene oxide, methanol-carbon dioxide.
- Quantify the safety benefits of using inert gases such as nitrogen and carbon dioxide during selective ethylene/propylene epoxidation.

Aspen Hysys® simulator [35] was used to predict the VLE of various systems and the concept is extended to lower molecular weight compounds for selective synthesis of their oxides.

## **1.6 Application of the Principles of Green Chemistry and Engineering**

The research to develop alternate processes for the epoxidation of alkenes is strongly driven by the principles of green chemistry and engineering. The operating conditions of the oxidation reaction developed by CEBC researchers are mild temperatures and pressures making the process less energy intensive than the conventional process. The reactants and the solvent used in the new process are environmentally benign in nature. This process maintains high atom efficiency as the



conversion of propylene is high with high selectivity to propylene oxide, due to high selectivity of the catalyst. These factors reduce the capital investment and operating costs, and the advantage is further improved because separation steps are facile. At the operating pressure, the propylene oxide formed in the reaction is in the liquid phase, due to its high solubility in methanol, and can be easily distilled off owing to its low boiling point. The choice of inerts, such as nitrogen to bring about pressure intensification, also aids in minimizing the risk of formation of an explosive mixture or the burning of substrate, solvent or products. All of these considerations plus the zero emissions of carbon dioxide makes the CEBC process green. The presence of inerts in the gas phase makes the process inherently safe and the absence of combustion of substrate and reaction product reduces emissions of carbon dioxide and eliminates any need for additional treatment. These qualitative conclusions will be later verified by quantitative environmental impact assessment.

### **1.7 Potential Impact of this Work**

Propylene oxide is a major chemical intermediate consumed in bulk by the chemical manufacturing industry. The commercialization of the CEBC technology will extend the use to hydrogen peroxide, an environmentally benign oxidant for industrial scale oxidation process for light olefin epoxidation. The advantages of this process are brought into light in terms of selectivity, separation and safety aspects. The accomplishments of the new proposed process are:

- Rational choice of solvents and operating conditions for enhancing the availability of light olefins in the liquid phase, thereby intensifying the process.
- The predictions of the phase behavior are very reliable. This information is essential for the rational interpretation of data in kinetic and reactor modeling.
- The safety calculations are essential for developing operating conditions for inherently safe operation by avoiding conditions that lead to explosive vapor-phase mixtures.

To describe these accomplishments the thesis is organized into 6 chapters. Chapter 2 involves the study of phase equilibria of propylene with the components of the reaction mixture as binary and ternary systems. In the third chapter the mass transfer of the ReactIR for transport of propylene into the liquid phase is estimated and a model is devised to estimate the rate of the reaction. Chapter 4 involves the study of phase equilibrium of ethylene, and a description of the present day commercial process. The fifth chapter provides the data on safety aspects due to the presence of inerts such as carbon dioxide and nitrogen in the epoxidation reaction. A summary of the conclusion and recommendations are provided in chapter 6.

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## Chapter 2

### Vapor Liquid Equilibria of Mixtures involving Propylene, Propylene Oxide, Water, Methanol and Nitrogen

#### 2.1 Introduction

Selective catalytic oxidation of propylene is a multi-billion dollar industry. As stated in the first chapter, propylene undergoes oxidation in the liquid phase in presence of hydrogen peroxide as oxidant. The rate of the reaction depends on the availability of gaseous propylene in the liquid phase. Hence, an accurate knowledge of the solubility of propylene in the solvent of choice is of the utmost importance.

The solubility of propylene in the liquid phase has been modeled using the “Aspen HYSYS®” simulator [1]. Aspen HYSYS® is a versatile software and is mostly used in the conceptual design, steady state, dynamic modeling and optimization of plant operations. In Professor Subramaniam’s group at KU, it has been mainly used for performing comparative economic and environmental impact analysis of conventional processes and CEBC processes. For performing the environmental impact analysis, the HYSYS® simulator has been linked to other programs such as SCENE (Simultaneous Comparison of Environmental and Non-Environmental Processes).

The Vapor-Liquid Equilibrium (VLE) of mixtures can be estimated with Aspen HYSYS® by flashing the feed at the required conditions. The most important factor in modeling the phase equilibria is the selection of the equation of state (EOS) that can adequately account for the non-idealities of the mixture of components. The

Aspen HYSYS® simulator has a compilation of various equations of state such as Peng Robinson, Virial, Saue Redlich Kwong etc. and activity models such as UNIQUAC, NRTL, Chein Null etc. of major thermodynamic importance that can be used based on the non-ideality of compounds present in the system. Activity models are used to represent the system of propylene, methanol, nitrogen and water due to the high non-ideality exhibited by these components at operating conditions of the CEBC process. A thorough literature search was done to compare the results of the simulation with published experimental data for the systems of propylene and methanol (Ogaki et al.), propylene and nitrogen (Yorizane et al.), propylene and water (Mcketta et al.), ethylene and methanol (Haneda et al.). The software also has an electronic version of Decehma Chemical Engineering database that contains the physical and chemical properties of the pure substances.

## **2.2 Activity Model**

Activity models provide a correlation between activity coefficients and mole fraction. There are many such correlations the most prominent of them being the Van Laar equation, Margules equation, Wilson's equation, Non-Random Two Liquid Theory (NRTL) and Universal Quasi Chemical Theory (UNIQUAC). These equations are derived from the Wohl's expansion of Gibbs free energy and are widely used. The UNIQUAC equation is used for modeling of the phase equilibria of the systems encountered in the present study and has advantages over the other equations. The generalized Wohl's expansion is given by

$$\frac{g^E}{RT(x_1q_1 + x_2q_2)} = 2a_{12}z_1z_2 + 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2 \dots \quad (2.1)$$

$$\text{Where } z_1 = \frac{x_1q_1}{x_1q_1 + x_2q_2} \text{ and } z_2 = \frac{x_2q_2}{x_1q_1 + x_2q_2} \quad (2.2)$$

The two parameters of the equation are the  $q$ 's which are effective volumes and the  $a$ 's which are interaction parameters. The various activity model equations are obtained by applying certain assumptions and their validity is limited to certain concentration regions and substances exhibiting certain characteristics. For example Van Laar's equation is not applicable to polar or associating components whereas Wilson's equation can be used to model such systems but cannot model liquid systems with limited miscibility.

The NRTL and UNIQUAC models can be used to represent the phase equilibria over the entire concentration range. The reason for choosing UNIQUAC model over NRTL is the fact that NRTL uses three parameters whereas UNIQUAC model uses two parameters to estimate the excess Gibbs free energy. It is very difficult to obtain reliable thermodynamic data for all the components of the system at the required conditions and an extra parameter introduces a higher level of uncertainty into the model. The interaction parameters of compounds used in this method can be estimated by the UNIFAC method which is also based on UNIQUAC theory [2].

### 2.3 Universal Quasi Chemical Theory (UNIQUAC Model)

Abrams derived an equation that extends the universal quasi chemical theory of Guggenheim for non-random mixtures to solutions containing the molecules of different sizes, thus the equation was called UNIQUAC equation [3]. The excess Gibbs free energy consists of two parts a combinatorial part that describes the entropic contribution and a residual part that is primarily due to intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined by the sizes and shapes of the molecules and requires only pure component data. The adjustable binary interaction parameters appear in the residual part. The UNIQUAC equation is given by

$$\frac{g^E}{RT} = \left( \frac{g^E}{RT} \right)_{\text{combinatorial}} + \left( \frac{g^E}{RT} \right)_{\text{residual}} \quad (2.3)$$

The equations for binary mixtures is given by,

$$\left( \frac{g^E}{RT} \right)_{\text{combinatorial}} = x_1 \ln \frac{\phi_1^*}{x_1} + x_2 \ln \frac{\phi_2^*}{x_2} + \frac{Z}{2} \left( x_1 q_1 \ln \frac{\theta_1}{\phi_1^*} + x_2 q_2 \ln \frac{\theta_2}{\phi_2^*} \right) \quad (2.4)$$

$$\left( \frac{g^E}{RT} \right)_{\text{residual}} = -x_1 q_1' \ln (\theta_1' + \theta_2' \tau_{21}) - x_2 q_2' \ln (\theta_2' + \theta_1' \tau_{12}) \quad (2.5)$$

$$\phi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \phi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \quad (2.6)$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \quad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \quad (2.7)$$

$$\theta_1' = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'} \quad \theta_2' = \frac{x_2 q_2'}{x_1 q_1' + x_2 q_2'} \quad (2.8)$$



The parameters  $r$ ,  $q$ ,  $q'$  are pure component molecular structure constants of any molecule and depend on the molecular size and external surface area. These adjustable parameters for binary mixtures are expressed in terms of characteristic energies. These parameters show a weak dependency on temperature.

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) = \exp\left(-\frac{a_{12}}{T}\right) \quad \tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) = \exp\left(-\frac{a_{21}}{T}\right) \quad (2.9)$$

The activity coefficients are represented by  $\gamma_1$  and  $\gamma_2$  and are estimated using in equations 2.10 and 2.11.

$$\begin{aligned} \ln \gamma_1 = & \ln \frac{\phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1^*} + \phi_2^* \left( l_1 - \frac{r_1}{r_2} l_2 \right) - q_1' \ln (\theta_1' + \theta_2' \tau_{21}) \\ & + \theta_2' q_1' \left( \frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} - \frac{\tau_{21}}{\theta_2' + \theta_1' \tau_{12}} \right) \end{aligned} \quad (2.10)$$

$$\begin{aligned} \ln \gamma_2 = & \ln \frac{\phi_2^*}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\phi_2^*} + \phi_1^* \left( l_2 - \frac{r_2}{r_1} l_1 \right) - q_2' \ln (\theta_2' + \theta_1' \tau_{12}) \\ & + \theta_1' q_2' \left( \frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} \right) \end{aligned} \quad (2.11)$$

$$\text{Where } l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1) \quad l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1) \quad (2.12)$$

This model is applicable to a wide variety of nonelectrolyte liquid mixtures containing non-polar and polar fluids such as hydrocarbons, alcohols, nitriles, ketones, aldehydes, organic acids, and water and also substances that are partially miscible over certain concentration ranges. The data obtained using these model are highly accurate. These equations can be extended to multicomponent systems as shown in equation 2.13.

$$\ln \gamma_i = \ln \left( \frac{\Phi_i^*}{x_i} \right) + \frac{z}{2} q_i \ln \left( \frac{\theta_i}{\phi_i^*} \right) + l_i - \left( \frac{\phi_i^*}{x_i} \right) \sum_{j=1}^m l_j x_j$$

$$+ q_i' \left( 1 - \ln \sum_{j=1}^m \theta_j' \tau_{ji} \right) - q_i' \sum_{j=1}^m \left( \frac{\theta_j' \tau_{ij}}{\sum_{k=1}^n \theta_k' \tau_{kj}} \right) \quad (2.13)$$

Equation 2.13 is embedded in the HYSYS® simulator determines the activity of the system. The equation for  $\tau_{ij}$  is modified as shown in equation 2.14 to accommodate temperature dependency term  $b_{ij}$  [2, 4].

$$\tau_{ij} = \exp \left[ \frac{-a_{ij} + b_{ij} T}{RT} \right] \quad (2.14)$$

The estimations of some of the Van der Waals area and volume parameters are done using empirical correlations (equations 2.15 and 2.16) with  $A_{wi}$ ,  $V_{wi}$  being the van der Waals area and volume given by Bondi. [1]

$$q_i = \frac{A_{wi}}{(2.5e9)} \quad (2.15)$$

$$r_i = \frac{V_{wi}}{15.17} \quad (2.16)$$

The accuracy of the model to simulate the phase behavior of multi component systems fails due to the inability of the model to account for interactions among the various molecules of the mixture; these calculations are very sensitive to the parameter  $(\tau_{ijk})$ .

## 2.4 Interaction Parameters

The interaction parameters appears in the residual part of the Gibbs free energy and contributes to the activity coefficient. Accurate values of the binary interaction parameters ( $a_{ij}$ ) are required to quantitatively estimate the contribution of residual Gibbs free energy. The sign of the interaction parameters are based on the effect on the total volume when pure liquids are mixed, if the total volume of the mixture is less than the sum of the volumes of pure components, the parameter is given a negative sign and if the mixture volume is more then the sum of the volumes it is given a positive sign. The most recent techniques that have been developed to estimate these interactions are based on the group contribution methods like Universal Quasi Chemical Functional Group Activity Coefficient (UNIFAC) and Analytical Solution of Groups (ASOG). The HYSYS® software is embedded with UNIFAC tool to estimate the interactions the details are discussed in the following section [1].

### 2.4.1 Universal Quasi Chemical Functional Activity Coefficient (UNIFAC) model

This method was originally developed by Fredenslund et al. [3] to estimate liquid phase activity coefficients and is based on combining the UNIQUAC model with the solution of group's theory developed by Wilson and Deal [3]. In this model, the mixture is assumed to be a solution of structural groups like methyl (CH<sub>3</sub>), hydroxyl (OH), acid (COOH) rather than a mixture of discrete molecules. The properties of the liquids are estimated from the properties of these groups. The

advantage of this method is that relatively small number of groups can build a large number of compounds and mixtures. In this theory the contribution of a hydroxyl group is treated as the same in primary, secondary or tertiary position thereby reducing the number of distinct groups. In the absence of experimental vapor-liquid equilibrium data, this method can be used to estimate the phase equilibria using the interaction parameters generated by these predictive tools. The VLE data obtained by using these fitted parameters are proven to generate data with high accuracy in comparison to experimental data.

The activity coefficient is assumed to consist of two parts (Equation 2.17), a combinatorial part (Equation 2.18) represented by the Staverman-Guggenheim term that accounts for the difference in shape and size of the molecule, which is obtained from the group volume and area constants, and a residual part (Equation 2.21) describing the interactions between different groups. The key assumption made in this technique is “the sum of individual contributions of each solute group in the solution is less than the individual contributions in the pure component environment”. The effect of temperature on the interaction parameters is assumed to be negligible. The assumption of assigning similar contribution to all isomers has a more profound effect on the ability of the model to simulate VLE accurately than temperature. Comparison of experimental data with that generated by the model has led to methanol being treated as a separate group than other alcohols. Similar treatment is given to the allyl group. A detailed study on the effect of temperature was carried out by Thomsen,[3] who modeled the vapor-liquid equilibrium for the system of 1-propanol and 2-

propanol with heptane at various temperatures. A well defined trend was observed in the activity coefficients. [5]

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2.17)$$

$$\ln \gamma_i^C = \ln \left( \frac{\Phi_i^*}{x_i} \right) + \frac{z}{2} q_i \ln \left( \frac{\theta_i}{\phi_i^*} \right) + l_i - \left( \frac{\phi_i^*}{x_i} \right) \sum_{j=1}^m l_j x_j \quad (2.18)$$

$\phi$ ,  $\theta$  are molecular volume and area fractions respectively.

$q_i$ ,  $r_i$  are the respective van der Waals volume and area parameters.

$$\psi_i = \phi_i = \frac{r_i x_i}{\sum r_j x_j} \quad (2.19)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (2.20)$$

$$\ln \gamma_i^R = \sum \nu_k^{(i)} \left[ \ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (2.21)$$

$\Gamma_k$  = Residual activity coefficient of group k (Equation 2.22).

$\Gamma_k^{(i)}$  = Residual activity coefficient of group k in reference solution containing only molecules of the type i, can be estimated by equation 2.22.

$$\ln \Gamma_k = Q_k \left( 1 - \ln \sum_m \theta_m \tau_{mk} - \sum_m \left( \frac{\theta_m \tau_{km}}{\sum_n \theta_n \tau_{nm}} \right) \right) \quad (2.22)$$

$\theta_m$  is the Group Surface Area Fraction and given by  $\theta_m = \frac{X_m Q_m}{\sum_n X_n Q_n}$

$X_m$  is the group fraction.  $X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j}$

$$\tau_{jk} = \exp\left[\frac{u_{jk} - u_{kk}}{RT}\right] = \exp\left[\frac{-a_{jk}}{T}\right] \quad (2.23)$$

The UNIFAC formulation can be applied to all systems in which the UNIQUAC model is used e.g. nonelectrolyte binary and multi component mixtures at temperature and pressure conditions removed from the critical region. This method fails for condensable mixtures and polymers containing more than ten functional groups. There have been recent developments to account for temperature dependency as described by Lyngby [5]. In spite of this versatility, it must be recognized that group contribution methods are only approximations as any group in a molecule is not completely independent of other constituent groups [3, 5-8].

## 2.5 Peng Robinson Equation of State

Peng Robinson equation of state was developed in the year 1976 to overcome the drawbacks of existing equations of state such as Saue Redlich-Kwong and Virial equation of state. The advantage of this equation of state is its ability to express the attractive and repulsive parameters in terms of critical properties. The compressibility factor and liquid densities may be predicted accurately even near the critical point. This equation can represent both the vapor phase and liquid phase of certain components over the entire range. This PREOS (Equation 2.24) can also be used to simulate the VLE of moderately polar liquids

$$P = \frac{RT}{(v-b)} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (2.24)$$

The parameter ‘a’, ‘b’ representing the attractive forces and the minimum distance within which molecules can approach can be expressed as a function of both acentric factor and temperature. These factors are dependent on the substance and are defined by its critical properties. The  $\beta$  parameter depends on the acentric factor ( $\omega$ ).

$$a(T_c) = 0.45724 \frac{(RT_c)^2}{P_c} \quad (2.25)$$

$$a(T) = a(T_c) \alpha(T) \quad (2.26)$$

$$\alpha(T) = \left[ 1 + \beta \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (2.27)$$

$$\beta = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (\text{for } 0 \leq \omega \leq 0.5) \quad (2.28)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (2.29)$$

These equations can be extended to mixtures by using van der Waals mixing rules as given below.

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \quad (2.30)$$

$$b = \sum b_i x_i \quad (2.31)$$

$$A = \frac{a_m P}{(RT)^2} \quad (2.32)$$

$$B = \frac{b_m P}{RT} \quad (2.33)$$

The fugacity coefficient of the component k in the system is estimated using equation 2.34. This value can be used in the modified Raoult’s law (equation 2.35) to account for any non-ideality of the gas phase because of interaction between the dissimilar molecules. These equations are embedded in the HYSYS® simulator and

aid in the estimation of the vapor and liquid phase compositions at equilibrium. The activity model in the simulator enables the user to treat the gas phase components as either ideal or non-ideal. Based, on the components ideal gas law or an equation of state such as Peng Robinson or Soave Redlich-Kwong can be used to represent the gas phase components [1, 2, 4].

$$\ln \varphi_i = -\ln \left( Z - \frac{Pb}{RT} \right) + (Z-1) \frac{b_i}{b} - \frac{a}{2\sqrt{2}bRT} \left[ \frac{1}{a} \left( 2\sqrt{a_i} \sum_{j=1}^N x_j \sqrt{a_j} (1-k_{ij}) \right) - \frac{b_i}{b} \right] \quad (2.34)$$

$$* \ln \left[ \frac{\nu + (\sqrt{2} + 1)b}{\nu - (\sqrt{2} - 1)b} \right]$$

$$\varphi_i P^t y_i = x_i P^{sat} \gamma_i \quad (2.35)$$

## 2.6 VLE Modeling using HYSYS® simulator

A suitable equation of state is selected based on the components of the system. The selection of an equation of state or an activity model to study the phase behavior is based on their ability to account for the non-ideality of the components. The inlet conditions of the feed are specified and the outlet vapor, liquid compositions and flow rates are estimated by the software. The software providers have developed an interface between the HYSYS® file and the Microsoft Excel® spreadsheet program in order to improve the ease of storing and processing data. The other factor that determines the prediction accuracy is the interaction parameters. HYSYS® has a built in tool to estimate the UNIFAC interaction parameters for activity models. Further interaction parameters for Peng Robinson and Redlich Kwong equations of state have to be provided by the user if they are not present on the electronic version of the



Dechema database embedded in the software. HYSYS® software given special emphasis to the Peng Robinson and Redlich-Kwong equations of state due to its versatility and compounds such as methanol, lower molecular weight alkanes, nitrogen, carbon dioxide and water are subjected to special treatment.

