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SIMULATION OF THE SYNTHESIS OF TERTIARY AMYL ETHYL
ETHER FROM TERTIARY AMYL ALCOHOL AND ETHANOL IN
REACTIVE DISTILLATION BY USING ASPEN PLUS PROGRAM



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อุกฤษฏ์ สหพัฒน์สมบัติ: การจำลองการสังเคราะห์เทอร์เชียรีเอมีลเอทิลอีเทอร์จากเทอร์เชียรีเอ
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ในงานวิจัยนี้จะทำการศึกษากลั่นแบบมีปฏิกิริยา (reactive distillation) ซึ่งปฏิกิริยาเคมี
และการแยกเกิดขึ้นภายในพร้อมกัน ถูกนำมาประยุกต์ใช้ในการสังเคราะห์เทอร์เชียรีเอมีลเอทิลอีเทอร์
(TAEE) จากสารตั้งต้นเทอร์เชียรีเอมีลแอลกอฮอล์ (TAA) และเอทานอล (EtOH) โดยใช้สมการ
อัตราการผลิตปฏิกิริยาอีเทอร์รีฟิเคชันในเฟสของเหลวและแบบจำลองชั้นสมดุลของการแยกเพื่อใช้ศึกษา
ในกลั่นแบบมีปฏิกิริยา การคำนวณจะทำโดยใช้ชุดโปรแกรมทางการค้าชื่อ ASPEN PLUS การ
จำลองถูกจัดทำขึ้นเพื่อตรวจสอบผลของตัวแปรที่ออกแบบขึ้น เช่น จำนวนชั้นของเรกติฟายอิง จำนวนชั้น
ของปฏิกริยา และจำนวนชั้นของสตีปปิงที่มีผลต่อระบบของกลั่นแบบมีปฏิกิริยา และได้พบว่าจำนวน
ชั้นของปฏิกริยา 4 ชั้น จำนวนชั้นของสตีปปิง 8 ชั้น และไม่มีชั้นของเรกติฟายอิงเหมาะสมสำหรับการ
สังเคราะห์เทอร์เชียรีเอมีลเอทิลอีเทอร์ นอกจากผลของจำนวนชั้นของกลั่นแบบมีปฏิกิริยาแล้ว ผลของ
ตัวแปรในการปฏิบัติงานต่างๆที่มีผลต่อค่าการเปลี่ยน (Conversion) ของเทอร์เชียรีเอมีลแอลกอฮอล์
(TAA) และค่าการเลือกเกิด (Selectivity) ของ เทอร์เชียรีเอมีลเอทิลอีเทอร์ (TAEE) ได้ถูกศึกษา
พบว่าค่าอัตราส่วนการป้อนกลับ (Reflux ratio) และความดันในกลั่น (Operating pressure) เป็น
ปัจจัยที่สำคัญที่สุดในการทำงานของกลั่นแบบมีปฏิกิริยา

นอกจากนี้ยังมีเพิ่มการใช้ระบบของเพอร์เวปอเรชันซึ่งเป็นกระบวนการแยกโดยใช้เมมเบรน
สำหรับทำการแยกส่วนผสมของเหลวที่แยกได้ยากหรือเป็นไปไม่ได้ที่จะแยกโดยระบบการแยกสารทั่วไป
ได้ถูกเพิ่มเข้าไปในระบบของกลั่นแบบมีปฏิกิริยา การแยกน้ำโดยใช้เพอร์เวปอเรชันเมมเบรนนี้จะ
ช่วยเพิ่มประสิทธิภาพของกลั่นแบบมีปฏิกิริยา

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ลายมือชื่ออาจารย์ที่ปรึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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UKRIT SAHAPATSOMBUT : SIMULATION OF THE SYNTHESIS OF
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In this research, a reactive distillation in which chemical reactions and separations occur simultaneously is applied for the synthesis of *tert*-amyl ethyl ether (TAE) from ethanol (EtOH) and *tert*-amyl alcohol (TAA). A rate-based kinetic model for liquid-phase etherification and an equilibrium stage model for separation are employed to study the reactive distillation. The calculation is carried out using the commercial software package, Aspen Plus. The simulations are performed to examine the effects of design variables; i.e., numbers of rectifying, reaction and stripping stages on the performance of reactive distillation. It has been found that an optimal column configuration for the TAE production under the range of study comprises no rectifying, 4 reaction and 8 stripping stages. With the optimum column, effects of various operating variables on the TAA conversion and TAE selectivity are further investigated and the results have shown that the reflux ratio and operating pressure are the most important factors for the operation of the reactive distillation.

In addition, the pervaporation, a membrane process for separation of liquid mixtures that are difficult or not possible to separate by conventional methods, is incorporated in the reactive distillation. Removal of water through the pervaporation membrane improves the performance of the reactive distillation.

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TABLE OF CONTENTS

	Page
ABSTRACT (IN THAI)	iv
ABSTRACT (IN ENGLISH)	v
ACKNOWLEDGEMENTS	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
NOMENCLATURE	xiii
CHAPTER	
1 INTRODUCTION	1
1.1 Tertialy-amyl ethyl ether (TAEE)	1
1.2 Reactive distillation	2
1.3 Hybrid process with pervaporation	4
1.4 Scope and objectives	4
2 THEORY	5
2.1 Oxygenates	6
2.1.1 TAEE	8
2.2 Reactive distillation	10
2.2.1 Reactive distillation configuration	11
2.2.2 Advantage of reactive distillation	13
2.3 Membrane definition	13
2.4 Pervaporation process	15
2.4.1 Definition of pervaporation process	15
2.4.2 Transport in membrane	16
2.4.3 Characterization of membranes	18
2.4.3.1 Permability and permeation rate	18
2.4.3.2 Membrane selectivity	20
2.4.3.3 Pervaporation process configurations	20