## **2.7 Results and Discussions**

### **2.7.1 Binary Systems**

The interaction parameters used in the model dictate the accuracy of the simulation. Various optimization tools that are in existence use the minimization of Gibbs Free energy approach to estimate the interaction parameters and are plagued by the problem generating data that represent a local minima. So, binary interaction parameters are often validated by simulating the equilibrium compositions of the liquid and vapor phases at the conditions at which experimental data is available. All components that are present in considerable quantities are modeled. The systems that are modeled here are propylene-methanol, propylene-nitrogen, propylene-water, and propylene-propylene oxide.

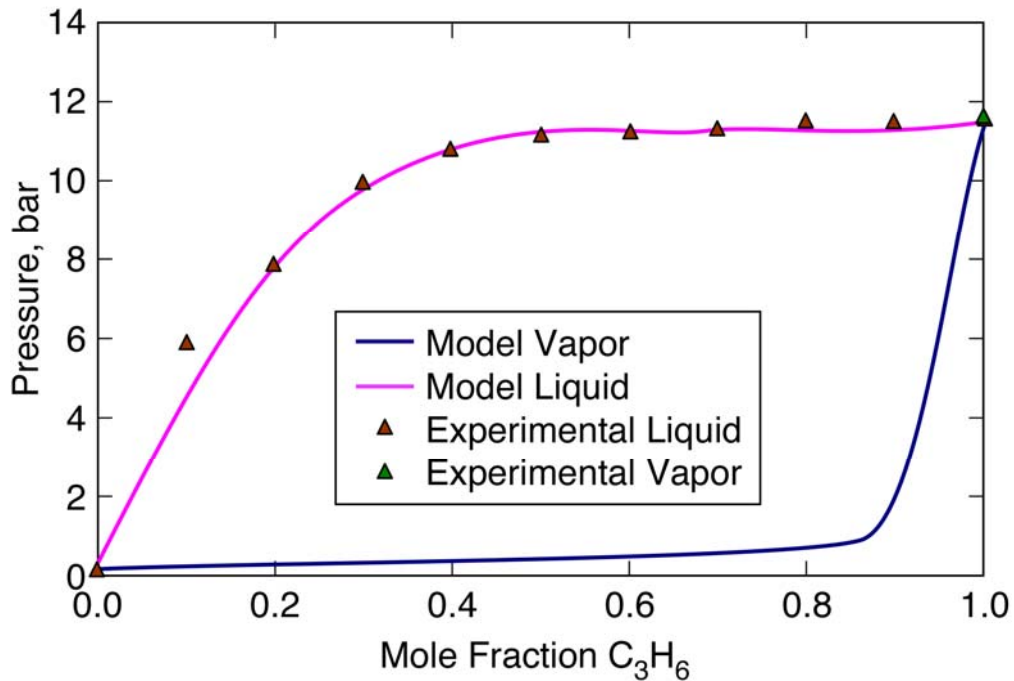
#### **2.7.1.1 Propylene (1) and Methanol (2)**

In the CEBC process, propylene is transported from the gaseous phase to the liquid phase where it reacts with hydrogen peroxide an oxidant to form propylene oxide. The rate limiting step of the reaction is very likely to be the diffusion of propylene from the gas phase into the liquid phase [9]. A good understanding of the

vapor-liquid equilibrium of propylene with solvent methanol and the knowledge of the mass transfer coefficient is required to overcome this limitation and operate outside the diffusion limited region. Propylene/methanol mixtures are non-ideal in nature; hence the UNIQUAC model was used to estimate its activity in the liquid phase while Peng Robinson equation of state was used to account for the fugacity of the gas phase components. The interaction parameters estimated using the UNIFAC method and are listed in Table 2.1.

**Table 2.1:** Binary Interaction Parameters of Propylene and Methanol at 25 °C [1]

Component	Propylene	Methanol
Propylene	-----	-109.345
Methanol	1620.271	-----



**Figure 2.1:** Vapor-Liquid Equilibrium of Propylene (1) and Methanol (2) at 25 °C

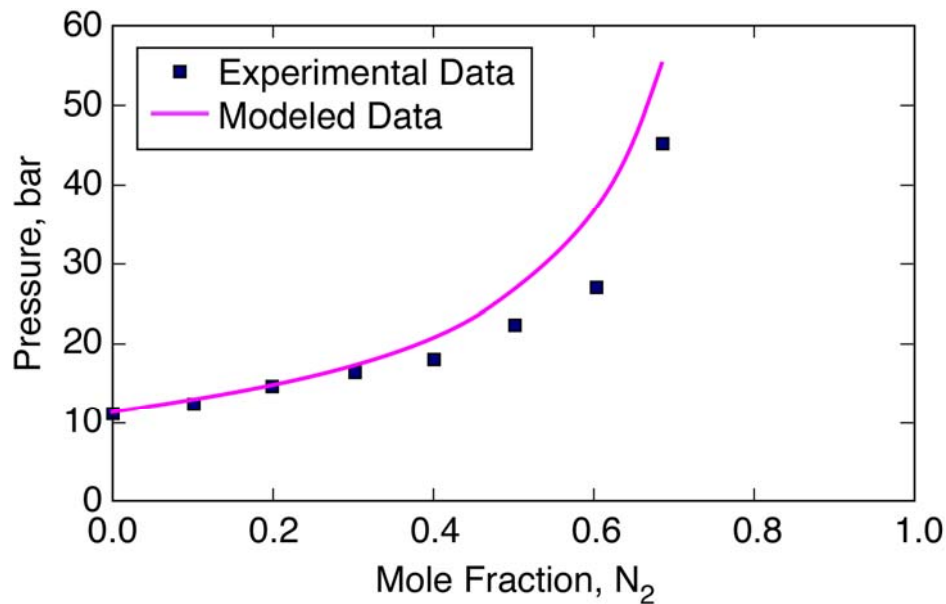
[10]

Using the interaction parameters as shown in Table 2.1 a good match was obtained between the model simulations and the experimental data obtained from the literature [10]. As shown in Figure 2.1, propylene dissolves in the liquid phase even at ambient conditions. The solubility of propylene is greater than 40 mol% under typical reaction conditions of 25 °C and 11 bars. The phase equilibria clearly indicate the advantages of using methanol in enhancing the solubility of propylene in the liquid phase.

#### **2.7.1.2 Propylene (1) and Nitrogen (2)**

Nitrogen is used in the liquid phase epoxidation process of propylene to bring about pressure intensification. The effect of nitrogen on the solubility of propylene in methanol and the yield of propylene oxide was measured. Propylene was charged into the reactor and the system was pressurized with nitrogen. An increased conversion of propylene was attained at higher nitrogen pressures and can be attributed to the enhanced solubility of propylene in methanol. A moderate pressure of 17 bars increased the yield of PO to 98+% from 80+% and reduced the reaction time by an hour. The reactor is maintained at 30 °C which is far below the critical temperature of propylene. Under these conditions, pressurization beyond the saturation vapor pressure results in condensation of propylene. Nitrogen, a non-condensable gas acts like a piston pushing propylene into the liquid phase thereby enhancing its solubility. The condensed propylene may then dissolve freely into the liquid phase and undergo conversion. ReactIR studies confirmed the increased concentration of propylene in

methanol+water mixtures at progressively higher nitrogen pressures. The vapor-liquid equilibrium of this system was modeled using the Peng-Robinson equation of state. The data revealed that a pressure of 10+ bars is needed to condense propylene at a temperature of 22.5 °C. The binary interaction parameter ( $k_{12}= 0.0637$ ) was obtained from literature [11]. The model predictions shows a good agreement with the experimental data at dilute  $N_2$  mole fractions deviating at higher mole fractions as shown in Figure 2.2 [9, 11].



**Figure 2.2:** Vapor-Liquid equilibrium of Propylene (1) and Nitrogen (2) at 22.5 °C [11]

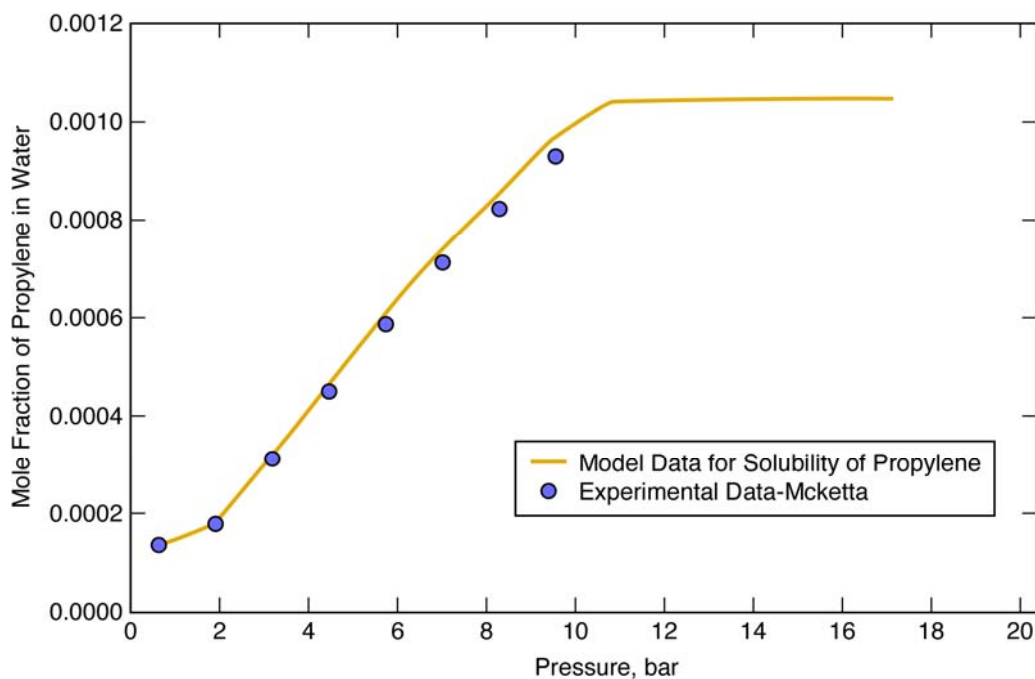
### 2.7.1.3 Propylene(1) and Water(2)

Propylene solubility in water is very low compared to that of methanol [12]. This binary system may be modeled, using the Kabadi Danner (KD) EOS which is a modification of Soave-Redlich-Kwong equation and is used for systems where the

solubility of water in the hydrocarbon is higher than the solubility of hydrocarbon in water. This modification is based on an asymmetric mixing rule, wherein the interactions in the water phase consisting of strong hydrogen bonds include those between the hydrocarbons and water as well as water-water interaction. These systems are highly non-ideal and activity models (UNIQUAC) was used in this thesis to model them. The binary interaction parameter used in the KD EOS is  $k_{12}= 0.44$  [1]. The propylene and water system showed the formation of a liquid-liquid phase at high pressures the UNIQUAC model can simulate the composition of the two liquid phases at low pressures [13], but at 30 °C and 20 bars, the system showed a single liquid phase. The equations given below describe the KD EOS.

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)} \quad (2.36)$$

KD equation includes a second energy parameter (a) which is a function of the hydrocarbon structure and expressed as a group contribution factor G that is assumed as zero for all the non-hydrocarbons. The solubility of propylene in water increases with increasing pressure and flattens at higher pressures as there is a phase split at these conditions. However, the mole fraction of propylene is only on the order of  $10^{-4}$  which is very low in comparison with that of methanol at operating temperature of 30 °C and pressure of 20 bars where 40 mol% of propylene dissolves into the liquid phase.

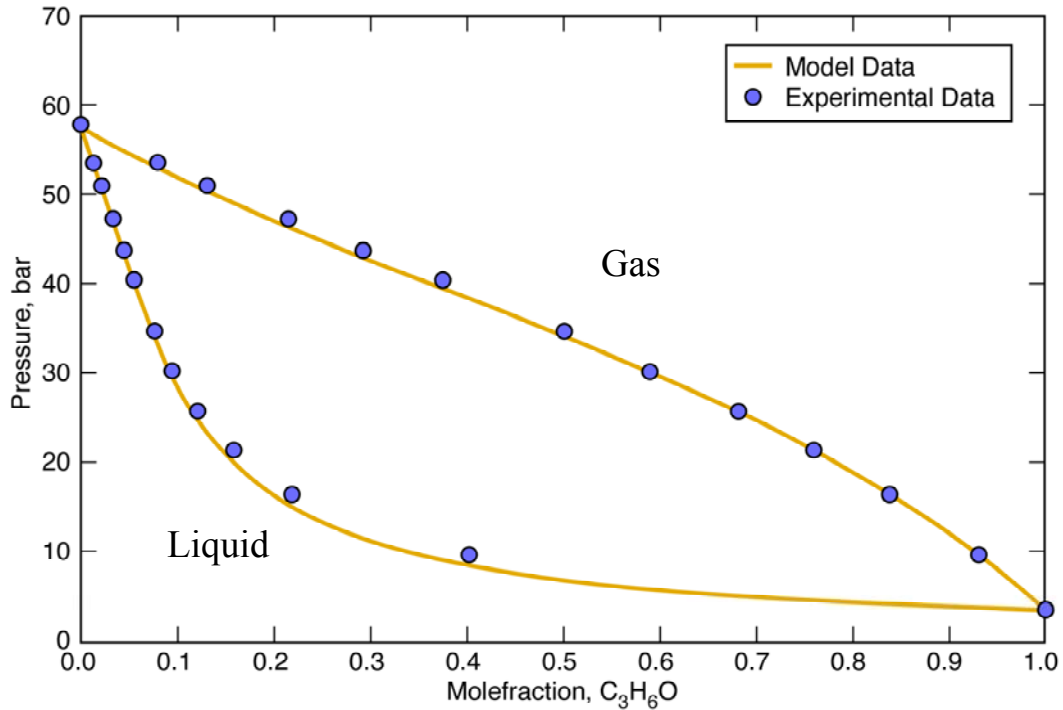


**Figure 2.3:** Solubility of Propylene (1) in Water (2) at 21 °C [12]

#### 2.7.1.4 Propylene Oxide (1) and Propylene (2)

The product of the epoxidation of propylene is propylene oxide. The presence of propylene oxide in the system will affect the vapor liquid equilibrium of propylene and methanol. The low normal boiling point of 34 °C for PO enables easy separation of the product by distillation following reaction. Further, the amount of propylene glycol generated in the CEBC process is negligible as the selectivity of catalyst towards the desired product is very high. The components of the binary system form a non-ideal mixture and the VLE data are simulated using the UNIQUAC model used in the HYSYS® simulation. The interaction parameters (100 for propylene/propylene oxide and 350 for propylene oxide/propylene) used are predicted using the UNIFAC method[10]. As shown in Figure 2.4, the model simulations match the experimental

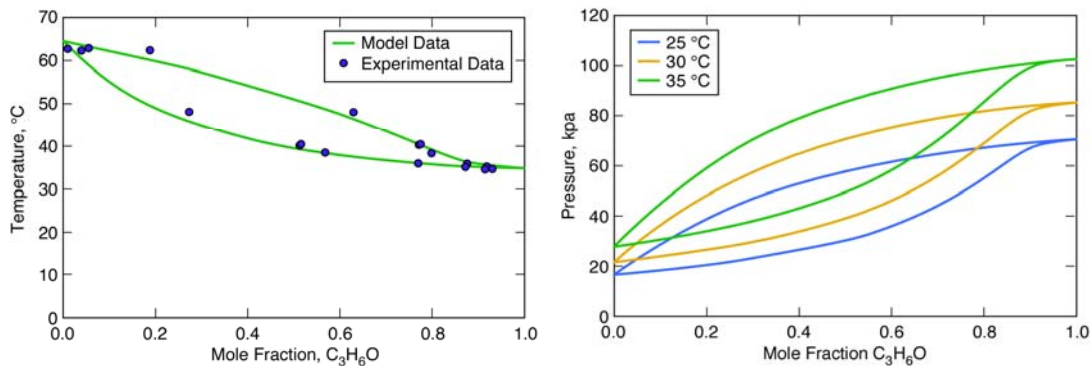
data very well. The vapor-liquid equilibrium data at 25 °C, shows a liquid phase with high concentration of propylene oxide.



**Figure 2.4:** Vapor-Liquid Equilibrium of Propylene Oxide (1) and Propylene (2) at 25 °C [10]

### 2.7.1.5 Propylene Oxide (1) and Methanol (2)

Propylene oxide and methanol mixtures are non-ideal in nature due to hydrogen bonding in methanol. UNIQUAC model is used in the simulation of the phase behavior the interaction parameters for this system are obtained from the literature. The values used in the simulation are  $k_{12}= 791.0185$  and  $k_{21}= -210.2403$ . At the operating pressure of 17 bars, the VLE data and simulations (Figure 2.5) reveal that the propylene oxide formed remains almost completely in the liquid phase at pressures above 2 bars [14].



**Figure 2.5:** Vapor-Liquid equilibrium of propylene Oxide (1) and methanol (2) at a) Isobaric Pressure of 1 bar [14] b) Isothermal conditions  $T= 25\text{ }^{\circ}\text{C}, 30\text{ }^{\circ}\text{C}, 35\text{ }^{\circ}\text{C}$ .

## 2.7.2 Multi-component Systems

The liquid phase of the reaction mixture contains the following components propylene, methanol, water, hydrogen peroxide. It is therefore necessary to investigate the effects of the presence of multiple components on the solubility of propylene. In particular, it is important to know if two liquid phases can be formed simultaneously. Since the catalyst, oxidant and substrate must be in the same liquid phase in order for the reaction to occur, the reaction would be sharply retarded by the formation of an organic rich liquid containing the substrate and a water-rich phase containing the oxidant. The limitation of the HYSYS® software to account for interactions among multiple components makes it unreliable to consider the system as a quaternary system. The hydrogen peroxide present in the system is 4.68 mmol which is low and hence its effect is assumed to be negligible. The system is treated as a pseudo ternary system and the interaction parameters obtained from modeling the binary systems are used. The modeled ternary systems include propylene-methanol-



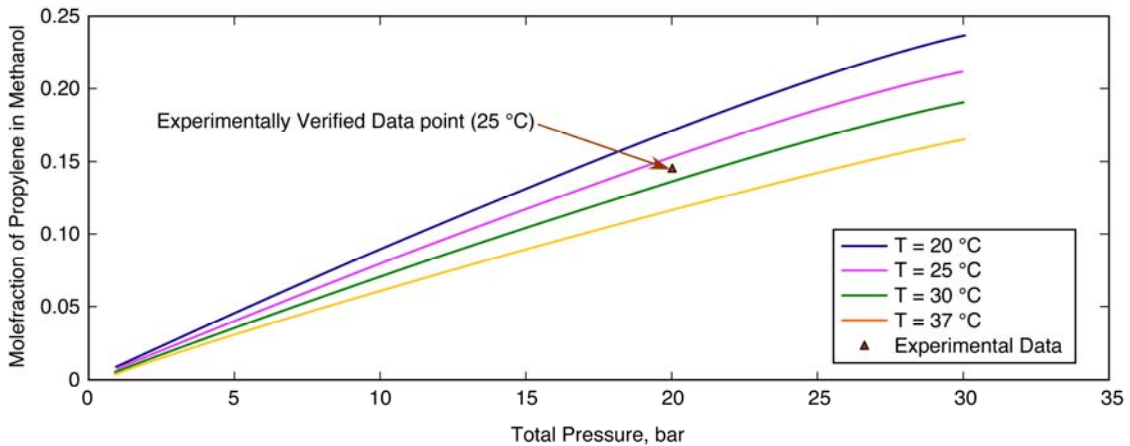
nitrogen, propylene-water-nitrogen, and propylene-methanol-water. All the ternary systems are modeled using the UNIQUAC model to represent the liquid phase and Peng-Robinson equation of state for the gas phase. The binary interaction parameters used are obtained from the binary systems and are shown in the Table 2.2.

**Table 2.2:** Binary Interaction Parameters used in the model

Component	Methanol	Nitrogen	Propylene	Water
Methanol	-----	20.032	1622.923	-----
Nitrogen	1518.723	-----	-583.963	602.209
Propylene	-110.944	20.032	-----	1021.644
Water	-----	20.032	-77.310	-----

### 2.7.2.1 Propylene (1), Methanol (2) and Nitrogen (3)

The system is modeled in a temperature range of 20-37 °C and the effect of temperature and pressure intensification (by the addition of nitrogen) on the solubility of propylene is shown in Figure 2.6.

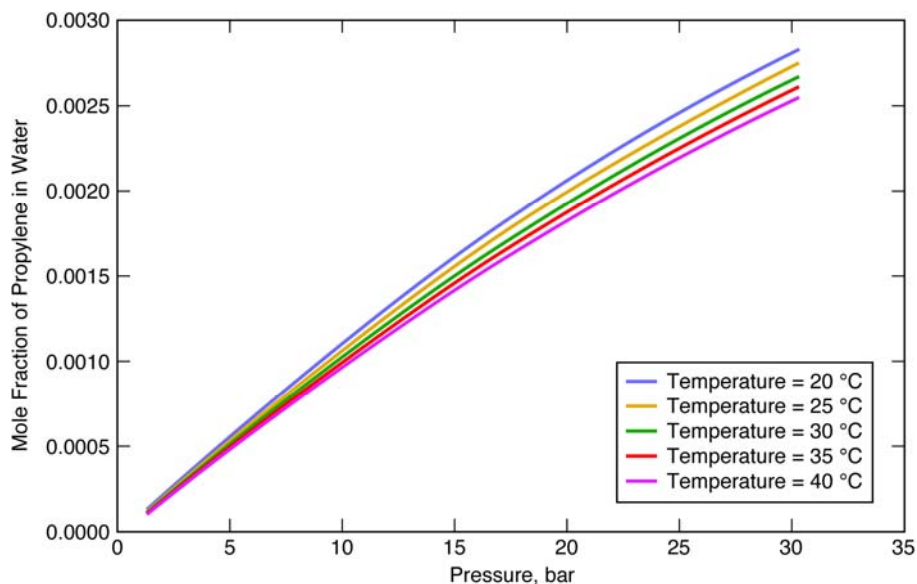


**Figure 2.6:** Solubility of propylene in methanol under varying nitrogen pressures [9]

The model simulation shows an enhancement in the propylene solubility in the liquid phase as the total pressure is increased by nitrogen (N<sub>2</sub>) addition. The solubility of propylene in the liquid phase decreases as the temperature is increased. There is good match between the model prediction and experimental solubility [9].

### 2.7.2.2 Propylene (1), Water (2) and Nitrogen (3)

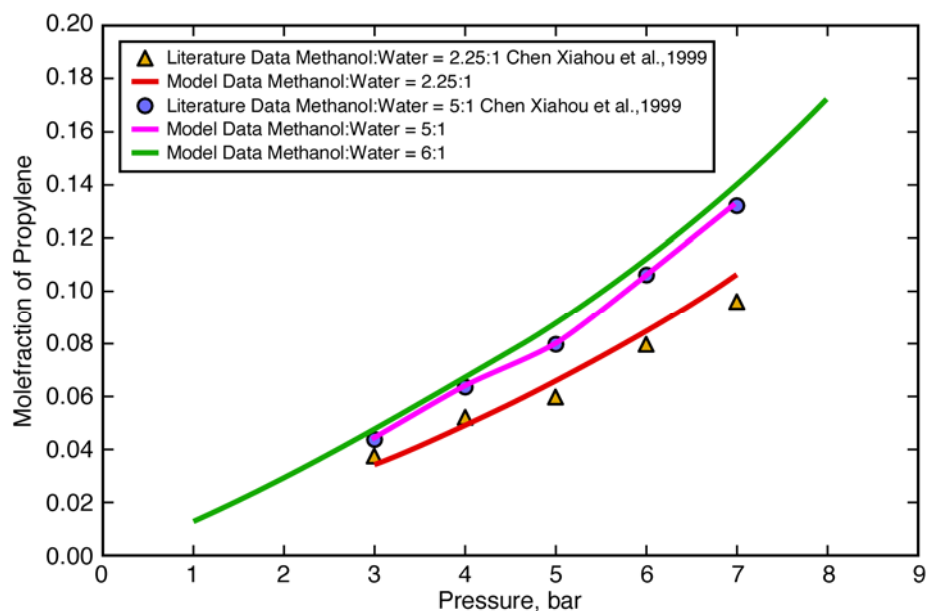
Water is present in the system along with hydrogen peroxide and is also formed during the epoxidation reaction. The catalyst is found to deactivate in excess water, especially in presence of base [15]. As shown in Figure 2.7 the solubility of propylene in water is quite low ( $10^{-4}$  mole fraction). Pressurization with nitrogen results only in a slight enhancement in the solubility of propylene in water.



**Figure 2.7:** Solubility of propylene in water under varying nitrogen pressure.

### 2.7.2.3 Propylene (1), Methanol (2) and Water (3)

There has been a lot of interest in the liquid phase epoxidation of propylene using environmentally benign substances with methanol being the preferred solvent [16]. Methanol and water are the two major components in the liquid phase of the CEBC process and are miscible with each other. Preliminary studies of propylene epoxidation with hydrogen peroxide were carried out in a 10 ml view cell reactor [9]. The feed composition is 4 ml of methanol, 0.1 ml 50 wt% H<sub>2</sub>O<sub>2</sub>, 20 mg methyl trioxorhenium catalyst and 0.06 g of PyNO<sub>x</sub> as accelerating ligand. The methanol to water mole ratio in the system at the beginning of the run is 6:1. The solubility of propylene in the liquid phase is estimated in the current modeling studies at the initial conditions. The validity of the binary interaction parameters to simulate solubility in the ternary system was verified by comparing with published experimental data of propylene, methanol, and water ternary system at methanol to water mole ratios of 5:1 and 2.25:1 [17]. As shown in Figure 2.8, the solubility of propylene in the liquid phase increases with increasing methanol content in the liquid phase, increasing propylene content in the feed and with increasing N<sub>2</sub> pressure. There is a decrease in the propylene solubility in the liquid phase as the temperature is increased [12, 13].



**Figure 2.8:** Solubility of propylene in methanol and water system at 25 °C [17]

## 2.8 Summary

The vapor-liquid equilibrium of various binary and ternary systems involving propylene epoxidation were predicted using appropriate equations of state such as UNIQUAC and PREOS and the results are compared with experimental data. The rate of the propylene epoxidation depends on the propylene content in the liquid phase, quantitative data on solubility of propylene in the liquid phase is essential. The increase in solubility of propylene in the liquid phase brought about by pressure intensification of nitrogen is demonstrated in the results of theoretical studies. The effects of temperature and pressure on the solubility of a gas in the liquid phase are understood and the advantages and disadvantages of the above models have been elaborated. The modeling of the ternary systems was done to study the effect of pressure of multiple components on the solubility of propylene, which reveals only an

insignificant effect. The information gained in this analysis equips CEBC researchers with a better understanding of the biphasic systems being developed in these laboratories with various modeling tools and their limitations.

### **Nomenclature**

$Z$  = co-ordination number in UNIQUAC model

$P$  = total pressure of the system, bar

$T$  = temperature of the system, K

$R$  = Universal gas constant,  $8.314 \cdot 10^{-5}$  (m<sup>3</sup> bar/mol K)

$x$  = mole fraction of a component

$k_{ij}$  = binary interaction parameter for PREOS

$Z$  = Compression Factor in PREOS

$a$  = attractive forces between the molecules

$b_i$  = minimum distance of approach between similar molecules

$b$  = minimum distance that molecules can approach in a mixture

$\nu$  = molar volume of a component, (m<sup>3</sup>/mol)

$\varphi$  = fugacity of a component

$\theta$  and  $\theta'$  = area fraction

$\phi^*$  = segment fraction

$\Delta u$  = characteristic energy (J)

$a_{ij}$  = binary interaction parameter for UNIQUAC model (J/gmol)

$\tau_{ij}$  = characteristic energy parameter

$\alpha_{jk}$  = It is the measure of difference in interaction between a group j and group k and between two k groups.

$Q_k, R_k$  = molecular volume and surface area contributions

$m_k$  = Number of occurrences of group k

$\gamma$  = activity coefficient of a component

$\nu_k^{(i)}$  = the number of molecules of kind k in molecule i.

$\Gamma_k$  = residual activity coefficient of group k

$G$  = Gibbs Free Energy, (J/mol)

$H$  = Enthalpy, (J)

$S$  = Entropy, (J/K)

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## **Chapter 3**

### **ReactIR Measurement of the Mass Transfer Coefficient for Propylene**

#### **Transport into the Liquid Phase**

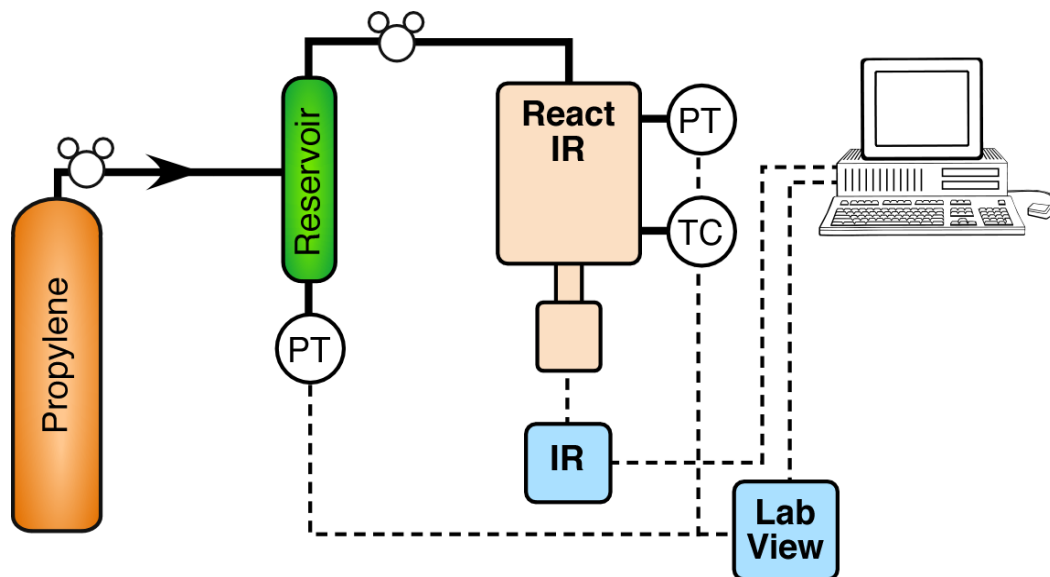
##### **3.1 Introduction**

To aid in rational process development and optimization, reliable estimates of mass transfer coefficients and reaction rate constants are essential. This chapter deals with the development of mathematical models for propylene uptake into the liquid phase in the absence of reaction. Complementary experimental investigations of mass transfer phenomenon, using a Mettler Toledo ReactIR instrument, that validate theoretical predictions are also presented.

##### **3.2 Mass Transfer Studies**

During the oxidation of propylene, the facile transport of propylene gas into the liquid phase requires adequate mechanical agitation to overcome interphase mass transfer limitations. This is essential to maximize the availability of propylene in the liquid phase. Under such conditions, the overall conversion of propylene would be controlled by the intrinsic kinetics of the reaction. In the present study, a stirred ReactIR is used to study the important mass transport step in the CEBC liquid phase epoxidation process.

The schematic of the experimental set up used in the estimation of mass transfer coefficient for the transport of propylene into liquid phase containing methanol is shown in Figure 3.1.



**Figure 3.1:** Schematic of the experimental set up

The IC-10 ReactIR is the latest model offered by Mettler Toledo. The ReactIR probe is made of silicon and can monitor the changes in baseline and the variations in intensities of the IR spectrum due to the changes in the concentration of the reactants and products. The pressure and temperature conditions of the reactor are monitored using Lab View 7.0® software. Propylene is charged into the reactor from a reservoir through a pressure regulator that is used to maintain a constant reactor pressure. The decrease in the reservoir pressure is logged by Lab View ®. The calibration chart of the pressure transducers used in the set up is shown in Appendix B.

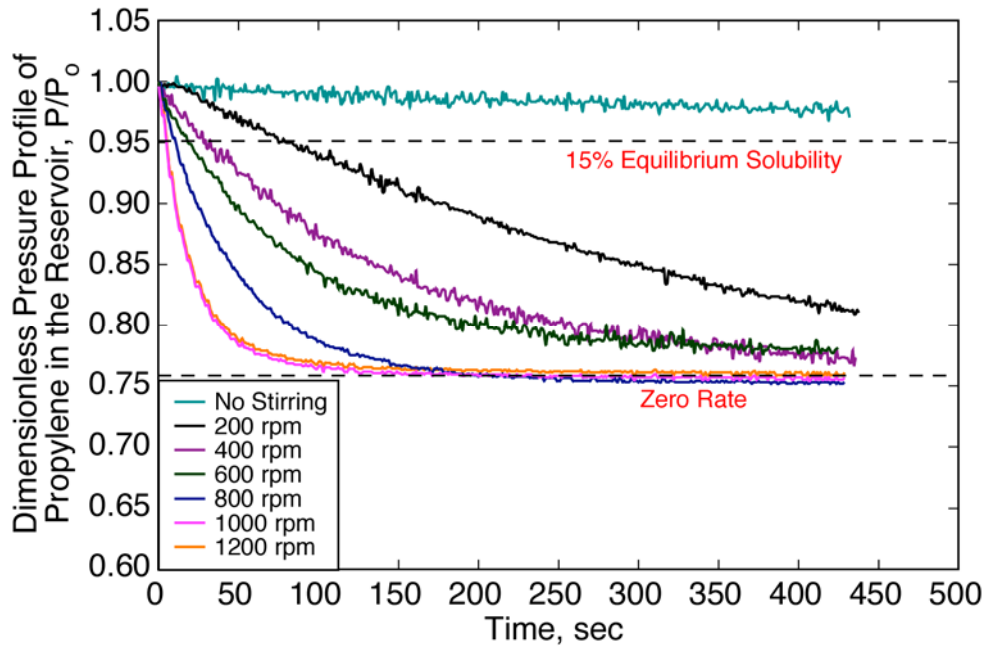
### **3.3 Experimental Procedure**

- Propylene is charged into an external reservoir at ambient temperature to a pressure of 12 bars.
- The reactor is cleaned thoroughly and the liquid consisting of 23 ml methanol is charged into the reactor.
- The reactor is purged with nitrogen followed by propylene gas at atmospheric pressure to remove any air present in the reactor. The equilibrium mole fraction of propylene in methanol at ambient pressure (0.01) is small compared to its solubility at 3.10 bar (0.1).
- Propylene is charged into the reactor from the external reservoir, to a set reactor pressure and then the stirrer is turned on, the pressure profile of propylene is monitored in the reservoir.

### **3.4 Mathematical Model to Estimate Mass transfer Coefficient from Constant Pressure Propylene Uptake Data in a Stirred Vessel**

The propylene uptake by dissolution into the liquid phase is performed following the procedure described in section 3.3. The propylene uptake experiments are performed at various stirring speeds while maintaining the reactor pressure constant by propylene addition from the external reservoir. Hence, the transient pressure profile from the reservoir provides a direct measure of the rate at which propylene dissolves into the liquid phase. As the stirring speed is increased, the rate of propylene dissolution into the liquid phase will increase in the presence of gas-

liquid mass transfer limitations. As shown in Figure 3.2 as the stirring speed is increased beyond 1000 rpm, there is no observed change in the slope of the pressure profile in the reservoir indicating that interphase gas-liquid mass transfer limitations are no longer a limitation. Intrinsic kinetics data should therefore be obtained at these stirrer speeds.



**Figure 3.2:** Effect of agitation on propylene dissolution into the liquid phase for reactor pressure of 3.1 bars and 25 °C

The pressure profile in the external reservoir may be employed to estimate the volumetric mass transfer coefficients. A model has been developed to estimate the  $K_L a$  of the system. The model assumes instantaneous equilibrium with the liquid at the gas liquid interface for the solubility of propylene in the liquid. At constant ReactIR pressure, the depletion of propylene in the external reservoir is equal to the rate at which propylene dissolves into the gas phase [1-4].

$$-\frac{V_g}{RT} \left( \frac{dP_g}{dt} \right) = k_l a (C_p^* - C_{p,l}) V_l \quad (3.1)$$

The concentrations of propylene at the gas-liquid interface and in the bulk liquid phase are estimated using equations 3.2 and 3.3.

$$C_{pl}^* = \left( \frac{\Phi P_{g,R}}{V_p (\gamma_i^* V_m)} \right) \quad (3.2)$$

$$C_{pl} = \left( \frac{P_{g,i} - P_g}{RT} \right) \frac{V_g}{V_l} \quad (3.3)$$

$V_p$  = Vapor Pressure of methanol is estimated by the Antoine equation

$$\ln P_{vp} = A - \frac{B}{T + C} \quad (3.4)$$

Where: A= 5.20409, B= 1581.341, C= -33.50

Substituting the terms 3.2 and 3.3 in the equation 3.1 and rearranging we obtain 3.5.

$$-\left( \frac{dP_g}{dt} \right) = k_l a \left( \frac{\phi P_{g,R} RT V_l}{V_p \gamma_i V_m V_g} - P_{g,i} + P_g \right) \quad (3.5)$$

Recognizing that the term  $\left( \frac{\phi P_{g,R} RT V_l}{V_p \gamma_i V_m V_g} - P_{g,i} \right)$  is constant for a particular run eq.

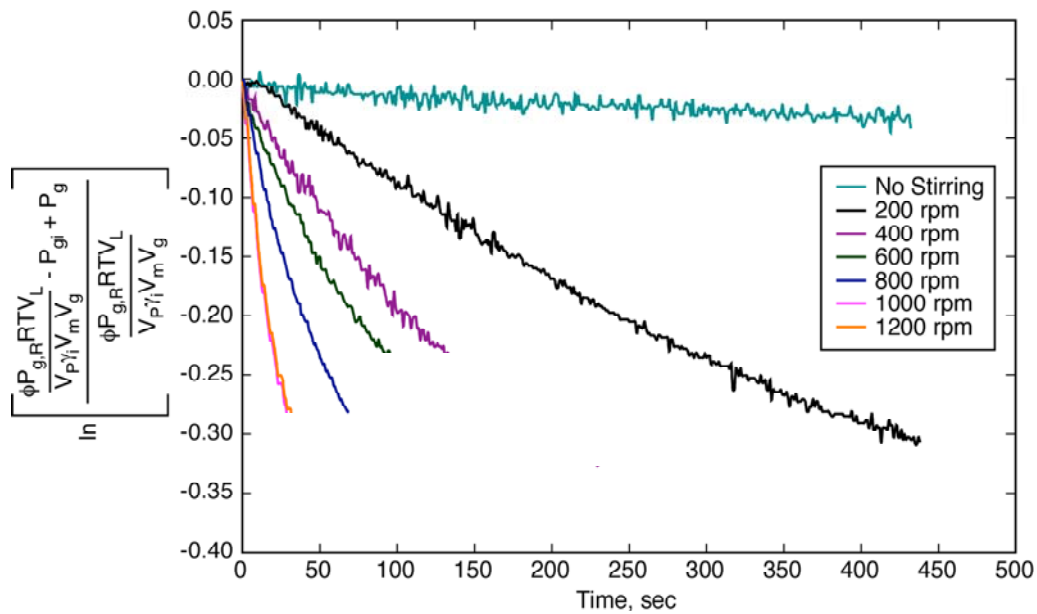
(3.5) is rewritten as

$$-\left( \frac{dP_g}{dt} \right) = k_l a (A + P_g) \quad (3.7)$$

Integrating the equation at the following limits;  $t = 0, P_g = P_{g,i}$   $t = t, P_g = P_g$  we get

$$-\left[ \ln(A + P_g) \right]_{P_{g,i}}^{P_g} = K_l a t \quad (3.8)$$

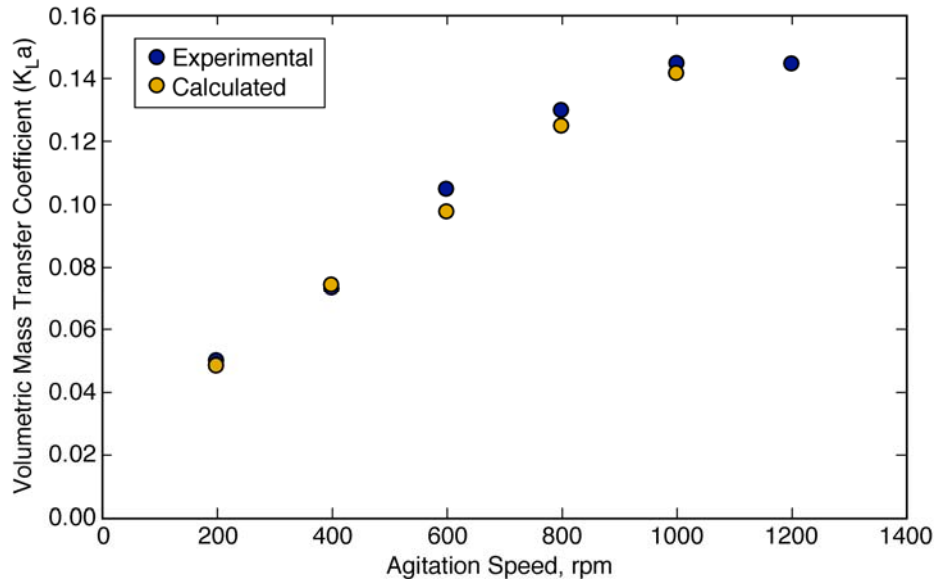
When the experimentally measured  $P_g$  versus  $t$  data are plotted according to eq. 3.8, the plot obtained are linear in the initial time period where solubility of propylene is almost 60% of the equilibrium solubility. The slope of the plot in the linear region yields the mass transfer coefficient as shown in figure 3.3. The sample calculation for the estimation of propylene concentration in the liquid phase is shown in Appendix C.