CHAPTER

	Page
2.4.4 Applications of pervaporation	21
2.4.4.1 Organophilic membrane	21
2.4.4.2 Hydrophilic membrane	22
2.5 Aspen Plus	22
2.5.1 Feature of Aspen Plus	23
2.5.2 Benefits of Aspen Plus	23
3 LITERATURE REVIEWS	24
3.1 Ethanol-based oxygenate production	24
3.1.1 TAEE synthesis from isoamylenes (IA)	25
3.1.2 TAEE synthesis from tert-amyl ethyl ether (TAA)	26
3.2 Hybrid processes of reaction and separation	27
3.2.1 Application of reactive distillation for octane enhancing ether production	28
3.2.2 Hybrid process of distillation-pervaporation	31
3.2.3 Hybrid process of reactive distillation (RD)- pervaporation	32
4 SIMULATION OF REACTIVE DISSTALLATION.....	34
4.1 Reactive distillation model	34
4.2 Kinetic model	36
4.3 Model validation.....	38
4.4 Results and discussions.....	39
4.4.1 Stardard condition	39
4.4.2 Effect of design variables	40
4.4.2.1 Number of reaction stages	42
4.4.2.2 Number of rectifying stages	42
4.4.2.3 Number of stripping stages	43
4.4.3 Effects of operating variables	45
4.4.3.1 Reflux ratio	45
4.4.3.2 Catalyst weight	46

CHAPTER

	Page
4.4.3.3 Operating pressure	47
4.4.3.4 Feed stage location	48
5 REACTIVE DISTILLATION WITH PERVAPORTATION	49
5.1 Hybrid process of reactive distillation and pervaporation model	49
5.2 Pervaporation model	51
5.2.1 Mass balance	52
5.2.2 Energy balance	53
5.3 Results and discussions	54
5.3.1 Standard condition with pervaporation	54
5.3.2 Effect of location of side stream pervaporation	56
5.3.3 Effect of side stream flowrate	56
5.3.4 Reactive distillation with two pervaporation modules ...	56
6 CONCLUSIONS AND RECOMMENDATIONS	58
6.1 Conclusions	58
6.1.1 Reactive distillation	58
6.1.2 Reactive distillation with pervaporation	59
6.2 Recommendations	59
REFERENCES	61
APPENDICES	
APPENDIX A. MODIFIED KINETIC PARAMETERS OF TAAE SYSTHESIS	66
APPENDIX B. PARAMETERS USED IN PERVAPORATION ...	70
APPENDIX C. FORTRAN USER MODEL	72
APPENDIX D. UNIFAC METHOD	74
VITA	80

LIST OF TABLES

TABLE	Page
2.1	Physical properties of oxygenates..... 7
2.2	Physical, Chemical and Thermal Properties of TAEE 9
4.1	Feed conditions and specification of reactive distillation column under the standard condition 36
4.2	Expressions of the parameters used in the kinetic model 38
4.3	Comparison of simulated results and experimental data from Aiouache and Goto (2003b) 39
4.4	Effect of feed separation on the TAA conversion and the TAEE selectivity 48
5.1	Feed conditions and specification of reactive distillation column with the pervaporation 51
5.2	Comparison of RD and RD connected with pervaporation from standard condition (Side stream flowrate = 0.0015 mol/s, membrane area = 0.01 m ²) 55
5.3	Effect of two pervaporation on the performance of reactive distillation (Side stream flowrate = 0.0015 mol/s, membrane area 0.01 m ² , reflux ratio = 2, reboiler duty 52 watts) 57

LIST OF FIGURES

FIGURE	Page
2.1	molecular structure of TAEE 8
2.2	Conventional process involving reaction followed by separation 12
2.3	Reactive distillation applied to the same process 12
2.4	Cross-section of membrane 14
2.5	Basic membrane separation principle 14
2.6	Schematic diagram of a pervaporation process 16
2.7	Schematic of pervaporation transport by solution-diffusion mechanism 17
2.8	Modes of operation at the permeate side 21
4.1	The configuration of a reactive distillation column 35
4.2	Mole fraction and temperature profiles inside the column at the standard operating condition (Feed molar flowrate = 2.71×10^{-3} mol/s, Reflux ratio = 2, Catalyst = 0.5 kg, Feed TAA:EtOH = 1:1) 41
4.3	Effect of the number of reaction stages on the reactive distillation performance 41
4.4	Effect of the number of rectifying stages on the reactive distillation performance 43
4.5	Effect of the number of stripping stages on the reactive distillation performance 44
4.6	Effect of the reflux ratio on the reactive distillation performance 45
4.7	Effect of the catalyst weight on the reactive distillation performance 46
4.8	Effect of the column pressure on the reactive distillation performance 47

FIGURE		Page
5.1	The configuration of combined process consisting of a reactive distillation column and a pervaporation unit	50
5.2	Schematic diagram of pervaporation membrane	52
5.3	Effect of location of side stream pervaporation on the performance of reactive distillation	55
5.4	Effect of side stream flowrate to pervaporation on the performance of reactive distillation	57



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จุฬาลงกรณ์มหาวิทยาลัย

NOMENCLATURE

a_i	activity of species i	[-]
A	effective surface membrane area	[m ²]
D	total distillate flowrate (= $LD+LI$)	[mol/s]
D/F	distillate to feed ratio	[-]
Dif	diffusivity coefficient	[m/s]
E_a	activation energy	[J/mol]
c_i	concentration of species i	[mol/m ³]
c_{pl}	heat capacity of liquid	[J/mol.K]
F	feed flowrate	[mol/s]
F_i	molar flow rate of species i in the reaction side	[mol/s]
H	enthalpy	[J/s]
H_{vap}	enthalpy of vaporization	[J/s]
J_i	permeate flux of species i	[mol/m ² .s]
k_i	kinetic constant base on mol fraction	[mol/(s mol-H ⁺)]
K_i	equilibrium constant	[-]
l	membrane thickness	[m]
LD	liquid distillate flowrate	[mol/s]
LI	liquid flowrate to return from stage 1 to stage 2	[mol/s]
m_r	mass of dry ion-exchange resin	[kg]
M_i	molecular weight of species i	[kg/mol]
N_i	number of mole of species i in the reactor	[mol]
P_i	permeability coefficient of species i	[mol/(m ² .s)]
Q	ion-exchange capacity (=4.9 resin]	[mol-H ⁺ /kg-dry resin]
Q_i	molar flow rate of species i in the permeate side	[mol/s]
Q_r	reboiler duty	[W]
r_i	reaction rate resin)]	[mol/(s kg-dry resin)]