**Figure 3.3:** Plot of pressure profile of propylene reservoir with varying agitation speed to check for linearity

The following experiments were carried out at room temperature of 22 °C, and the reactor pressure was maintained constant at approximately 3.1 bars. The reactor was charged with 23 ml of methanol and the pressure relaxation profiles were obtained at different stirrer speeds. As shown in Figure 3.2, the decrease in pressure occurred faster as the stirrer speed was increased from 200 rpm and the profiles

became invariant beyond 1000 rpm. The decrease in pressure in the reservoir is clearly due to dissolution of propylene in the liquid phase. The faster decrease in pressure at higher rpm is attributed to improved propylene-to-liquid mass transfer rates brought about by the increased turbulence at the higher rpm. Beyond 1000 rpm, the pressure profiles in Figure 3.2 merge signifying that mass transfer rates are maximized and equilibrium solubilities are achieved. Indeed, the amount of propylene transferred into the liquid phase at equilibrium is consistent with what is predicted from thermodynamic model predictions (presented in Chapter 2). The plot of logarithmic value of  $K_L a$  vs time is linear in nature validating the model as shown in Figure 3.3. The experiments are conducted until there is no further pressure drop in the reservoir but the  $K_L a$  is estimated at finite solubility of 15% of the equilibrium solubility. The variation of  $K_L a$  with agitation speed shows an asymptotic behavior as shown in Figure 3.4. The equilibrium mole fraction of propylene in methanol is 0.0894 which is a close match to the published literature data [5].



**Figure 3.4:** Comparison of the Mass Transfer Coefficient estimated from the empirical equation and that obtained from experiments conducted in a 50 ml Parr Reactor

The experimental values of  $K_La$  obtained from the (equation 3.8) were compared to that with empirical correlation [6].

$$k_L a = 1.48 * 10^{-2} (N)^{2.18} \left( \frac{V_G}{V_L} \right)^{1.88} \left( \frac{d_I}{d_T} \right)^{2.16} \left( \frac{h_1}{h_2} \right)^{1.16} \quad (3.9)$$

The volume based on 50 ml Parr reactor are given in Table 3.1. The comparison of the  $K_La$  estimated from the empirical equation and that obtained from the experiments is shown in Figure 3.4.



**Table 3.1:** Values of Parameters based on Vessel Geometry

<b>Ratio</b>	<b>Value</b>
$\frac{V_G}{V_L}$	1.7
$\frac{d_I}{d_T}$	0.58
$\frac{h_1}{h_2}$	0.54
N (rpm)	0,200,400,600,800,1000,1200

### 3.6 Summary

The phase behavior of propylene (discussed in Chapter 2) reveals a high solubility of propylene in methanol. The mass transfer studies have indicated the use of mechanical agitation at a speed of 1000 rpm as an effective speed to dissolve propylene in sufficient quantities to operate outside the diffusion limited region [7]. The  $K_{La}$  of gas-liquid transport of propylene into liquid phase containing methanol is estimated to be  $0.140 \text{ sec}^{-1}$  at 1000 rpm through the development of an empirical model.

### Nomenclature

$V_g$  = Volume of the Propylene Reservoir = 0.3 ltr

$V_l$  = Volume of the liquid in the reactor, ltr

$C_{pl}$  = Concentration of propylene in the liquid phase, gmol/ltr

$C_p^*$  = Concentration of propylene at the interface, gmol/ltr

$P_{g,R}$  = Pressure in the reactor

$(\phi)$  fugacity coefficient in the gas phase

$(\gamma)$  activity coefficient in the liquid phase

$P_{g,i}$  = Pressure in the constant volume reservoir at the start of the experiment, bar

$P_g$  = Pressure of propylene in the reservoir at any instant of time, bar

$T$  = Operating Temperature, K

$d_I$  = Diameter of Impeller, m

$d_T$  = Diameter of Reactor, m

$h_1$  = Height of Impeller from the bottom, m

$h_2$  = Height of Liquid in the Reactor, m

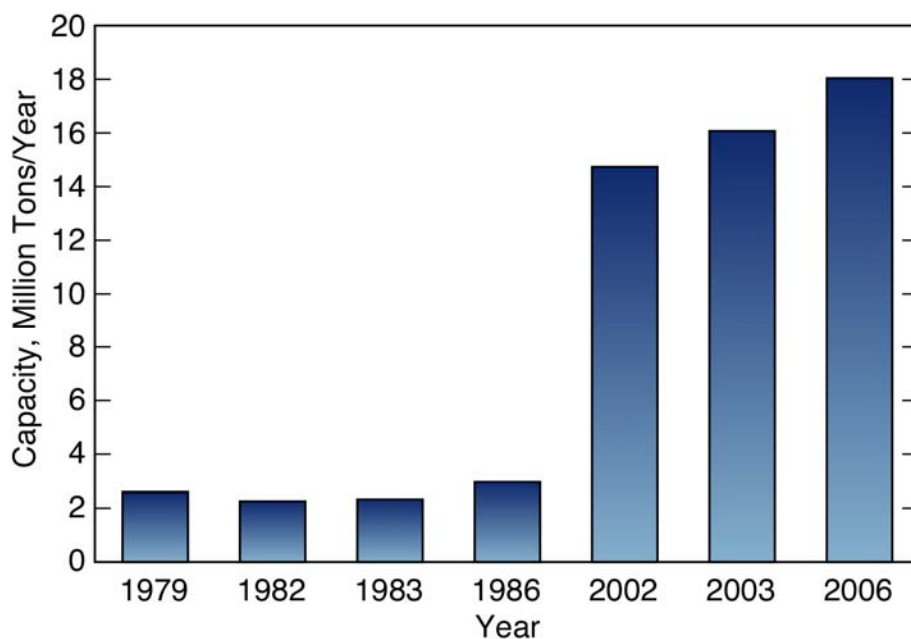
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## **Chapter 4: Liquid Phase Epoxidation of Ethylene and Investigation into the Phase behavior of its components**

### **4.1 Introduction**

Ethylene Oxide (EO) has a worldwide consumption capacity of 18 million tonnes per annum and is a raw material for various substances such as glycol ethers, polyols, ethanolamines etc. The major producers of ethylene oxide are BASF, Dow Chemicals and SABIC. The largest outlet of ethylene oxide is ethylene glycol which accounts for 70% of ethylene oxide manufactured. The products obtained by further processing of ethylene oxide have a wide variety of applications in various industries. The world consumption capacity of ethylene oxide has steadily increased due to high demand in the emerging markets of China and India. The historical average growth rate of this chemical has been 4% but the demand is predicted to grow at a rate of 5.7% in the years 2006-2011 [1, 2]. The consumption trends of ethylene oxide are shown in the Figure 4.1.



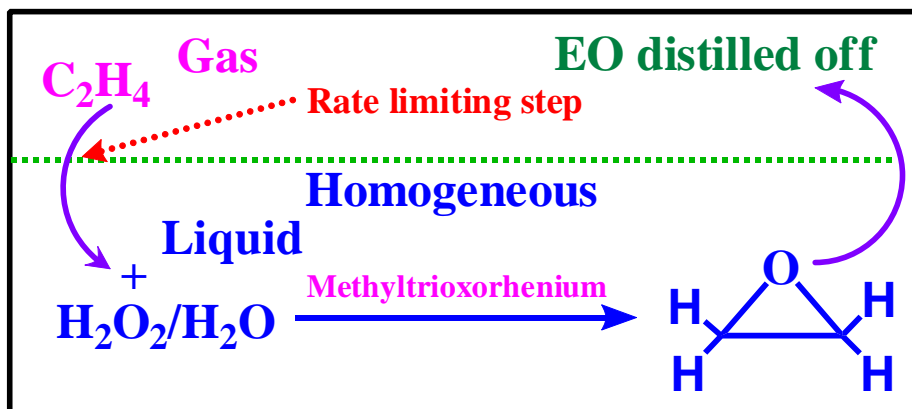
**Figure 4.1:** World Consumption trends of Ethylene Oxide [1, 4].

The growth rate in the US is expected to be 2.5% annually below the global average but the demand is expected to grow from 3.84 million tonnes to 4.24 million tonnes as of 2010 according to ICB Americas. The price of ethylene oxide has increased consistently and is around 70 cents/lb. The percentage of ethylene oxide that is converted to glycols is the highest in the middle-east. Surfactants are the second major outlet of ethylene oxide, accounting for 9% of ethylene oxide world wide consumption (highest consumption in the US). In 2002, 61% of U.S. ethylene oxide was hydrolyzed to ethylene glycol [3].

Ethylene Oxide has a very large market and the conventional route has a lot of drawbacks as discussed in chapter 1, in light of these facts development of an alternative process for the manufacture of EO has a much economic incentive [5].

## 4.2 Liquid Phase Epoxidation of Ethylene

The liquid phase epoxidation of ethylene to ethylene oxide is a novel concept that has been developed by CEBC researchers who happen to be the first group to generate quantitative data on the conversion and yield of ethylene oxide based on hydrogen peroxide as shown in Figure 4.2.

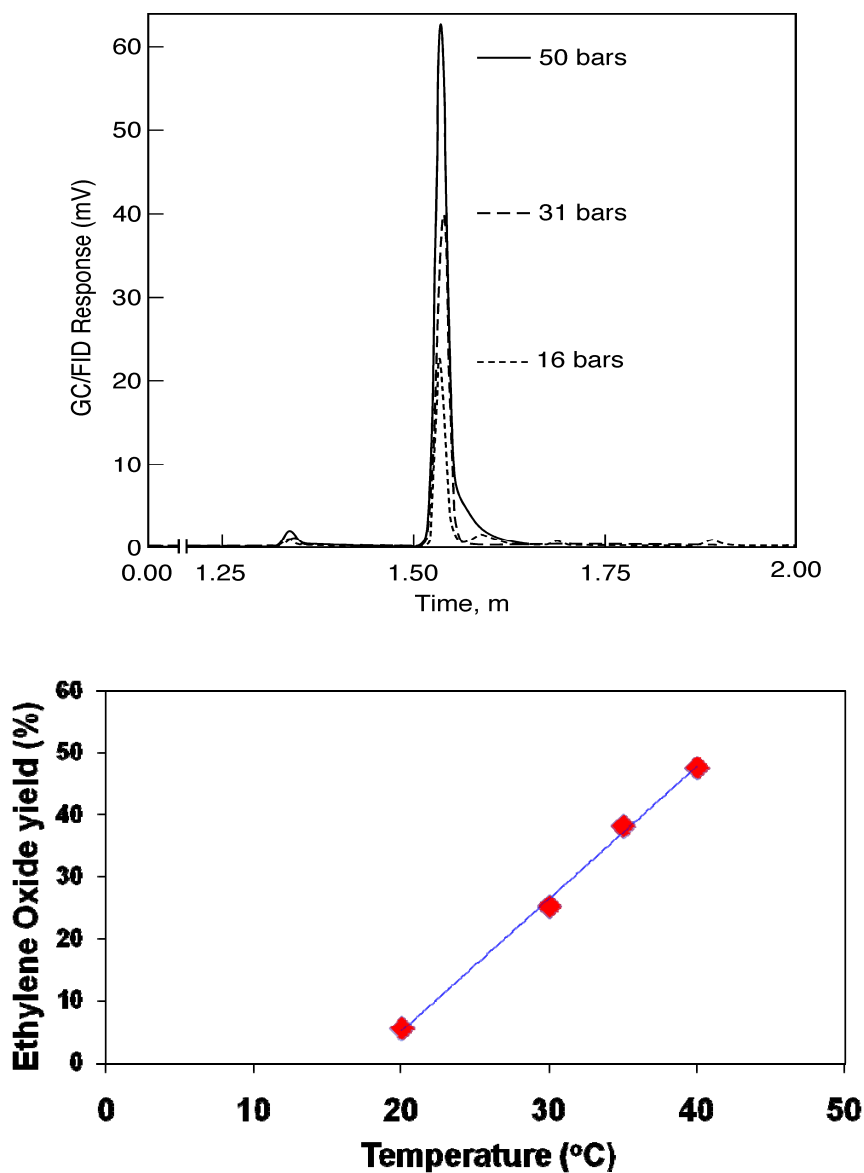


**Figure 4.2:** Schematic of the biphasic process for ethylene epoxidation.

In this process gaseous ethylene is brought into the liquid phase containing the solvent methanol (4.1 ml), 50 wt% hydrogen peroxide (10.4 mmoles) as oxidant, catalyst methyl trioxorhenium (0.084 mmoles), and a base pyridine N-oxide (0.61 mmoles), where it undergoes epoxidation with atomic oxygen of the hydrogen peroxide to form ethylene oxide and water as a byproduct. The availability of ethylene in the liquid phase is among the rate limiting steps of the reaction. Availability of ethylene in sufficient amounts is a key to enhancing the rate of the reaction. EO undergoes a ring opening reaction due to the acidic nature of the system; this ring opening reaction is mitigated by the addition of any base, but basic media leads to catalyst decomposition. Pyridine N-Oxide, is a very weak base, has a dual

advantage. First, it increases the activity of methyl trioxorhenium catalyst but, second, because of its low basicity its low basicity PyNO does not affect the lifetime of the catalyst. Finally, being slightly basic, it does not promote the ring opening reaction, which is favored in acidic media.

The product of the reaction ethylene oxide is a highly combustible substance and is known to have a wide flammability limit. Liquid phase epoxidation of ethylene has a unique advantage; ethylene oxide owing to its high solubility in alcohols dissolves completely in the liquid phase thereby eliminating the possibility of explosions or further combustion reactions. Ethylene Oxide, a low boiling liquid can be easily recovered by distillation. Preliminary reactions were carried out at a temperature of 25 °C and moderate pressures of 31 bars but the yield of ethylene oxide was low. Modeling studies equipped us with quantitative data on the solubility of ethylene in methanol facilitating in optimizing reaction conditions that ensured sufficient availability of ethylene in the liquid phase which resulted in increase in productivity of EO. By, increasing the reactor pressure to 50 bars the ethylene conversion has increased to 4% with 90+% selectivity. By, increasing the operating temperature incrementally to 40 °C the yield of ethylene oxide increased progressively to 48%, based on hydrogen peroxide, for a reaction time period of 6 hrs, clearly indicating kinetic control of the reaction. At higher temperatures the catalyst is more quickly deactivated as found in the studies for the propylene epoxidation system. The effect of pressure and temperature on the yield of EO is shown in Figure 4.3 [6].



**Figure 4.3:** Effect of pressure and temperature on the yield of Ethylene Oxide [6].

GC analysis of the gas phase from the reactor, post reaction showed absence of carbon dioxide and oxygen proving that there is no rapid burning of ethylene or EO, both of which are major drawback for the conventional gas phase process.

The cost of hydrogen peroxide and catalyst methyl trioxorhenium controls the economic feasibility of the process at the industrial scale. Low turnover numbers may



create an economic constraint which might be overcome by using an alternative catalysts, such as Titanium Silicate (TS-1) [7] which is known to exhibit good activity even at higher temperatures and is currently used in hydroperoxidation processes for the manufacture of propylene oxide from propylene by industrial giants such as Huntsman, Shell etc. The CEBC process for the manufacture of ethylene oxide provides the greenest alternative that has been designed for the epoxidation of ethylene. The knowledge of the solubility of ethylene in the presence of other components of the reaction mixture is of importance and can be realized by modeling of the vapor-liquid equilibrium.

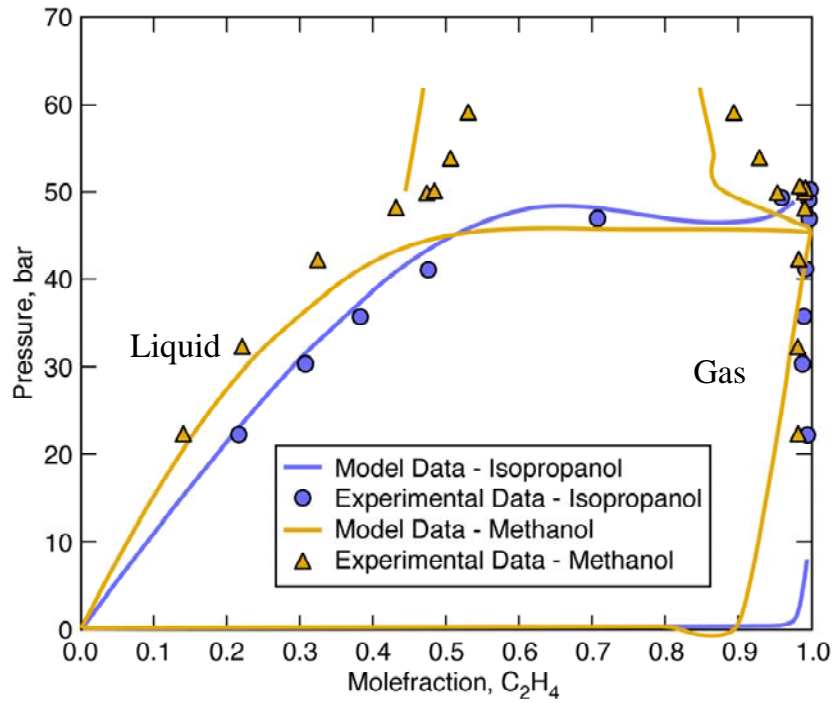
### **4.3 Results and Discussions**

The reaction system and conditions developed in the laboratories for propylene epoxidation were adapted for the epoxidation of ethylene. The vapor-liquid equilibrium of ethylene with various alcohols is presented below:

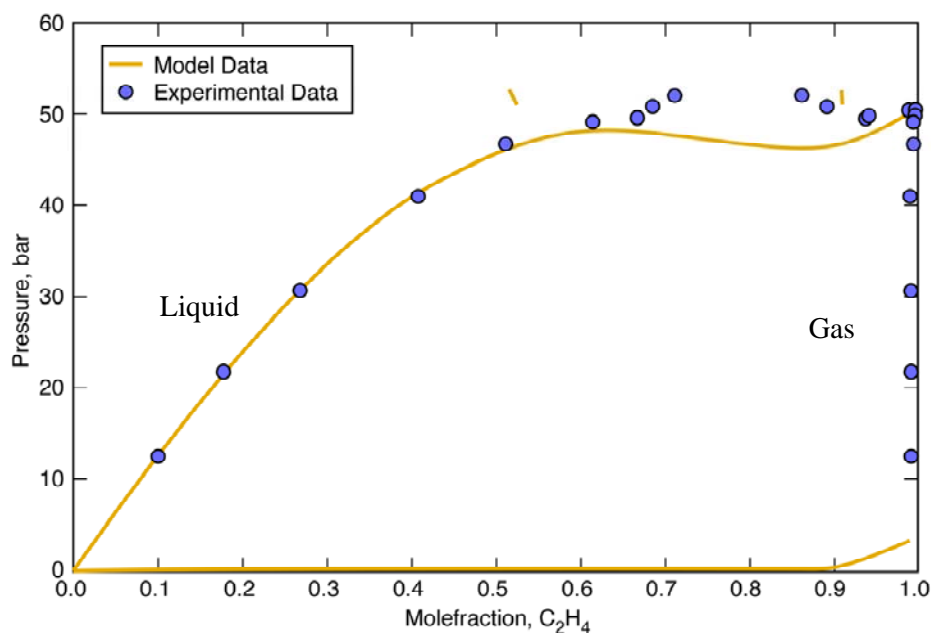
#### **4.3.1 Ethylene (1) and Alcohols (2)**

The vapor-liquid equilibrium of ethylene with methanol, ethanol, n-propanol, and isopropanol was studied. The vapor-liquid equilibrium of ethylene with various alcohols revealed the formation of two liquid phases at high pressures, a water phase and an alcohol phase. This behavior persists even in the presence of higher molecular weight alcohols. However, the behavior ceases to exist in branched alcohols i.e. there is no second liquid phase formation in isopropanol, as observed in n-propanol.

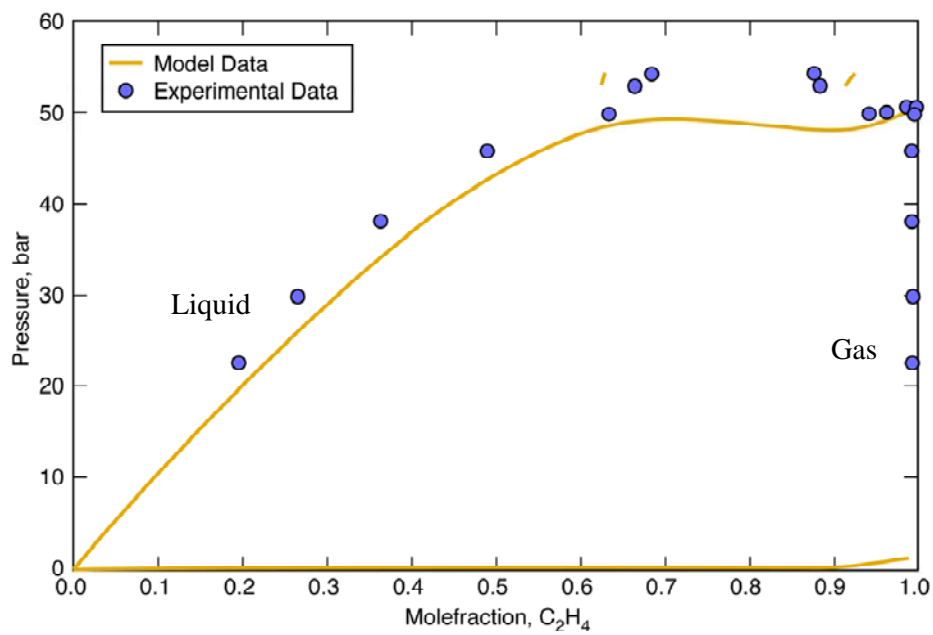
Temperature has a profound effect on the VLE; at higher temperatures, higher pressures are required to obtain the same solubility of ethylene but there is no liquid phase formation. As, stated above these have enabled us in the optimization of the reaction condition.



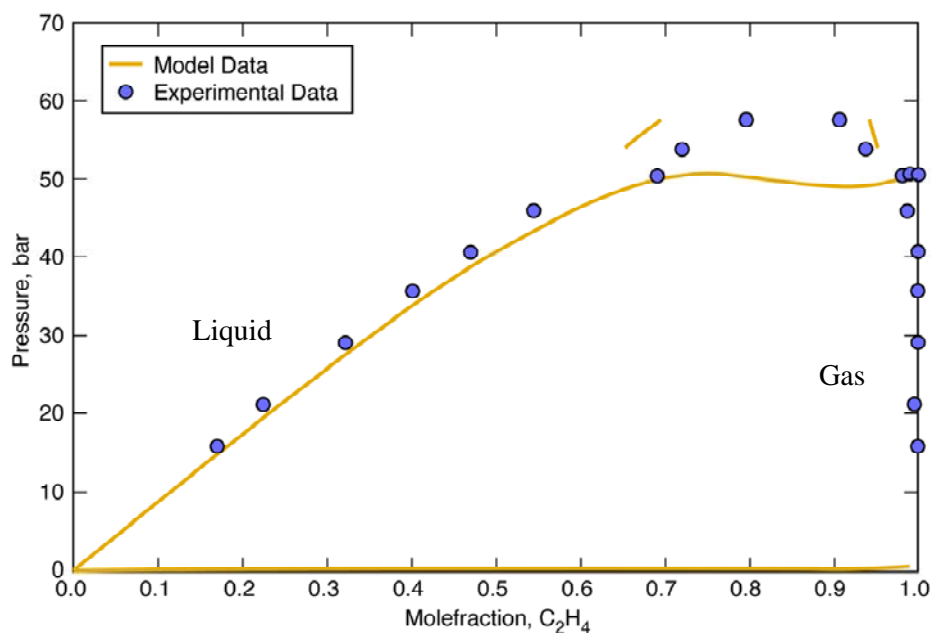
**Figure 4.4a:** Vapor-Liquid equilibrium of ethylene (1) - methanol (2) and ethylene (1) iso-propanol (2) solvents at 10 °C. [8, 9]



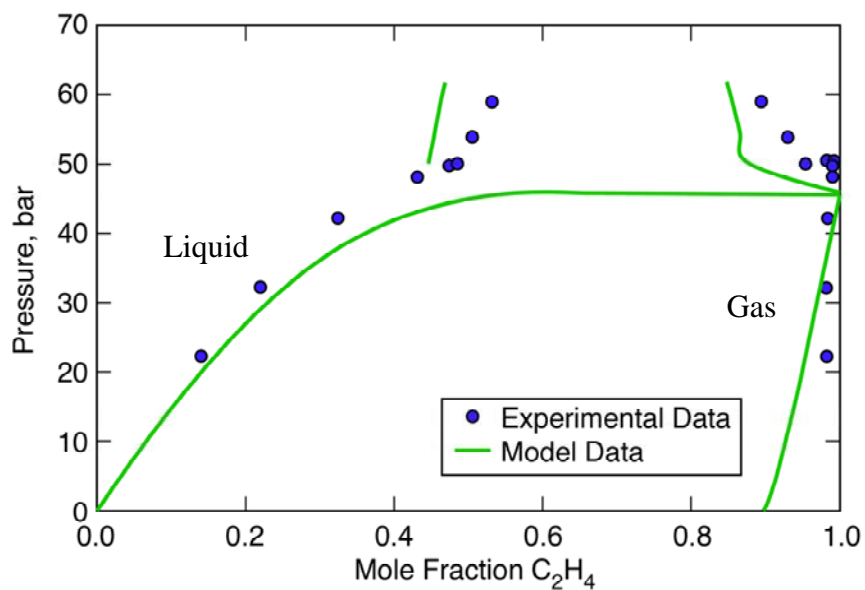
**Figure 4.4b:** Vapor-Liquid equilibrium of ethylene (1) and ethanol (2) at 10 °C. [10]



**Figure 4.4c:** Vapor-Liquid equilibrium of ethylene (1) and 1-propanol (2) at 10 °C. [11]



**Figure 4.4d:** Vapor-Liquid equilibrium of ethylene (1) and 1-butanol (2) at 10 °C.  
[12]



**Figure 4.4e:** Vapor-Liquid equilibrium of ethylene (1) and methanol (2) at 25 °C.  
[13]

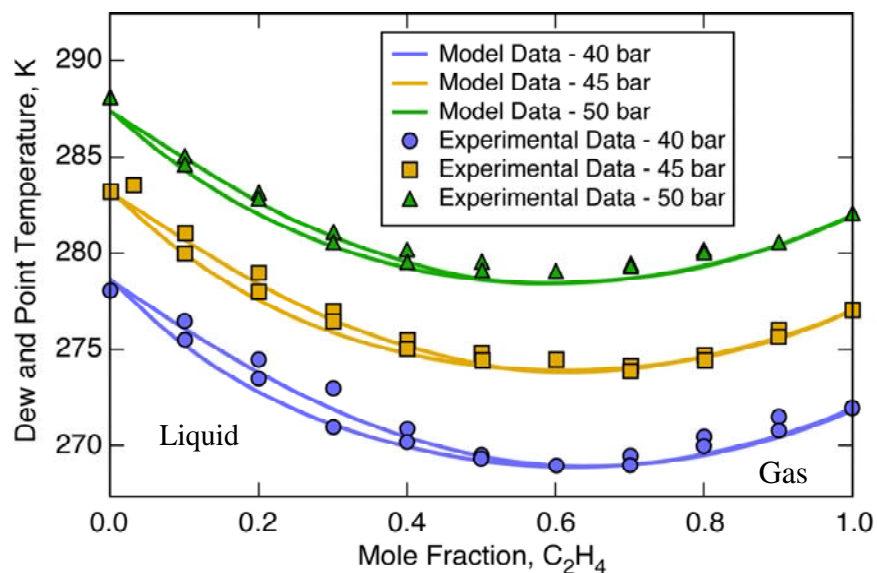
A homogeneous single liquid phase containing the catalyst, substrate and oxidant is necessary to operate the reaction at optimum conditions to obtain maximum yield. Ethylene has a critical temperature of 9 °C and a critical pressure of 50.9 bars. This reaction is carried out at 40 °C, which is above the critical conditions of ethylene. The two reasons for choosing methanol as the solvent; firstly the pressure required to obtain a fixed mole fraction of ethylene in the liquid phase is the least compared to other alcohols and second the preliminary data on the life and activity of catalyst methyl trioxorhenium were available for the propylene epoxidation system where methanol was used as a solvent and the data were found to be encouraging. It is observed that under pressure the ethylene solubility increases in the liquid phase and the system behaves like an olefin expanded liquid. The systems are modeled using Peng Robinson equation of state using the interaction parameters (shown in Table 4.1) and the results so obtained gave a good match to the experimental data from the literature [14].

**Table 4.1:** Binary Interaction coefficients of ethylene with various alcohols

<b>Components</b>	<b>Binary Interaction Parameters (<math>k_{ij}</math>)</b>
Ethylene and Methanol	0.010
Ethylene and Ethanol	0.0224
Ethylene and 1-Propanol	0.056
Ethylene and 2-Propanol	0.052
Ethylene and 1-Butanol	0.0788

### 4.3.2 Ethylene (1) and Carbon dioxide (2)

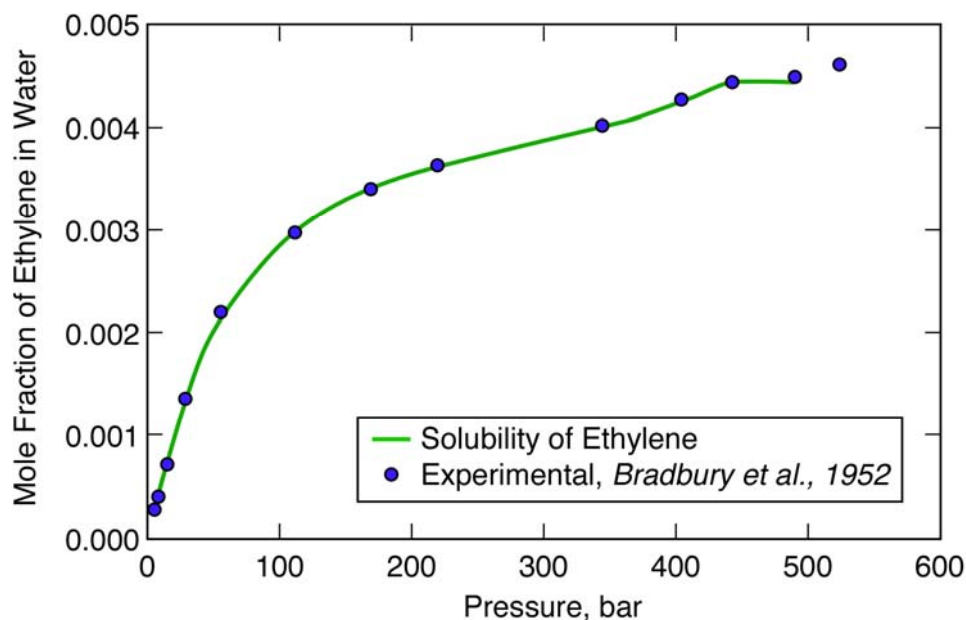
Ethylene is a flammable gas and may easily form a flammable mixture in the presence of air. The use of carbon dioxide or nitrogen as a diluent is a proven method to mitigate runaway combustion reactions. These runaway reactions are a major drawback for the existing commercial process. The presence of carbon dioxide affects the vapor-liquid equilibrium of ethylene with the liquid phase. The dew and bubble point temperatures of ethylene-carbon dioxide mixture were studied in the vicinity of operating conditions. Carbon dioxide being a condensable gas enters into the liquid phase thereby acts as a diluent for ethylene in the vapor phase and forms a carbon dioxide expanded liquid (CXL). The system is modeled in the HYSYS® simulator using Peng Robinson equation of state and provides a good match with the experimental data. The binary interaction parameter used is  $k_{12} = 0.06672$  is obtained from literature [14]. The vapor-liquid equilibrium shows that an azeotropic mixture is formed in composition ranges with higher ethylene concentration as the operating conditions are near the critical temperature of ethylene [14, 15].



**Figure 4.5:** Dew and Bubble Point Curves of ethylene (1) and carbon dioxide (2).

### 4.3.3 Ethylene (1) and Water (2)

Water, which is also formed during the reaction, is present in the reaction mixture along with the oxidant which is 50 wt% hydrogen peroxide. As, the concentration of water increases in the liquid phase it has a profound effect on the solubility of ethylene in methanol. The solubility of ethylene in water is very low compared to that in methanol. At a fixed temperature, the solubility of ethylene increases with increasing pressure and reaches a steady value at high pressures. The solubility decreases as the temperature is increased. This system is modeled using UNIQUAC model in HYSYS® simulator. The interaction parameters between ethylene and water ( $k_{12}= 100$ ,  $k_{21}= -217.74$ ) used in the model are predicted by UNIFAC VLE tool embedded in the software.

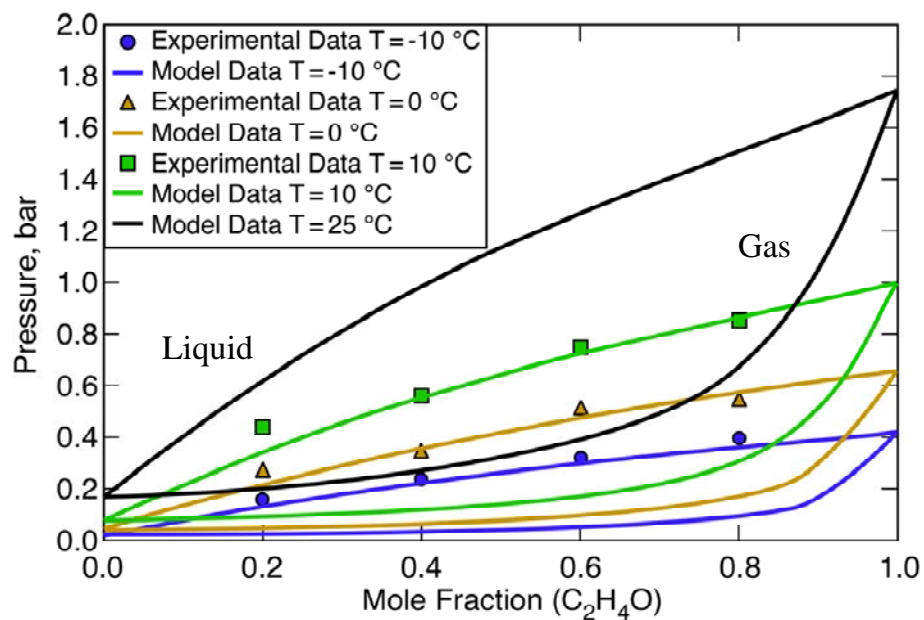


**Figure 4.6:** Solubility of ethylene (1) in water (2) at 35 °C.

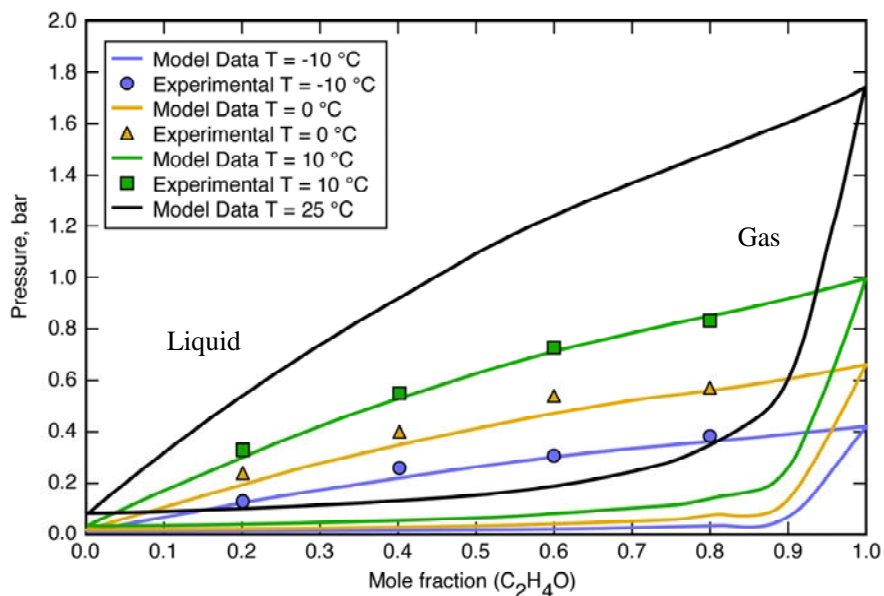
#### 4.3.4 Ethylene Oxide (1) and Alcohols (2)

Ethylene oxide (EO) is a highly combustible substance and has a wide flammability limit that extends from 3 mol % (lower flammability limit) to 100 mol% (upper flammability limit). The complete combustion of ethylene oxide to form water and carbon dioxide a side reaction of the vapor phase oxidation process has a major effect on the economics of the process. Thus, the understanding of the phase behavior of ethylene oxide is of utmost importance; EO is highly soluble in alcohols. At the operating temperature, any pressure above 2 bars is sufficient to dissolve the ethylene oxide completely into the liquid phase. This property of ethylene oxide totally eliminates the possibility of the combustion of EO which is highly exothermic in nature. Higher pressures are required to observe the same effect as the temperature of the system is increased.