R	reflux ratio	[-]
R_g	gas constant (=8.314)	[J/(mol/K)]
S	solubility coefficient	[mol/m]
T	operating temperature	[K]
T_c	condenser temperature	[K]
x_i	mole fraction of component i	[-]

Greeks letters

α_i	separation factor of species i	[-]
γ_i	activity coefficients of species i	[-]

Subscripts

0	initial value at $t = 0$
d	desired reagent to be removed
f	feed to pervaporation
i	species i
p	permeate side
R	retentate side
$EtOH$	ethyl alcohol
H_2O	water
IA	isoamylene
TAA	<i>tert</i> -amyl alcohol
$TAAE$	<i>tert</i> -amyl ethyl ether

CHAPTER 1

INTRODUCTION

Oxygenated compounds are an important additive to gasoline in order to improve octane number, which is a measure of a fuel's antiknock performance. In the past, lead compounds, e.g., tetraethyl lead, had been used for such a purpose; however, these compounds were removed from gasoline due to the awareness that lead has an environmental impact. As a result, gasoline producers have presently used oxygenates to compensate the loss in octane from the removal of lead compounds. More recently, oxygenates have also been used in an emission control strategy to reduce carbon monoxide (CO) and, to a lesser extent, hydrocarbon emission from motor vehicles. However, it is known that the use of oxygenates can usually increase the emission of oxides of nitrogen (NO_x); therefore, the amount of oxygen contents in the gasoline for automobile engines is limited to control NO_x emission.

1.1 Tertiary-amyl ethyl ether (TAEF)

There are several kinds of oxygenated compounds that can be used to meet oxygen requirements in gasoline. They are generally divided into two groups: alcohols (e.g., methanol (MeOH) and ethanol (EtOH)) and ethers (e.g., methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and higher tertiary ethers). At present, tertiary ethers have become important additives to gasoline as they are used to improve octane number in gasoline and also to enhance the combustion of gasoline. Among of the tertiary ethers, 2-methoxy-2-methyl propane (methyl *tert*-butyl ether, MTBE) has been widely used in many countries and currently produced in large-scale production. However, it has been reported that MTBE may pollute underground water due to its high water solubility (Dai, 2000). Therefore, the production of other oxygenated compounds such as tertiary-amyl methyl ether (TAME) and tertiary-amyl ethyl ether (TAEF) have been of present interest (Thiel *et al.*, 1997; Kitchaiya and Datta, 1995). Higher ethers, i.e., TAME and TAEF can be attractive alternatives since

they have lower water solubility and lower blend Reid vapor pressure (bRVP) than MTBE.

By comparing TAEE and TAME, TAEE seems to be more interesting due to the fact that

1. TAEE can be produced from ethanol (EtOH) which can be obtained from renewable sources such as sugar cane, corn and molasses.
2. Although TAEE has lower octane number (105) than TAME (112), the vapor pressure of TAEE is lower (0.21 psi) than that of TAME (2.5 psi). Thus, TAEE is more suitable for tropical countries.

Several reports in the production of TAEE have focused on the method in liquid phase synthesis from isoamylene (IA) and ethanol (EtOH) in reactive distillations (Kitchaiya and Datta, 1995; Linnekoski *et al.*, 1997). IA can be produced from the dehydration of amyl alcohols which are included in fusel oil. Fusel oil is a by-product of a fermentation process for ethanol production and can also be obtained during distillation of crude ethanol. However, it is noted that *tert*-amyl alcohol (TAA), a main component in fusel oil, can be an alternative reactant instead of IA (Aiouache and Goto, 2003a). The synthesis of TAEE from TAA and ethanol should be a promising route as both reactants are derived from renewable resources (Chang *et al.*, 1998). Generally, there are two routes to produce TAEE from TAA and ethanol. Firstly, in the indirect method, TAA is dehydrated to IA and then IA reacts with EtOH to produce TAEE. Secondly, in the direct method, TAA and EtOH directly react at the same time in one reactor.

1.2 Reactive distillation

Reactive distillation, sometimes called “catalytic distillation”, has drawn considerable attention from both academic and industrial sectors over the past decades. Reactive distillation which combines a catalytic reactor and a distillation in

one single unit operation is a promising process for equilibrium limited liquid-phase chemical reactions. Its four potential benefits are:

- shifting an equilibrium conversion
- reacting away azeotropic mixtures
- improving selectivity
- saving energy due to the efficient use of reaction heat for separation (Baur *et al.*, 2000)

Reactive distillation has been applied to many esterification and hydrolysis processes involving alkyl acetate and glycols, alkylation for cumene, and the formation of fuel oxygenates in chemical and petrochemical industries. Reactive distillation was first used by the chemical and petrochemical industry in esterification processes to separate reaction products from reactants to increase product yields (Venkataraman *et al.*, 1990). Other applications of commercial reactive distillations can be found in many processes such as methyl acetate process, MTBE process (Doherty and Buzad, 1992) and ETBE process (Quitain *et al.*, 1999a). Since effects of operating conditions and design parameters on the performance of reactive distillation can be investigated via simulation, there are many simulation studies on reactive distillation for ether synthesis. Sneesby *et al.* (Sneesby *et al.*, 1997) studied the simulation of synthesis ETBE in reactive distillation focusing on the design aspects. Moreover, Quitain *et al.*, (1999b) proposed a process for industrial production of ETBE by using the ASPEN PLUS program. Another simulation of reactive distillation column for ETBE was introduced by Yang *et al.*, (2001) who developed a mathematical model of continuous reactive distillation. In addition, there is a simulation study of reactive distillation for removal of water ethanol (Christina *et al.*, 2004). However, there are limited numbers of works in studying a sensitivity analysis of the effect of the operating factors on the performance of RD column for the production of TAAE from TAA and EtOH.