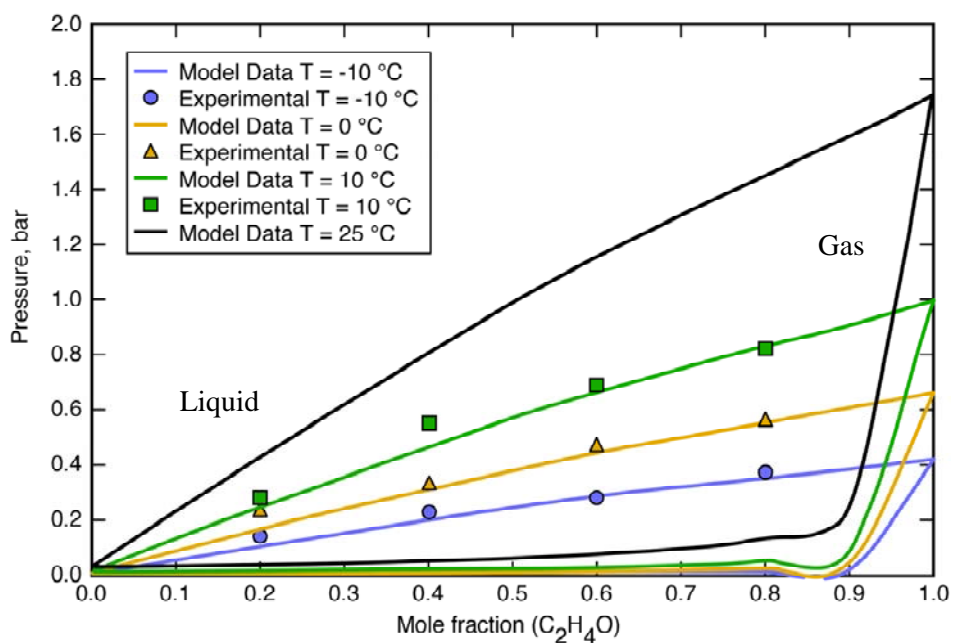




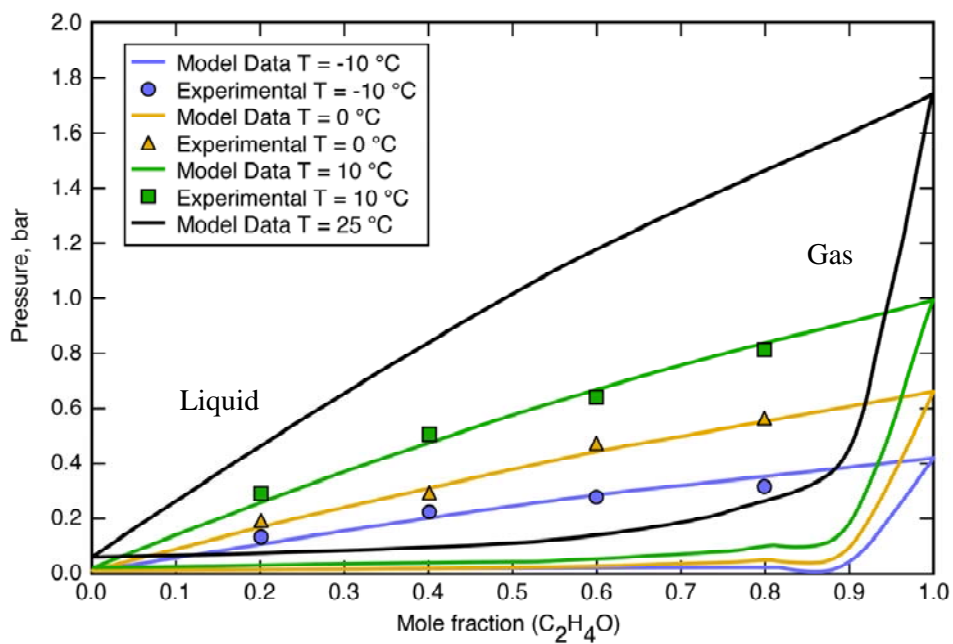
**Figure 4.7a:** Vapor-Liquid equilibrium of ethylene oxide and methanol at a) -10 °C b) 0 °C c) 10 °C d) 25 °C. [16]



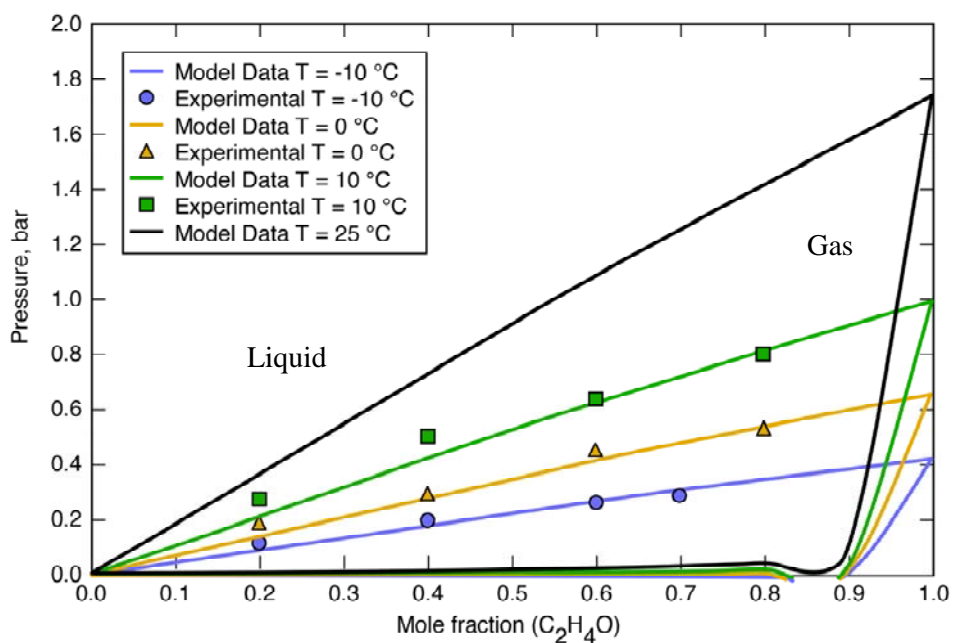
**Figure 4.7b:** Vapor-Liquid equilibrium of ethylene oxide with ethanol at a) -10 °C b) 0 °C c) 10 °C d) 25 °C. [16]



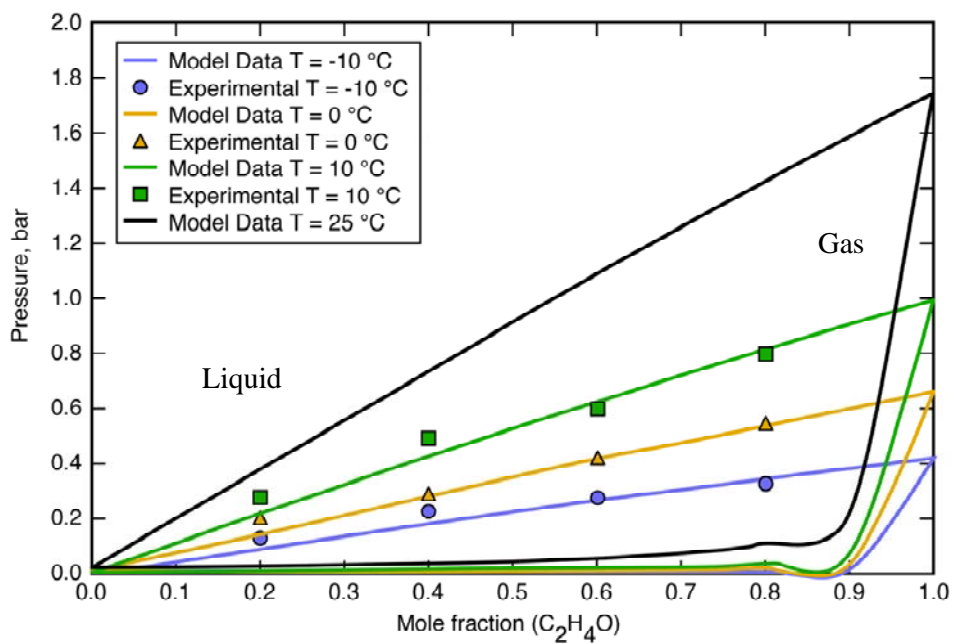
**Figure 4.7c:** Vapor-Liquid equilibrium of ethylene oxide with n-propanol at a) -10 °C b) 0 °C c) 10 °C d) 25 °C. [16]



**Figure 4.7d:** Vapor-Liquid equilibrium of ethylene oxide with isopropanol at a) -10 °C b) 0 °C c) 10 °C d) 25 °C. [16]



**Figure 4.7e:** Vapor-Liquid equilibrium of ethylene oxide with n-butanol at a) -10 °C b) 0 °C c) 10 °C d) 25 °C. [16]



**Figure 4.7f:** Vapor-Liquid Equilibrium of ethylene oxide with iso-butanol at a) -10 °C b) 0 °C c) 10 °C d) 25 °C. [16]

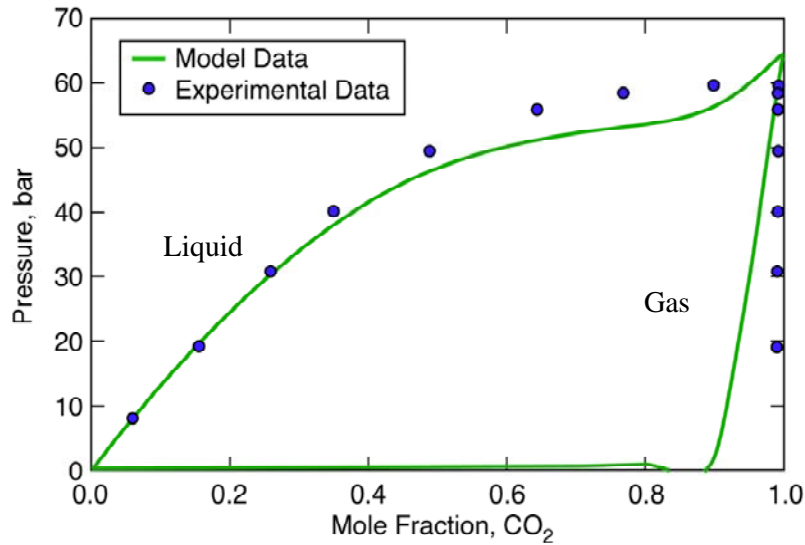
The VLE of the ethylene oxide and alcohol mixture was modeled using the UNIQUAC model, because of the high non-ideality of ethylene oxide. The interaction parameters between ethylene oxide and alcohol were predicted using the solution of group's theory. The values that are used in the HYSYS® simulator for modeling are given in the table 4.2.

**Table 4.2:** Binary Interaction parameters for various ethylene oxide (EO) and alcohol systems.

System	Interaction Parameter	System	Interaction Parameter
EO-Methanol	-245.7	Methanol-EO	629.7
EO-Ethanol	-123.6	Ethanol-EO	413.5
EO-1-Propanol	-82.6	1-Propanol-EO	272.6
EO-2-Propanol	-82.6	2-Propanol-EO	272.9
EO-1-Butanol	-28.1	1-Butanol-EO	168.2
EO-2-Butanol	-26.7	2-Butanol-EO	166.5

#### 4.3.5 Carbon dioxide (1) and Methanol (2)

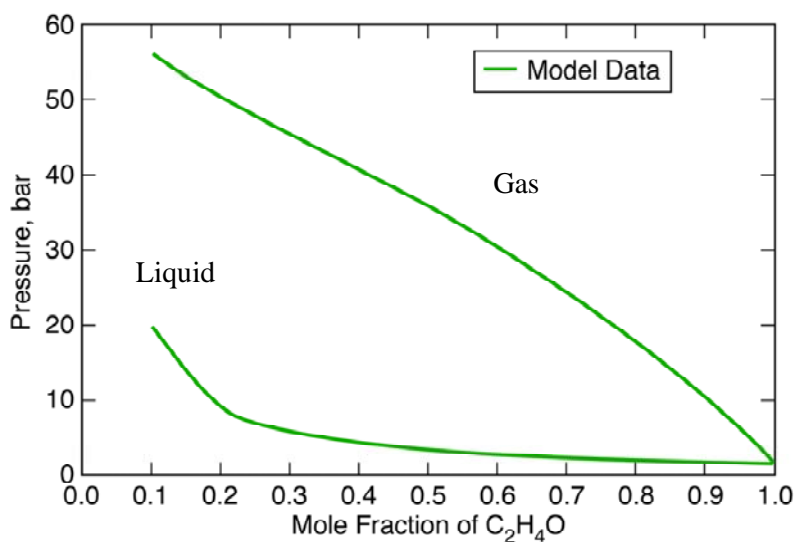
The system of methanol and carbon dioxide has been extensively studied over a wide temperature and pressure ranges. The solubility of carbon dioxide in methanol increases with increasing pressure and decreases with increasing temperature. The mixture can be classified as Type 1 based on the extent of interactions (based on Van Konynenburg phase studies). This system was modeled using the Peng Robinson equation of state using the HYSYS® simulator. The interaction parameters between methanol and carbon dioxide ( $k_{12} = 0.040$ ) are obtained from HYSYS® database. The data so obtained from the model matches very closely with the experimental data provided by Brunner et.al.[17], Ohgaki et.al.[13], K. Bezahehtak et.al... ,[18].



**Figure 4.8:** Vapor-Liquid equilibrium of methanol and carbon dioxide at 25 °C [18, 19]

#### 4.3.6 Ethylene Oxide (1) and Ethylene (2)

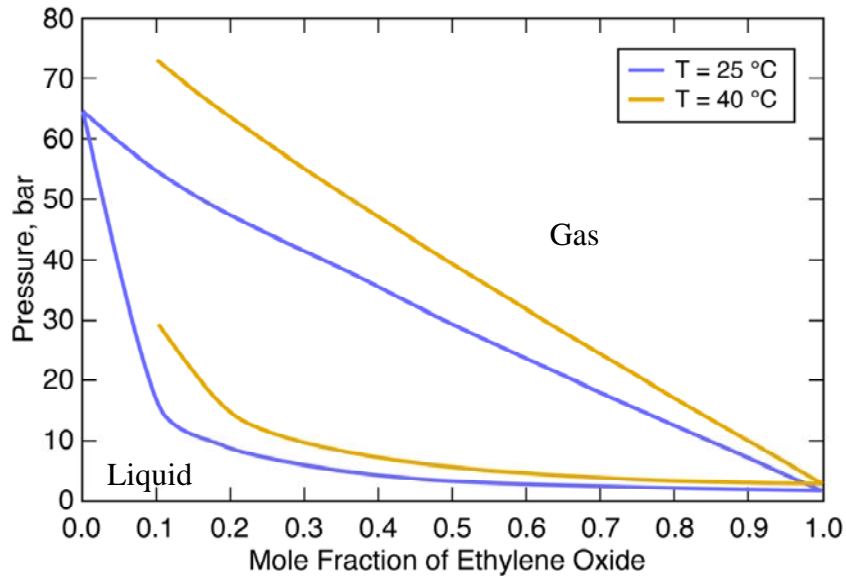
The solubility of ethylene oxide in alcohols being very high, and the effect of the presence of such high concentrations in the liquid phase on the phase behavior can be understood by modeling the VLE of ethylene and EO. Peng Robinson equation of state is used to model the system in HYSYS® simulator. The experimental data for this system is not available in literature, but the data generated by the model has been proven to give accurate results for a number of systems for which literature data is available. The results of the model at 25 °C show that the amount of ethylene present in the liquid phase is sufficiently high such that ethylene does not become a limiting reagent.



**Figure 4.9:** Vapor-Liquid equilibrium of ethylene and ethylene oxide at 25 °C.

#### 4.3.7 Ethylene Oxide (1) and Carbon dioxide (2)

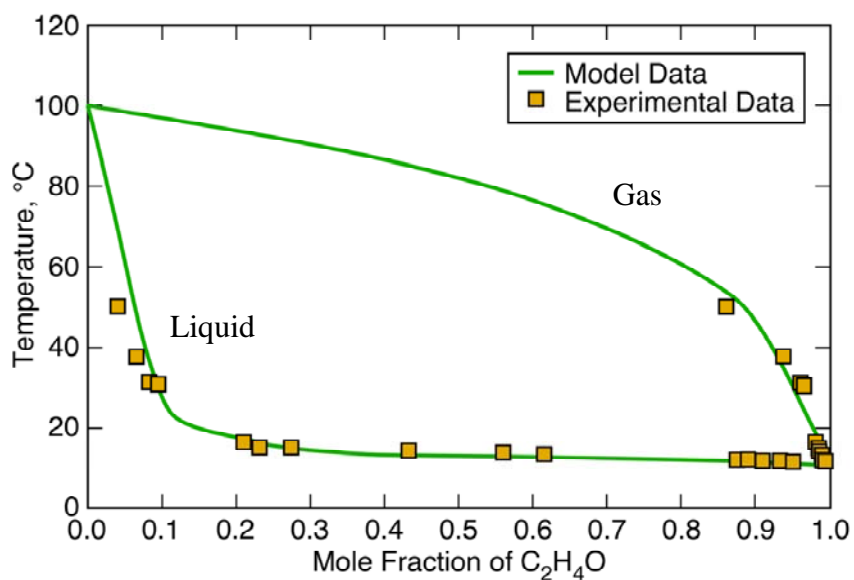
Ethylene Oxide is a highly inflammable gas and is generally stored under an inert atmosphere of carbon dioxide or nitrogen [20]. Carbon dioxide to ethylene volume ratio is recommended to be 7.5 to operate outside the flammability envelope [21]. The phase behavior of ethylene oxide in the presence of high inert concentrations gives an insight into the design of these storage vessels. The system was modeled using the Peng-Robinson equation of state and the interaction parameters were predicted using the UNIFAC tool. The model data reveals that EO condenses at moderate pressures of 10 bars for the temperatures of 25 and 40 °C. [21, 22]



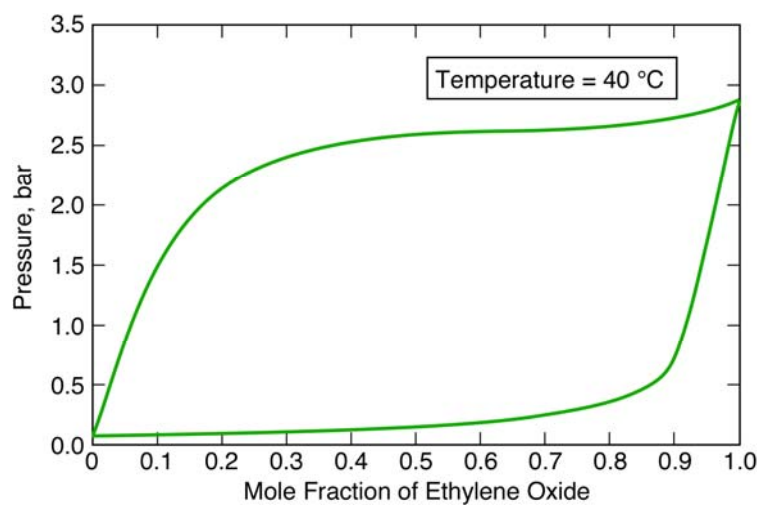
**Figure 4.10:** Vapor-Liquid equilibrium of ethylene oxide (1) and carbon dioxide (2).

#### 4.3.8 Ethylene Oxide (1) and Water (2)

Ethylene Oxide reacts with water to form glycols; the knowledge of the VLE of this system is of high industrial importance. EO is known to be highly soluble in methanol and water. The vapor-liquid equilibrium of ethylene oxide with water is modeled using the UNIQUAC model and compared with published data. The interaction parameters used in the model were predicted using the UNIFAC VLE and the values are  $k_{12} = -132.905$ ,  $k_{21} = 893.771$ . The model predictions show a high solubility of ethylene oxide in water at moderate pressures. At higher temperature, higher pressures are required to obtain similar solubility of ethylene oxide. As, shown in Figure 4.11a at low pressures of 2.5 bars the concentration of ethylene oxide in water is around 30 mol % [23, 24].



**Figure 4.11a:** Vapor-Liquid equilibrium of ethylene oxide (1) and water (2) at 1 bar pressure [23]



**Figure 4.11b:** Vapor-Liquid equilibrium of ethylene oxide (1) and water (2) at 40 °C.

#### 4.4 Summary

A novel biphasic process for the manufacture of EO is introduced. Extensive literature search has been done to find an appropriate solvent for ethylene and the effect on the solubility of ethylene due to the presence of other substances has been



studied using modeling techniques. Methanol is found to be a suitable solvent based on high solubility of ethylene in the liquid phase at moderate pressures. The error between the experimental data and model predictions is negligible but the model fails to predict data as we approach the critical conditions. The knowledge of the VLE has led to devising optimum operating conditions to obtain maximum yield of EO thus fulfilling the CEBC vision for developing sustainable technologies.

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## Chapter 5

### Investigation of Flammability Envelope of Components in the Epoxidation system in the presence of inerts such as CO<sub>2</sub> and N<sub>2</sub>.

#### 5.1 Introduction

The previous chapter reveals that the conversion of ethylene in the vapor phase epoxidation of ethylene is limited due to the combustion of ethylene and ethylene oxide to carbon dioxide and water [1]. The objective of this chapter is to address the ability of inerts such as carbon dioxide and nitrogen to mitigate the flammability hazards when used as a diluent for oxidants such as oxygen and air.

Humphrey Davy and Robert Bunsen were the original pioneers in the subject of flammability as they responded to explosions in coal mining [2]. The requirement for the propagation of flame is an oxidant, fuel, and an ignition source. Fuel is a substance that undergoes and maintains combustion under specified conditions. Oxidant is any substance that supports combustion. Combustion reactions are highly exothermic reactions raising the temperature of the system, such that the flame can be self sustained until one of the components is consumed. This auto-thermal process results in rapid pressure increase that can lead to pressure release.