1.3 Hybrid process of reactive distillation with pervaporation

The increased world-wide competitiveness in production has forced industry to improve current process designs. Consequently, the development of new process designs, and the reorganization of present process designs (with the possible integration of new technologies into them) is of growing importance to industry (Lipnizki *et al.*, 1999). Membrane technologies have recently emerged as an additional category of separation processes to the well-established mass transfer processes. Membrane separation technologies offer advantages over existing mass transfer processes. Pervaporation (PV) offers potential solutions in a wide range of applications from the dehydration of organic compounds to the recovery of organic compounds from water and the separation of organic mixtures. Generally, PV alone may not supply products suitable for further processing. Thus, hybrid processes of PV with other units are regarded as one means of overcoming these limitations. Recently, Rautenbach *et al.*, (1998) and Chen *et al.*, (2002) studied the hybrid process of PV and distillation for the production of MTBE. In addition, the pervaporation are also combined with the reactive distillation. Steinigewag *et al.*, (2004) studied the transesterification processes by combination of reactive distillation and pervaporation. Furthermore, this hybrid process was applied to the production of TAAE by Aiouache and Goto (2003b). They studied the etherification of *tert*-amyl alcohol with ethanol in a RD column inserted by a zeolite NaA membrane. However, there are a limited number of works in studying the hybrid process for the production of TAAE.

1.4 Scope and objectives

The objective of this research is to investigate the synthesis of TAAE from TAA and ethanol in a reactive distillation by using Aspen Plus. The kinetic parameters for the synthesis of TAAE with Amberlyst 15 catalyst used in this work are obtained from the literature (Aiouache and Goto, 2003a). Emphasis is placed on the determination of an appropriate configuration of the reactive distillation column for the TAAE production. In addition, an analysis of the effects of various key operating parameters such as reflux ratio, operating pressure, and feed stage location,

on the conversion of TAA conversion and the selectivity of TAEE in the reactive distillation is performed. In order to further improve the performance of the reactive distillation, a hybrid process of reactive distillation and pervaporation is proposed and studied in this work. The use of pervaporation in reactive distillation to remove water from the process is suggested to increase reaction rates towards the desired product, TAEE.



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CHAPTER 2

THEORY

This chapter provides some background information and definition on oxygenates, reactive distillation process, pervaporation process and Aspen Plus simulator. Details are as follows.

2.1 Oxygenates

Oxygenates are compounds containing oxygen in a chain of carbon and hydrocarbon atoms. It is known that although they cannot provide energy to an engine, their structure give a reasonable anti-knock value. As a result, oxygenates are good substitutes for aromatics to improve octane rating of gasoline and may also reduce the smog-forming tendencies of the exhaust gases. Over the past two decades, oxygenates have been used to increase the volume and octane of gasoline. In the late 1970s and early 1980s, as lead compounds were removed from gasoline, gasoline producer used oxygenates to compensate the loss in octane from the removal of lead compounds. More recently, oxygenates have been used in an emission control strategy to reduce carbon monoxide (CO) and, to a lesser extent, hydrocarbon emission from motor vehicles. However, oxygenates can generally increase the emission of oxides of nitrogen (NO_x). Therefore, the oxygen contents in the gasoline for automobile engines have been limited to control NO_x emission.

Most oxygenates used in gasoline are either alcohols (C_x-O-H) or ethers (C_x-O-C_y), and contain 1 to 6 carbon atoms. Alcohols have been used in gasoline since the 1930s while MTBE was first used in commercial gasoline in Italy in 1973 and in the US by ARCO in 1979. In general, oxygenates can be produced from either fossil fuels or biomass. Methanol (MeOH), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) are examples of oxygenate compounds derived from fossil fuels, while ethanol (EtOH), ethyl tertiary butyl ether (ETBE), tertiary amyl ethyl ether

(TAEE) are from biomass. Table 2.1 shows physical properties of various oxygenates. Initially, oxygenates were added to hydrocarbon fractions that were slightly-modified unleaded gasoline fraction, and these were commonly known as “oxygenated” gasolines. In 1995, the hydrocarbon fraction was significantly modified, and these gasolines are called “reformulated gasolines” (RFGs). The change to reformulated gasoline requires oxygenates to improve octane rating. It is noted that the hydrocarbon composition of RFG must be significantly more modified than the existing oxygenated gasolines to reduce degree of unsaturation, volatility, benzene, and the reactivity of emissions. Oxygenates are beneficial to gasoline function in two ways. Firstly, they have high blending octane, and so can replace high octane aromatic compounds in the fuel. These aromatics are responsible for disproportionate amounts of CO and HC exhaust emissions. This is called the “aromatic substitution effect”.

Table 2.1 Physical properties of oxygenates

	Motor Octane Number	Research Octane Number	Reid Vapour Pressure (kPa)	Boiling Point (K)	Water Solubility (mg/l)
<i>Ethers</i>					
MTBE	101	117	55	328	43,000 - 54,300
ETBE	101	118	28	345	26,000
TAME	98	112	10	359	20,000
TAEE	95	105	0.15	374	4,000
<i>Alcohols</i>					
MeOH	91	123	32.1	338	Miscible
EtOH	96	123	124.1	351	Miscible
TBA	89	106	48.1	356	Miscible
<i>Gasoline</i>	82-88	92-98	70-100	299-503	N/A

* From The Handbook of MTBE and Other Gasoline Oxygenates

Secondly, Oxygenates cause engines without sophisticated engine management systems to move to the lean side of stoichiometry, thus reducing emission of CO (2% oxygen can reduce CO by 16%) and HC (2% oxygen can reduce HC by 10%). However, on vehicles with engine management systems, the fuel volume will be increased to bring the stoichiometry back to the preferred optimum setting. Oxygen in the fuel cannot contribute energy and consequently, the fuel has less energy content. For the same efficiency and power output, more fuel has to be burnt, and the slight improvements in combustion efficiency that oxygenates provide on some engines usually do not completely compensate for the oxygen.