The terminologies used in this chapter to describe the flammability envelope of a fuel are:

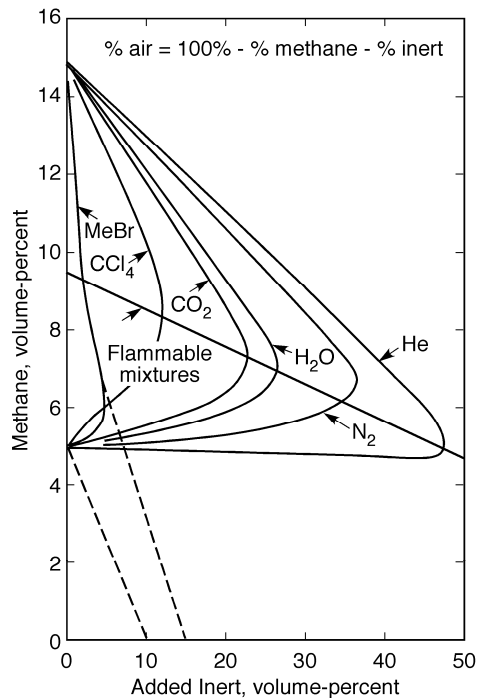
- **Lower Flammability Limit (LFL):** The minimum concentration of the fuel in the vapor phase of a fuel/oxidant atmosphere at which flame propagation occurs in the presence of an ignition source.
- **Upper Flammability Limit (UFL):** The maximum concentration of the fuel in the vapor phase of a fuel/oxidant atmosphere at which flame propagation occurs in the presence of an ignition source.
- **Flash Point:** The lowest temperature at which the vapor of a flammable substance can form a flammable mixture in air. Note that flash point is in terms of temperature and LFL and UFL, in terms of concentration.
- **Autoignition Temperature:** The temperature at which the fuel self ignites, in the absence of an ignition source in a fuel/oxidant atmosphere.
- **Freeze Out Temperature:** Combustions reactions producing carbon dioxide and water have a freeze out temperature which is the minimum temperature required for carbon monoxide to propagate a self-sustaining flame. Literature search reveals a value of 1000-1500 K as a good approximation for most of substances.
- **Calculated Adiabatic Flame Temperature:** The maximum temperature attained by the products of an adiabatic combustion reaction.

The concentrations of fuel and oxidant between the lower and upper flammability limits define the range of flammable mixtures. The flammability envelope can be estimated by upward or downward propagation of the flame most of the literature data has been based on the downward propagation of the flame. These studies help in

the design of safe operating conditions and enable operations in fuel enriched environments. Propagation of flame in the vapor phase of the gaseous mixture occurs when the ignition source supplies energy to the fuel at a faster rate than the fuel loses energy; then these mixtures are susceptible to thermal runaway reactions.

### 5.1.1 Inerts Gases to reduce Flammability Envelope

Inert gases when present in substantial quantities can be used to mitigate the risk of ignition and flame propagation. Inert gases, owing to their high heat capacities, can affect ignition temperature, and the ability of the fuel and oxidant to sustain combustion reaction. The flammability envelope for methane in the presence of various inerts is shown below in Figure 5.1[3].



**Figure 5.1:** Flammability Envelope of methane in presence of various inerts [3], [4].

The concentration of inert components in the mixture clearly reveals that carbon dioxide lowers that flammability envelope of a combustible gas to a greater extent than nitrogen. This is attributed to the heat capacity of the gas, which increases with increase in number of constituent atoms of the molecule. An inert gas with high heat capacity and low thermal conductivity reduces the flammability envelope to a greater extent. As, the concentrations of an inert gas in the mixture increases, the flammability envelope reduces and vanishes beyond a certain concentration. This data clearly reveals that a lower concentration of carbon dioxide can thwart the hazard of an accidental explosion, in comparison with nitrogen.

## **5.2 Computational methods to estimate Flammability Envelopes**

There are many software products that have been designed to evaluate the flammability envelopes of combustible substances. SuperChems 3.0® is commercially available software that has embedded tools for this purpose. It is based on the estimation of a *Calculated Adiabatic Reaction Temperature* (CART). CART is the most widely used method to estimate this kind of hazardous behavior. The temperature rise of a given reaction is calculated under adiabatic conditions and it provides the most reliable information for the estimation of flammability envelope [5-7].

### **5.3 Methodology**

This analysis involves the estimation of CART to study the vapor phase flammability envelope using the Gibbs free energy minimization approach for ambient pressures using HYSYS® software. Using this approach quantifiable data can be generated which clearly underlines the advantages of using inerts such as carbon dioxide and nitrogen. Here, the analysis is restricted to the combustion of reactants and products associated with the liquid phase epoxidation process of propylene and ethylene as developed at CEBC [5].

#### **5.3.1 Gibbs Free Energy Minimization-HYSYS**

This method has been used for predicting flammability of various fuels including lower alkanes, esters and carboxylic acids and serves as an alternative approach to conducting experiments. This technique is based on the correlation between the explosive limits and parameters characteristic of the mixture. The starting materials are considered to be in metastable states and a progress towards equilibrium is estimated by the minimization of the Gibbs Free energy. Freeze out temperature is defined and any mixtures whose combustion products attain an adiabatic temperature higher than that defined temperature are considered to be explosive and susceptible to thermal run away reactions. The freeze-out temperature is commonly chosen to be 1400 K [5, 7].

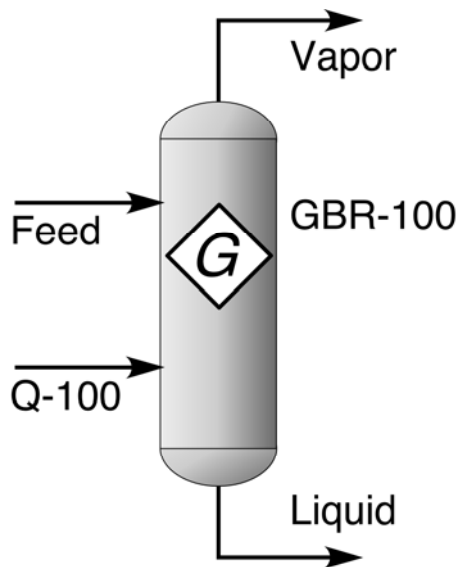


### 5.3.2 Computational Procedure for the Model

The following assumptions are made in the model:

1. Combustion is instantaneous.
2. Operation is under steady state adiabatic conditions.
3. Kinetic and Potential energy effects are ignored.
4. The fuel and oxidant are well mixed.

The implementation of this process in HYSYS®, involves the construction of a flow sheet to model the vapor-liquid equilibrium of the mixture using an appropriate equation of state and the CART of the vapor stream is measured in a Gibbs free energy reactor with a zero heat duty as shown in the Figure 5.2.



**Figure 5.2:** Gibbs Reactor for estimation of flammability envelope [8].

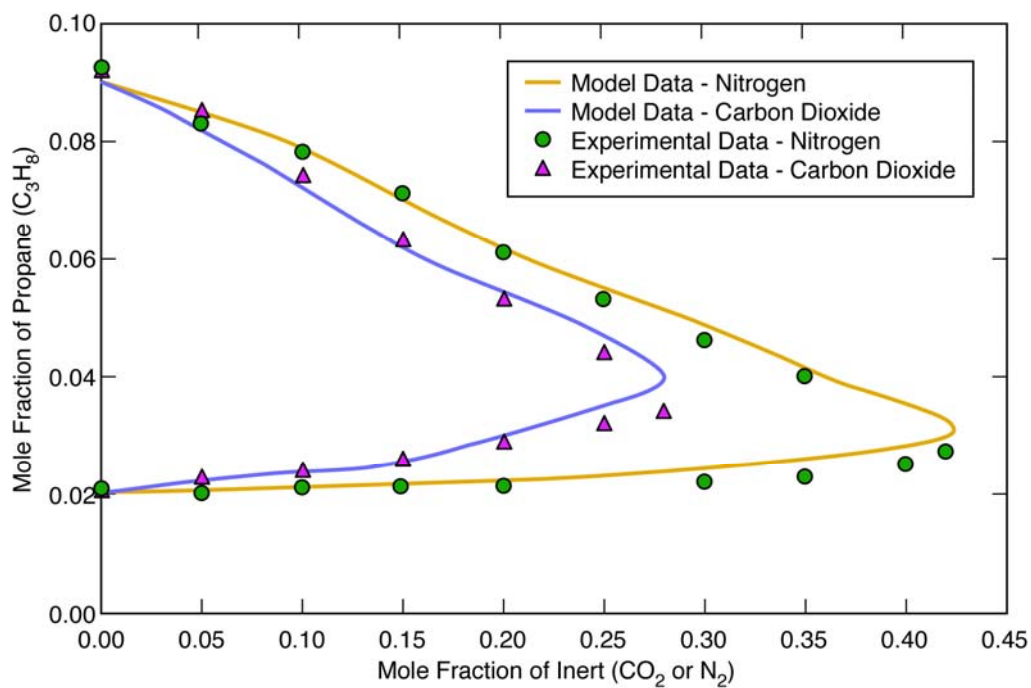
The heat generated upon combustion and the ability of the reaction mixture to absorb the heat determines the temperature rise. The lowest fuel concentration that leads to the formation of explosive mixtures is termed the lower flammability limit

(LFL). As the fuel/oxidant mixture becomes richer in fuel, the temperature rise diminishes and eventually falls below the freeze out temperature resulting in an upper flammability limit (UFL). The LFL and UFL are computed for various compositions of inerts, fuel and oxidant to generate the flammability envelope, subject to the following constraints.

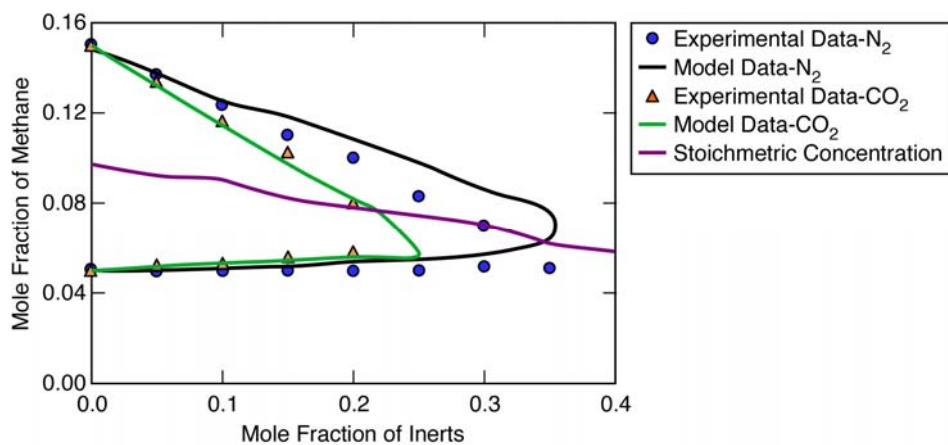
$$\sum G_{products} - \sum G_{reactants} = 0 \quad (5.1)$$

$$G = H - TS \quad (5.2)$$

The input conditions of the stream are defined and all possible complete and partial combustion reactions involving the flammable substance are assumed to be at equilibrium are defined in HYSYS® software with their stoichiometries manually. The Peng Robinson equation of state is used to estimate the thermodynamic properties of all the combustion products in the gas phase when subjected to the Gibbs Free minimization constraints described in the equations 5.1 and 5.2. to obtain the calculated adiabatic reaction temperature (CART) [9]. This method is validated by estimating the flammability envelope of methane and propane and comparing with the experimental data available from literature as shown in Figure 5.3 and 5.4.



**Figure 5.3:** Flammability envelope for propane at 1 atm and 25 °C [3].

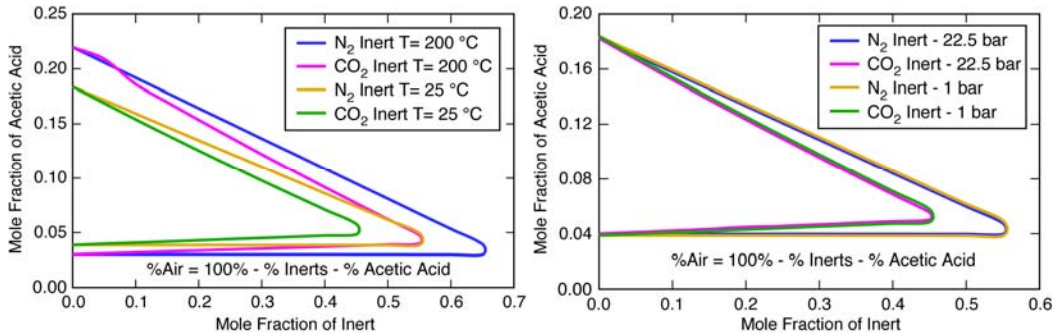


**Figure 5.4:** Flammability envelope for methane at 1 atm and 25 °C [3].

## 5.4 Results and Discussions

The CART was calculated using the various compositions of the reactants and products of the liquid phase epoxidation process at atmospheric pressure and room

temperature. The CART at various compositions that intersect the defined threshold temperature represents the upper and lower flammability limits. The effect of temperature and pressure on the flammability envelope are studied for the mixture of acetic acid/air/inert system. It is observed that the temperature of the input stream does not affect the lower flammability limit but widens the UFL profoundly. Pressure does not have a significant affect on the flammability envelope as shown in the Figures 5.5 a & b.

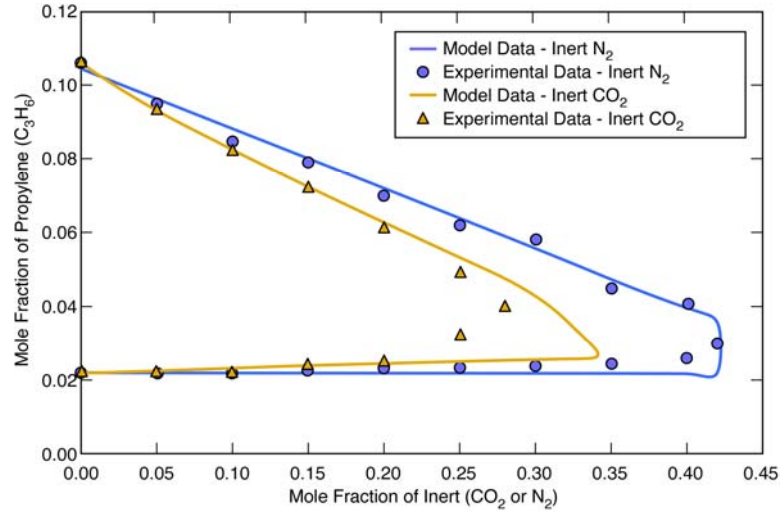


**Figure 5.5:** Flammability envelope of acetic acid (a) Effect of pressure (b) Effect of temperature

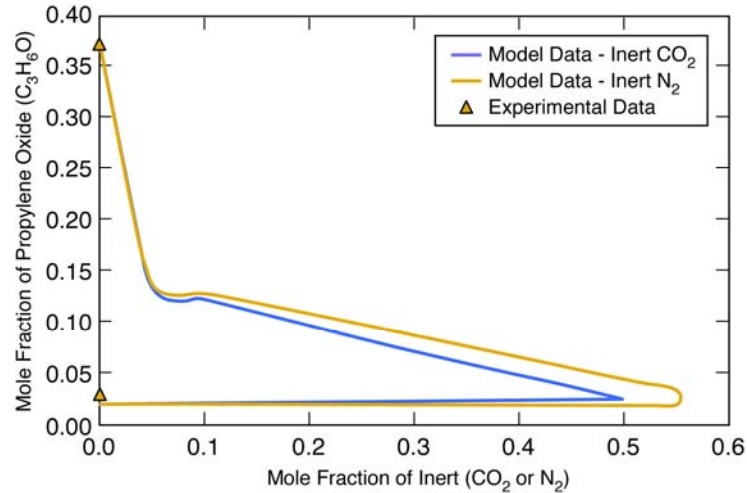
#### 5.4.1 Propylene and Propylene Oxide

Propylene and propylene oxide, the reactants and products of the liquid phase epoxidation process form a flammable mixture with a vapor phase containing  $O_2$ . The knowledge of the flammability envelope of propylene and the effect of the presence of inerts enables the conduct of operations under a propylene enriched atmosphere in a safe manner. Nitrogen, a non condensable gas, is added to the gas phase to enhance

the solubility of propylene in methanol, where it undergoes the catalytic epoxidation reaction to form propylene oxide.



**Figure 5.6:** Flammability envelope of propylene at 1 atm and 25 °C [3].



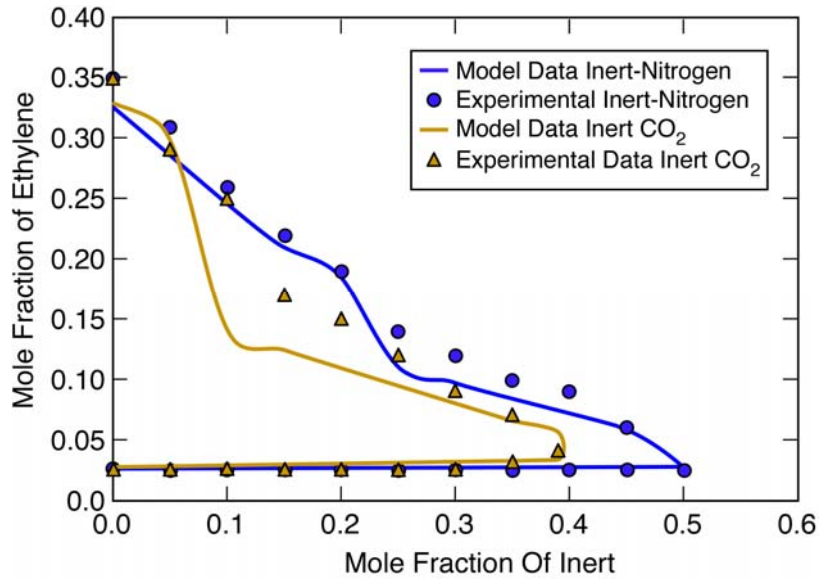
**Figure 5.7:** Flammability envelope of propylene oxide at 1 atm and 25 °C [3].

As seen in the Figure 5.7, a steep drop in the upper flammable limit of propylene oxide is observed when a small amount of nitrogen is present in the gas phase. The flammability limit of propylene extends from 3 mol% to 10.5 mol% and, in the case of propylene oxide, from 3 mol% to 37 mol%. The use of nitrogen to bring

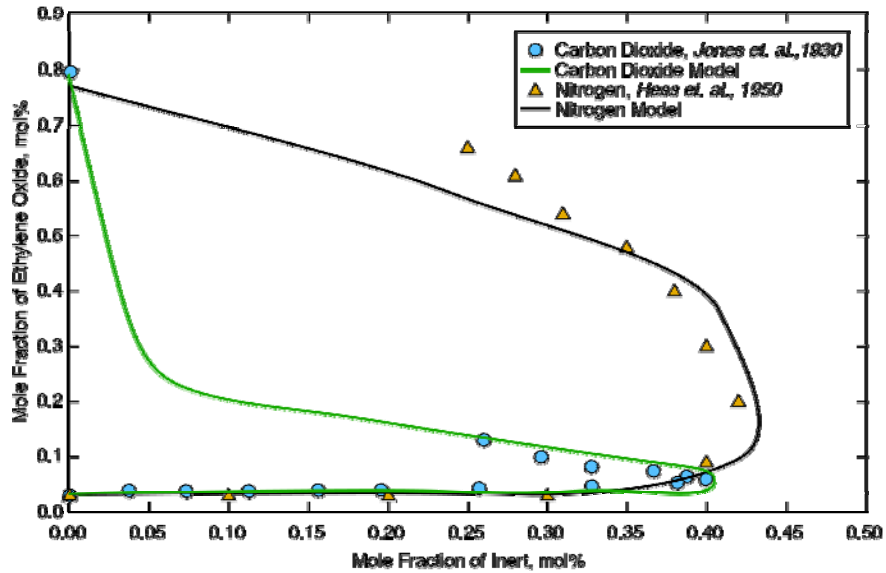
about pressure intensification has an added advantage in preventing the formation of an explosive mixture. Carbon dioxide is known to have a higher heat capacity than nitrogen and can bring about a greater decrease in the flammability envelope for a similar amount of inert, reducing the fixed capital investment of the reactor. The drawback of using carbon dioxide is the adverse effect on conversion of propylene due to its condensable nature; it forms a CXL and has a diluting effect on the dissolved reactants. Higher conversions are obtained due to the pressure intensification brought about by the relatively insoluble nitrogen. So, nitrogen is preferred over carbon dioxide to provide a safety blanket for this process.

#### **5.4.2 Ethylene and Ethylene Oxide**

Ethylene and Ethylene Oxide were also subjected to similar analyses. These gases are highly combustible substances with a wide flammability envelope. It is known that the conversion of ethylene is restricted to around 8% in the conventional vapor phase epoxidation process to minimize the side reactions of complete combustion of ethylene and ethylene oxide which results in the generation of carbon dioxide. The economics of the conventional process is controlled by the cost of ethylene which accounts for 75% of the cost of the product and combustion of 25-30% of the converted ethylene to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  represents a considerable monetary loss.



**Figure 5.8:** Flammability envelope of ethylene at 1 atm and 25 °C [3].



**Figure 5.9:** Flammability envelope of ethylene oxide at 1 atm and 25 °C [10-13].

Figures 5.8 and 5.9 show that ethylene has a LFL of 3 mol% and UFL 35 mol%. In contrast, ethylene oxide has a flammability envelope extending from 3 mol% in O<sub>2</sub> to 85 mol%. Moreover pure EO undergo thermal decomposition by a free radical mechanism to a concentration of 85 mol% EO, and the byproducts being

acetaldehyde, formaldehyde and ethane [14]. The conditions of the storage vessel are monitored continuously to prevent this decomposition as it brings the ethylene oxide concentration within the flammability limit and may undergo spontaneous combustion. Comparison of the modeling results with the available experimental data showed a deviation of 15% in some composition ranges, due to the inability of the model to account for the difference in the interactions among the gases as the number of components increase and also non-availability of this interaction parameter data in the literature. In the regions with low or high inert gas concentrations, the presence of other gases does not have a dominant effect on the interaction parameters since in one case ethylene/ethylene oxide are the dominant gases while in the other case the inerts are present in high concentration. The availability of reliable interaction parameter data dictates the precision of the model at intermediate concentration of the mixture.

## **5.5 Summary**

A quantitative analysis of the flammability envelope compares the advantages of using carbon dioxide and nitrogen inerts in mitigating the flammability envelope using the Calculated Adiabatic Reaction Temperature (CART) approach. The systems analyzed are the reactants and products of the olefin epoxidation reaction. The region in which the combustible substance forms a flammable mixture is smaller in the presence of carbon dioxide than in the presence of nitrogen owing to the high heat capacity of carbon dioxide. Thus operating in inert atmospheres provides inherent safety benefits.



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## Chapter 6

### Conclusions and Recommendations

#### 6.1 Conclusions

Extensive modeling studies for the estimation of the vapor-liquid equilibria of various binary and ternary systems of propylene and ethylene gas with liquid phase constituents (containing water and alcohols) were conducted in this thesis using HYSYS® software to understand the phase behavior in liquid phase epoxidation systems. The modeled data are generally shown to have high accuracy when compared with published experimental data, including those from our research group. Based on the modeling, it was confirmed that methanol addition to the aqueous liquid phase favors significant dissolution of the light olefins in the liquid phase (on the order of tens of mole percent) with simple pressure tuning reaction temperatures (20-40°C). In the case of propylene, pressures as low as 10 bars, with either propylene or N<sub>2</sub> as the pressurizing gas, are sufficient to enhance propylene availability in the liquid phase. In the case of ethylene ( $T_c = 9\text{ }^\circ\text{C}$ ), ethylene dissolution is significantly enhanced as the pressure is increased in the vicinity of the critical pressure of ethylene ( $P_c = 50\text{ bars}$ ). These phase behavior trends provide a clear explanation of the pressure-induced rate enhancement observed during propylene epoxidation. Further, they have also guided the choices of solvent and operating conditions (P&T) for obtaining enhanced rates in the case of liquid phase ethylene epoxidation using aqueous H<sub>2</sub>O<sub>2</sub> as the oxidant and methyltrioxorhenium as the catalyst.

Experimental mass transfer investigations, performed using a stirred reactor, established that at stirrer speeds exceeding 1000 rpm was required to overcome mass transfer limitations for propylene dissolution into the liquid phase containing methanol. The volumetric mass transfer coefficients (0.140 cm/s) estimated from transient propylene profiles (i.e., uptake data) showed good agreement with those predicted with empirical correlations. Further, the measured propylene uptake at equilibrium is in agreement with the value predicted by phase behavior modeling. These results establish operating conditions needed to avoid mass transfer limitations.

Flammability calculations, based on the calculated adiabatic reaction temperature (CART), were performed to delineate the flammability envelopes of combustible olefins in the presence of inert gases such as nitrogen and carbon dioxide. Carbon dioxide owing to its higher heat capacity, reduces the flammability envelope to a greater extent than does nitrogen. The calculations agree with published experimental data and demonstrate that as long as hydrogen peroxide decomposition to O<sub>2</sub> is avoided (by operating at ambient temperatures or lower), flammable vapors involving ethylene and propylene are totally avoided. Furthermore, pressures that favor ethylene oxide to be predominantly confined to the liquid phase (thereby minimizing its vapor phase concentration) are preferred to avoid flammable ethylene oxide vapors.

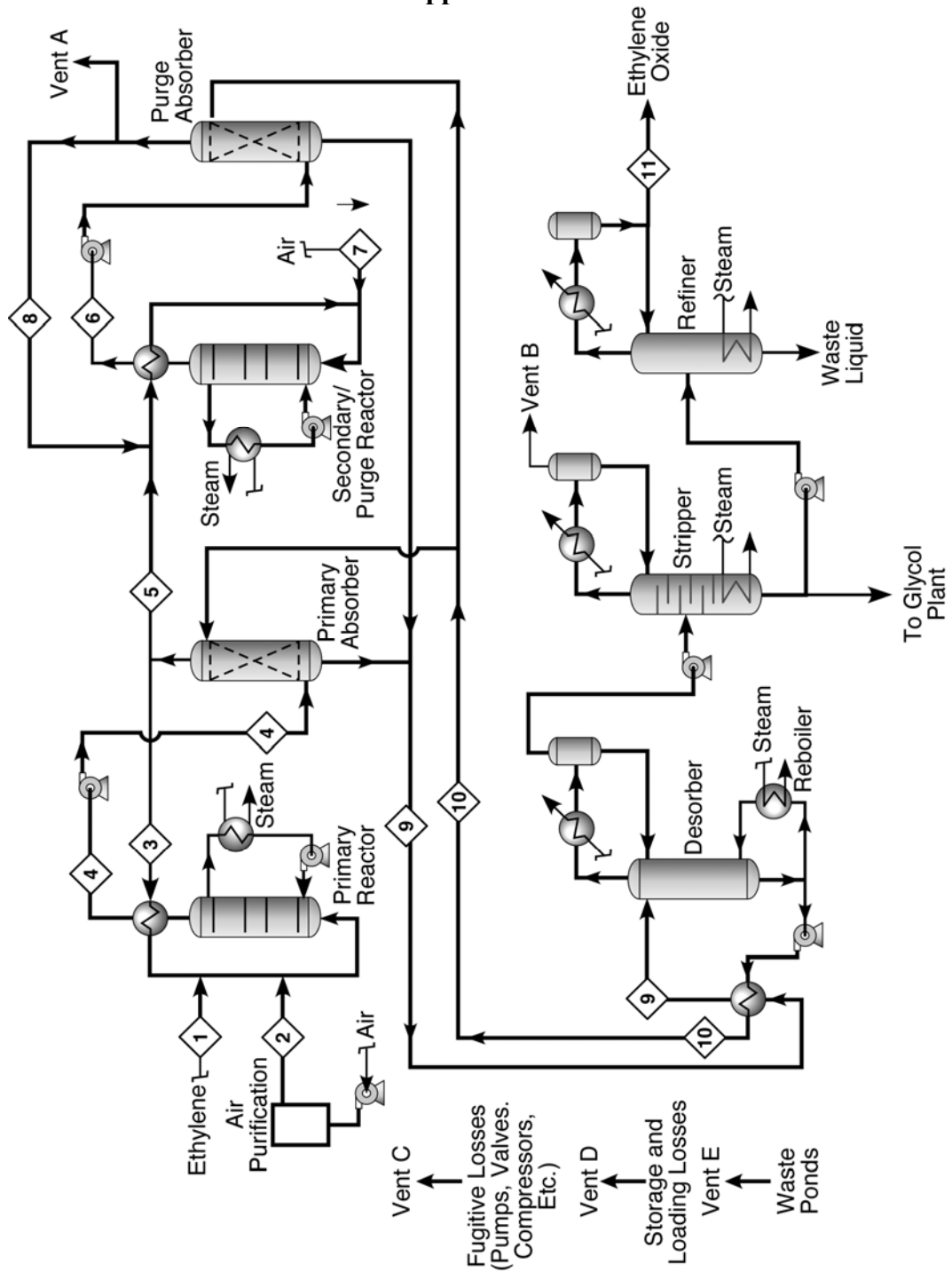
## **6.2 Recommendations**

Based on the foregoing results, several recommendations are made as follows:

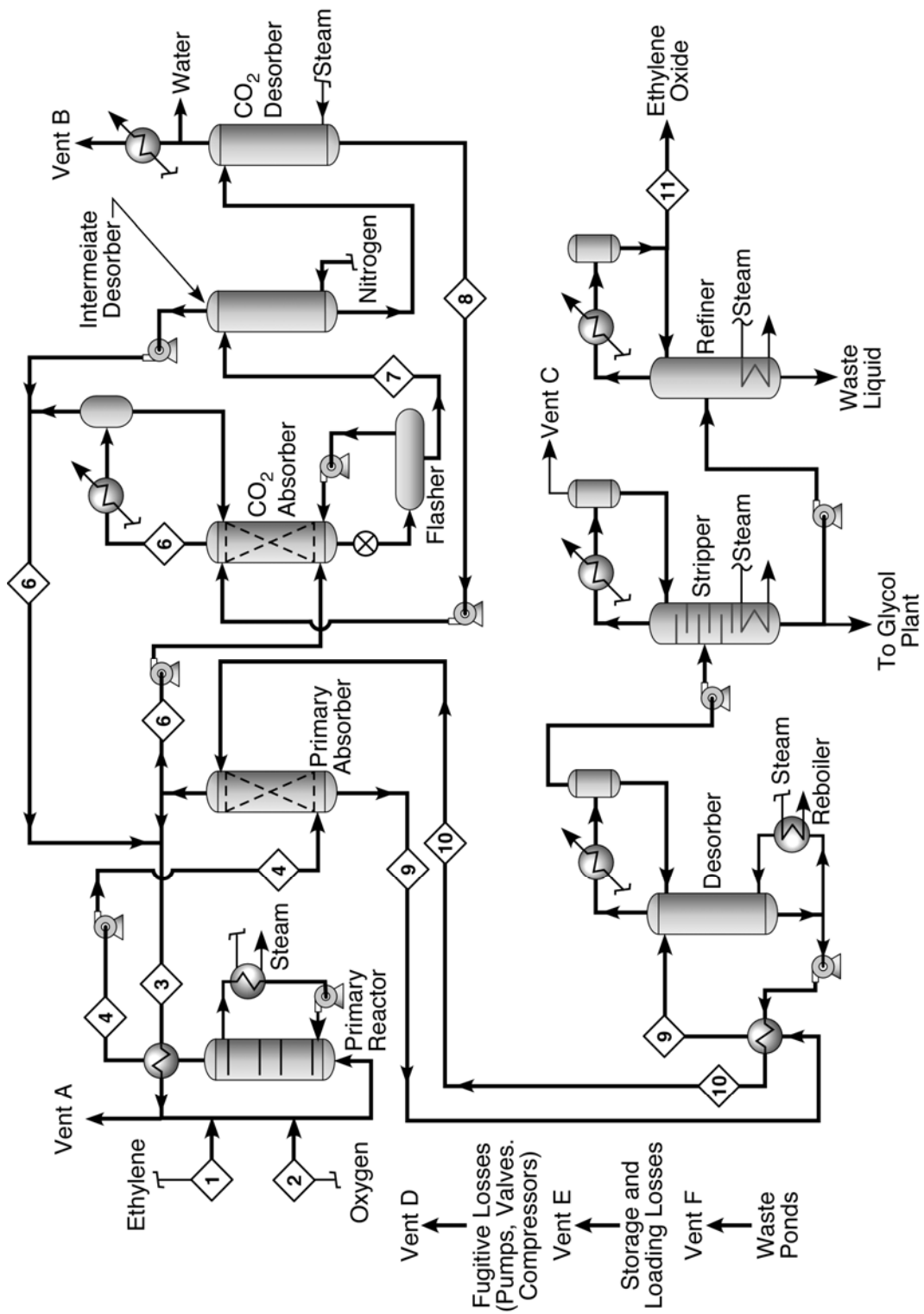
The HYSYS® VLE prediction model fails as the number of components increases beyond three in the system being modeled; this is due to the lack of interaction parameter data in literature and the inability of the model to simulate such systems using the UNIFAC tool embedded in the HYSYS® software. The UNIFAC method is based on group contribution theory which treats the system as a solution of various groups whose interactions are fixed and independent of the chain length or presence of other groups. The limitations associated with this theory can be overcome by using the COSMO solvation models to estimate the electrostatic interactions between the molecules. The estimation of the repulsive parameters ( $k_{ij}$ ) based on these estimates can improve the accuracy of the simulations for multi-component systems.

The mass transfer studies show that the solubility of propylene in the liquid phase can be the rate limiting step of the reaction. Mechanical stirring at high speeds of 1000 rpm can overcome this difficulty, but at these speeds there is vortex formation requires the use of baffles to break these vortices for proper dispersion of bubbles. This suggests that the sparging the gas into the liquid phase or use of bubble column may serve as alternate configuration especially for ethylene epoxidation.

### Appendix A



**Figure A1:** Schematic of Ethylene Epoxidation using Air as the Oxidant

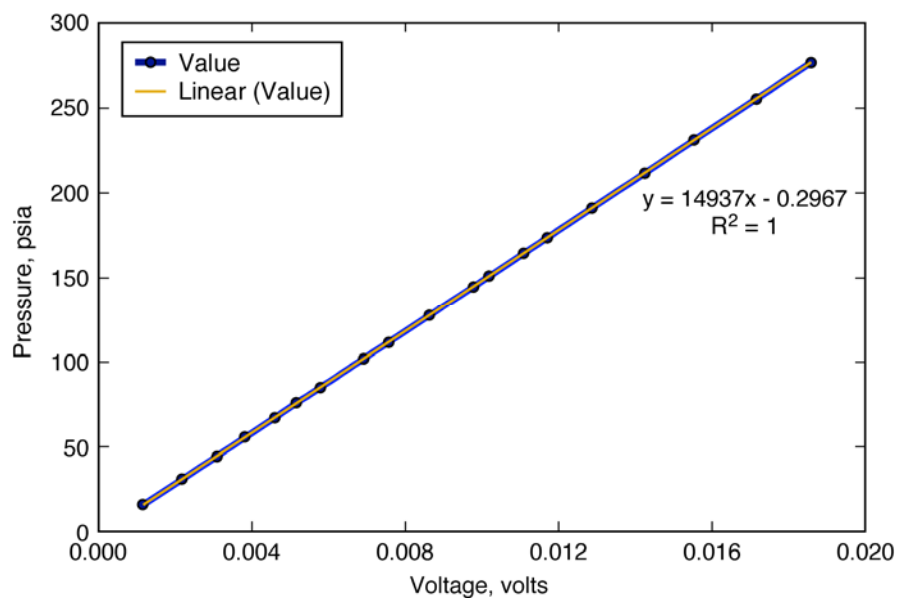


**Figure A2:** Schematic of Ethylene Epoxidation using oxygen as the oxidant.

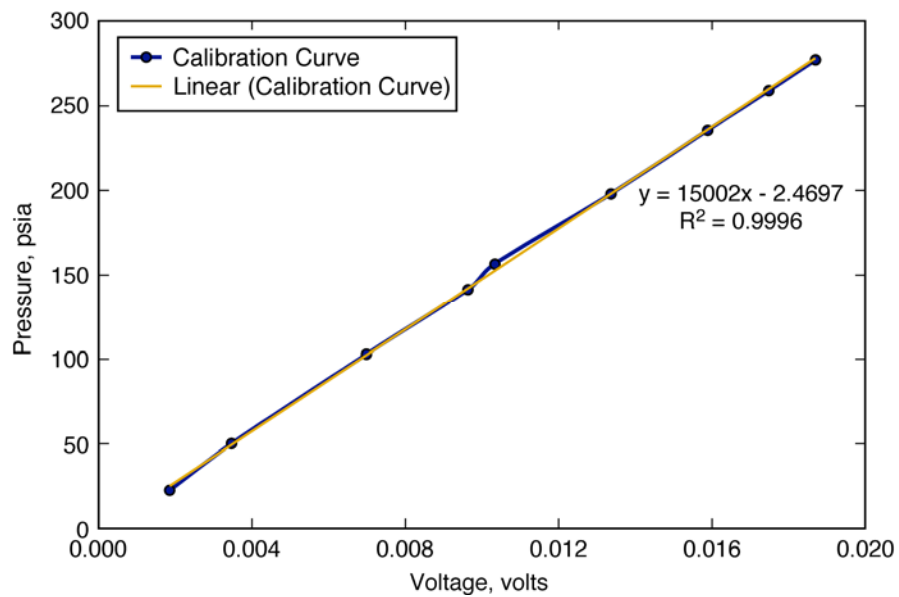
## Appendix B

### **Calibration of Pressure Transducer**

1. The cell is first pressure tested and ensured to be leak free.
2. An analog gauge (HEISS® guage), calibrated against a dead weight gauge is connected between the cylinders and the transducer.
3. The cell is pressurized and depressurized with an inert gas like helium or nitrogen at over a pressure range of (1- 20 bars) in a random manner.
4. The cell is pressurized to a fixed value of pressure and held constant until the transducer response stabilizes. The response to the transducer was measured in terms of the voltage output, directly read from Lab View® as the transducer's output. The above procedure is repeated for various pressures that span the complete operating conditions of the desired experiments.
5. A linear relationship is obtained by plotting the response of the transducer (voltage) against the actual pressure as shown in Figure Fig C1& C2. The value of the slope and intercept are recorded in the data acquisition software. The voltage is not always zero for the zero gauge pressure and hence the line does not pass through the origin although linearity still holds good.



**Figure B1:** Calibration of pressure transducer attached to the ReactIR



**Figure B2:** Calibration of pressure transducer attached to the propylene reservoir



## Appendix C

### Sample calculation for the estimation of propylene mole fraction in methanol

Volume of the reactor = 50 ml

Reactor Pressure = 45 psi = 3.10 bar

Operating Temperature of the reactor = 22 °C

Volume of Methanol charged in the reservoir = 23 ml

Density of Methanol = 0.791 (g/cc)

Moles of Methanol present in the reservoir = 0.569 moles

Volume of the Reservoir = 0.3 ltr

Initial Pressure of Propylene in the reservoir = 138.96 psi = 9.58 bar

Final Pressure of Propylene in the reservoir = 68.73 psi = 4.738 bar

Pressure drop in the reservoir = 4.842 bar

Temperature of Reservoir = 22 °C

Volume occupied by the gas = 27 ml

#### Using ideal gas law to estimate the following quantities

Moles of Propylene pumped into the reactor = 0.05941 moles

Moles of propylene that must present in the gas phase to maintain a reactor pressure of 3.1 bar = 0.00342 moles

Moles of propylene that are present in the liquid phase = (0.05941- 0.00342)  
= 0.0559 moles

Total moles in the liquid phase =  $(0.0559 + 0.569) = 0.624$  moles

Mole fraction of methanol in the liquid phase = 0.9105

Mole fraction of propylene in the liquid phase = **0.0894**

The literature data published by Ogaki shows the mole fraction of propylene in methanol to be **0.09**.