2.1.1 TAEE

Tertiary-amyl ethyl ether (TAEE) is a higher analog to TAME, produced by reaction of a branched C₅ olefin called tertiary-amylene with ethanol. TAEE has a higher boiling point, a somewhat lower octane value than MTBE, and is fully compatible with gasoline hydrocarbon blends. Typical properties of TAEE are listed in Table 2.2 and its molecular structure is given below.

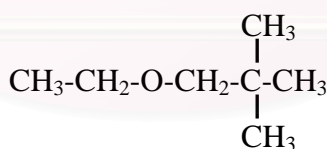


Fig 2.1 Molecular structure of TAEE

Several reports in the production of TAEE have focused on the method in liquid phase synthesis from EtOH and isoamylene (IA). IA can be produced from dehydration of amyl alcohols which are included in fusel oil. Fusel oil is a by-product of an alcoholic fermentation process and also obtained during distillation of crude ethanol. However, an alternative reactant instead of IA is tert-amyl alcohol (TAA), one of the major products of fusel oil obtained from biomass fermentation (Aiouache and Goto, 2003a). Hence, the synthesized TAEE is absolutely produced from

renewable resources. There are two routes to produce TAE. First, in the indirect method, TAA is dehydrated to IA and then IA reacts with EtOH to produce TAE. Secondly, in the direct method, TAA and EtOH react at the same time in one reactor. The simultaneous etherification and hydration of TAA are presented by the following stoichiometric equations

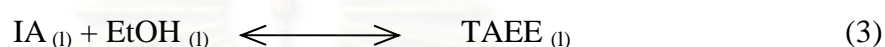


Table 2.2 Physical, chemical and thermal properties of TAE

Molecular formula	C ₇ H ₁₆ O
Molecular weight	116
Elemental analysis	
Carbon content, wt%	72.4
Hydrogen content, wt%	13.8
Oxygen content, wt%	13.8
C/H ratio	4.5
Specific gravity, g/cm ³	0.70
Reid vapor pressure at 25 °C, mmHg	1.2
Boiling point at 760 mmHg, °C	101
Solubility of TAE in water at 20 °C, wt%	0.4
Blending octane number ^a	
RON	105
MON	95
(RON+MON)/2	100

^a Obtained by adding 10 vol% TAE to a base gasoline having RON clear = 94.3 and MON clear = 84.3

2.2 Reactive distillation

In the chemical process industries, chemical reaction and the purification of the desired products by distillation are usually carried out sequentially. In many cases, the performance of this conventional chemical process structure can be significantly improved by integrating both reaction and distillation in a single multifunctional process unit. This integration concept leads to a reactive distillation (RD). It is noted that when heterogeneous catalysis is applied, the term 'catalytic distillation' is often used. Reactive distillation (RD) is a key opportunity for improving the structure of a process. The combination of distillation and reaction is possible, of course, only if the conditions of both operations can be combined. This means that the reactions have to show data for reasonable conversions at pressure and temperature levels that are compatible with distillation conditions. The type of catalysis is also important. Homogeneous catalysis is possible in most cases but needs a separation step to recycle the catalyst. This can be avoided in heterogeneous catalysis, but special constructions are necessary to fix the catalyst in the reaction zone.

The integration of reaction and separation results in many advantages. For examples, chemical equilibrium limitations can be overcome, higher selectivity can be achieved, the heat of reaction can be used in situ for distillation, auxiliary solvents can be avoided, and azeotropic or closely boiling mixtures can be more easily separated than in ordinary distillation. Increased process efficiency and reduction of investment and operational costs are the direct results of this approach. Some of these advantages are realized by using reaction to improve separation; others are realized by using separation to improve reaction. Most important industrial applications of RD are in the field of esterification processes such as the famous Eastman Chemical process for the synthesis of methyl acetate (Agreda *et al.*, 1990). This process combines reactive and non-reactive sections in a single hybrid RD column and thereby replaces a complex conventional flowsheet with 11 process units. With this RD technology investment and energy costs were reduced by factor five. Another success story of RD was started in the 1980s by using this technology for the preparation of the ethers

MTBE, TAME, and ETBE, which are produced in large amounts as fuel components because of their excellent antiknock properties.

2.2.1 Reactive distillation configurations

A conventional configuration for a process involving a catalytic chemical reaction with a solid catalyst involves two steps of chemical reaction and subsequent separation. In the chemical reaction step, reactants are brought into contact with solid catalysts at appropriate process conditions in one or more reactors. The stream leaving the reactor section then goes to one or more separation steps where unconverted reactants are separated from the products of the reaction and the inerts. The unconverted reactants, in some cases, may be recycled to the reaction section. When a substantial amount of inerts are present in the system, at least two separation units for separation of high purity product and for separation of the unconverted reactants from the inerts are required. The separation process typically chosen is distillation.

A conventional process configuration is shown in Figure 2.2. The separation process is distillation. In the case, a reaction product is less volatile than reactants and inert. The flow diagram of the application of reactive distillation to this process is shown in Figure 2.3. The middle section of the column is the reactive distillation section. For a non-azeotropic chemical system, separation of the inerts takes place in the rectification section of the column and the purification of the product takes place in the stripping section.

In the other configuration, the reaction and distillation proceed in alternating steps. Here, the reactive distillation section of a column contains both the catalyst contact device and the distillation device. A reaction occurs in the catalyst contact device and then the reacting phase passes to the distillation device for vapor/liquid contact and separation. These two steps occur alternately. By making the steps of infinitely small size, this configuration becomes equivalent to the first one. In both configurations, a rectification section may be located above the reactive distillation

section of the column and a stripping section may be located below it, depending upon purity specifications.

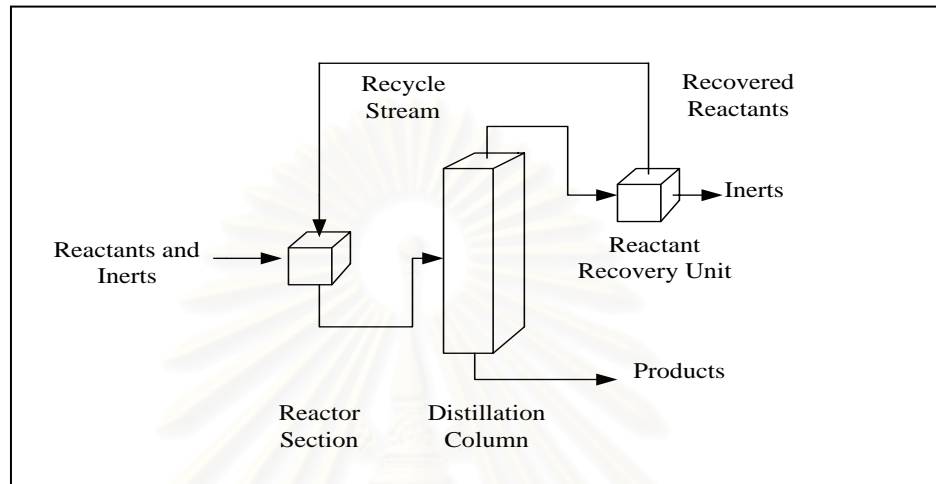


Figure 2.2 Conventional process involving reaction followed by separation

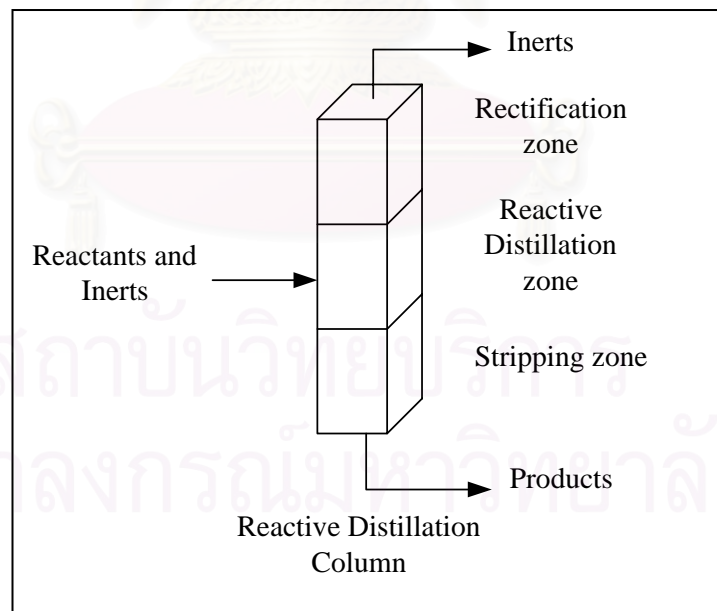


Figure 2.3 Reactive distillation applied to the same process

2.2.2 Advantages of reactive distillation

Application of RD to a catalytic chemical reaction using solid catalysts leads to a substantial cost savings compared to a conventional process. These savings result from:

- An important benefit of RD technology is a reduction in capital investment, because two process steps can be carried out in the same device. Such integration leads to lower costs in pumps, piping and instrumentation.
- If RD is applied to exothermic reaction, the reaction heat can be used for vaporization of liquid. This leads to savings of energy costs by the reduction of reboiler duties. Endothermic reactions are not suitable for the RD-technology because of vapor condensation. Although endothermic reactions require more reboiler duty and therefore exhibit no large energy savings, there are no restrictions to the application of RD.
- The maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture, so that the danger of hot spot formation on the catalyst is reduced significantly. A simple and reliable temperature control can be achieved.
- Product selectivity can be improved due to a fast removal of reactants or products from the reaction zone. By this, the probability of consecutive reactions, which may occur in the sequential operation mode, is lowered.
- If the reaction zone in the RD column is placed above the feed point, poisoning of the catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems.

2.3 Membrane definition

A membrane is a permeable or semi-permeable barrier at the boundary of every cell, often in the form of a thin film deposited on a support material as shown in

Figure 2.4. It can be made from a variety of materials ranging from inorganic solids to different types of polymers. The main function of membrane is to control the exchange of mass between two adjacent fluid phases as shown schematically in Figure 2.5. For this function, the membrane must be able to act as a barrier, which separates different species either by sieving or by controlling their relative rate of transport through itself. The separation

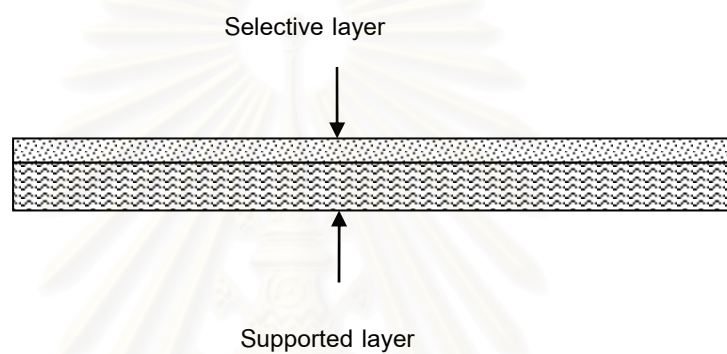


Figure 2.4 Cross-section of membrane

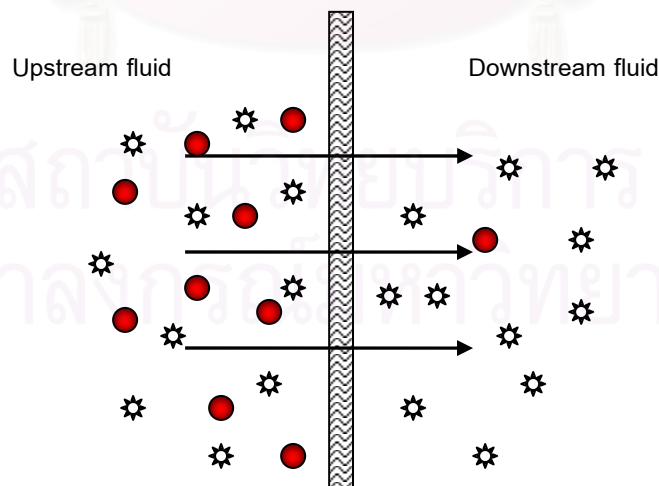


Figure 2.5 Basic membrane separation principle

by membrane results in a fluid stream (defined as the retentate), which is depleted from some of its original components, and another fluid stream (defined as the permeate), which is concentrated in these components. Exchange between the two bulk phases across the membrane is caused from the presence of a driving force, which is typically associated with a gradient of pressure, concentration, temperature and electrical potential, etc. The types of membranes used for separation can be classified using different criteria such as by membrane structure (porous and non-porous) and by type of material used to prepare the membrane (organic, polymeric, inorganic, metal, etc.). The ability of a membrane to affect separation of mixtures is determined by two parameters, its permeability, defined as the flux, and selectivity, defined as the ratio of the individual permeabilities for the two species.

2.4 Pervaporation process

2.4.1 Definition of pervaporation process

Pervaporation is a membrane separation process for separation of liquid mixtures. In the process, a liquid feed mixture is in contact with one side of a permeate selective dense membrane in a membrane module. Partial vapor pressure of each component near the membrane surface is assumed at its saturation vapor pressure. A gradient in vapor pressure between the feed and the permeate sides of the membrane is a driving force for the permeation and it is maintained at high value by reducing the permeate side pressure. The permeate leaves the membrane as a vapor and is usually condensed and removed from the system as liquid. Heat necessary for evaporation of the permeate stream has to be transported through the membrane, and this transport of energy is coupled to the transport of matter. The evaporation enthalpy is taken from the sensible heat of the liquid feed mixture, leading to a reduction in the liquid mixture temperature. It makes pervaporation unique compared to all other transport processes involving in the membrane processes. A schematic of the pervaporation process is shown in Figure 2.6.

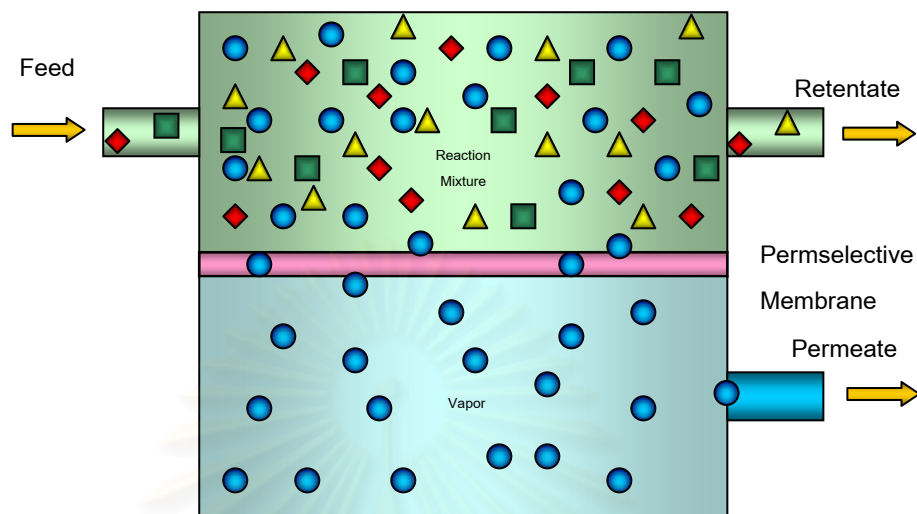


Figure 2.6 Schematic diagram of a pervaporation process

2.4.2 Transport in membrane

Transport of a component through a membrane in the pervaporation process can be described by the solution-diffusion model (Feng *et al.*, 1997). The mechanism consists of three consecutive steps (see Figure 2.7) as follows:

- 1) sorption of reagent from the liquid feed to the membrane
- 2) diffusion of reagent in the membrane and
- 3) evaporation or desorption of reagent in vapor phase from the downstream side of the membrane.

It is assumed that a component of the feed having a high affinity to the membrane is easily and preferentially adsorbed and dissolved in the membrane substance. Swelling effect is a major problem for pervaporation membrane compared to membranes for other membrane processes. This is because the membrane contacts with a high density fluid at high temperature.

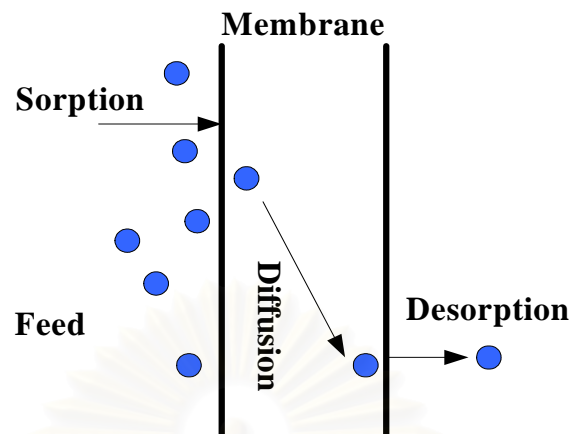


Figure 2.7 Schematic of pervaporation transport by solution-diffusion mechanism

Following a concentration gradient, the components migrate through the membrane by a diffusion process and are desorbed at the downstream side of the membrane into a vapor phase. In the pervaporation, the components passing through the membrane are sorbed out of a liquid phase but desorbed into a vapor phase.

Substances with lower or no solubility in the membrane material cannot be dissolved or slightly dissolved and thus the transport rate is low. As the diffusion coefficients of small molecules in a polymer matrix do not differ significantly, the separation characteristics of the membrane is primarily governed by the different solubilities of the components in the membrane material and to a lesser extent by their diffusion rates.

The transport of a single component through a nonporous homogeneous membrane has been relatively well described. The concentration dependence of diffusivity is often expressed by exponential or linear forms. Assuming thermodynamic equilibrium exists at both membrane interfaces, the steady-state flux equation can be readily derived on the basis of Fick's equation for one-dimensional diffusion normal to the membrane surface. For binary mixtures, the mass transport is complicated by the permeant-permeant and permeant-membrane interactions, and no overall explaining theory exists.

It is noted that using the same approach as in single-component pervaporation, the solution-diffusion model has been modified by introducing different empirical parameters, most of which arise from the concentration dependence of diffusivities. Assuming that the diffusivities of individual permeants are proportional to the total concentration of permeants in the membrane. However, this model does not apply to non-ideal cases such as the pervaporation of alcohol/water mixtures. The concentration dependence of diffusivity is due at least in part to the plasticizing action of the permeants on the polymer, while different components may have different plasticizing effects. Hence, it is generally not appropriate to assume the contribution of permeants to their diffusivities to be linearly additive.

Further, as commonly observed, diffusivities are very sensitive to permeant concentration, especially when the membrane has a strong affinity to the permeating species. A simple linear relationship is often inadequate to describe the concentration dependence of diffusivity.

2.4.3 Characterization of membranes

2.4.3.1 Permeability and permeation rate

The phase change of the permeating species is one of the most distinguishing features of pervaporation. Based on the solution-diffusion model, the flux equation can be written as (Wijmans and Baker, 1995):

$$J_i = \frac{P_i}{l} \left(c_{io} - \frac{p_{il}}{H_i} \right) \quad (2-1)$$

where c_{io} is the concentration of components i at the membrane surface and p_{il} is the partial vapor pressure of the permeant at the permeate side and l is the membrane thickness. P_i is the permeability coefficient of the membrane with respect to the

driving force expressed in terms of partial vapor pressure and is related to the solubility coefficient (S) and diffusivity coefficient (D).

In the pervaporation process, when the permeate pressure (p_{il}) is kept at low value, the Eq. (2-1) can be expressed as:

$$J_i = \frac{P_i}{l} c_{i0} \quad (2-2)$$

and the permeation rate can be expressed as

$$Q_i = P_i A c_i \quad (2-3)$$

where Q_i and c_i are the permeate rate and the concentration of component i , respectively. A is effective membrane surfaces.

The permeability in Eqs. (2-1) to (2-3) are defined as:

$$P_i = D_i S_i \quad (2-4)$$

where D and S are normally dependent on temperature and the temperature dependence can be expressed as Eqs. (2-5) and (2-6), respectively.

$$D_i = D_{i,0} \exp\left(-\frac{E_{aD}}{R_g T}\right) \quad (2-5)$$

$$S_i = S_{i,0} \exp\left(-\frac{E_{aS}}{R_g T}\right) \quad (2-6)$$

Thus, the permeability can be written as the following equation.

$$P_i = P_{i,0} \exp\left(-\frac{E_a}{R_g T}\right) \quad (2-7)$$

2.4.3.2 Membrane selectivity

Membrane selectivity of component i is defined as the ratio of the permeability of a desired component to be removed to that of the component i as follow:

$$\alpha_i = \frac{P_d}{P_i} \quad (2-8)$$

where α_i is the separation factor, P_d is the permeability of the desired component to be removed and P_i is the permeability of the component i .

2.4.3.4 Pervaporation process configurations

Transport through pervaporation membrane is produced by maintaining a vapor pressure gradient across the membrane. Figure 2.8 shows three potential ways to achieve the required vapor pressure gradient.

- 1) Vacuum driven pervaporation: This method is applicable when the volume of permeating vapour is relatively small. Although it is not a practical choice due to high energy consumption, this method is usually employed for small-scale operation in laboratory.
- 2) Temperature gradient driven pervaporation: The partial vacuum can be created by condensing the vapor into liquid. This method is preferable for commercial operations, because the cost for providing the required cooling is much less than the cost of a vacuum pump and the process is operationally reliable.
- 3) Carrier gas pervaporation: The permeate side of membrane is swept with an inert gas in which the partial vapour pressure of the critical component

is kept sufficiently lower than that on the feed side. This method is attractive if the permeate has no value and can be discarded without condensation.

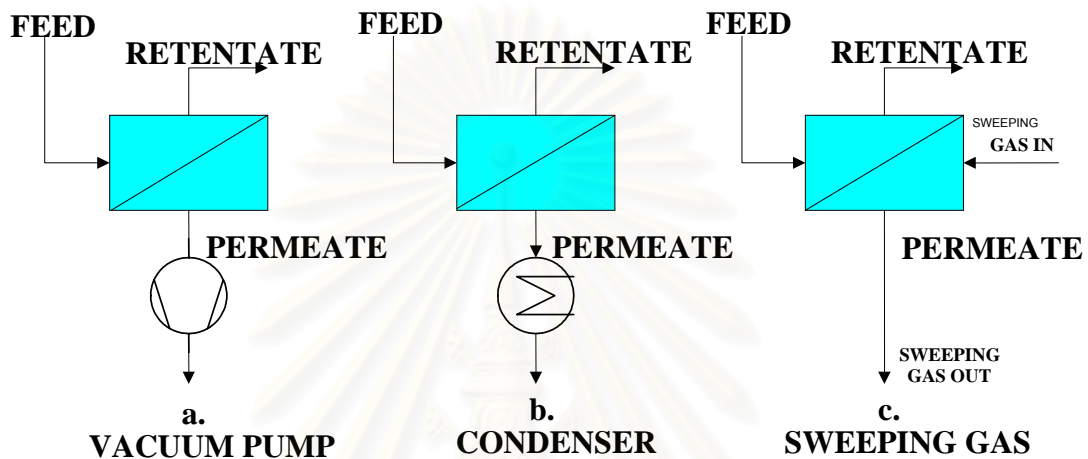


Figure 2.8 Modes of operation at the permeate side

2.4.4 Applications of Pervaporation

The applications of pervaporation process can be defined according to two different membrane classes as follows.

2.4.4.1 Organophilic membrane

Organophilic membranes are mostly applied for removal of volatile organic components (VOC's) from gas stream like waste air or nitrogen. Main applications are treatment of streams originating from evaporation of solvents in coating processes in film and tape production, from purge of products like polymers, from breathing of solvent storage tanks and especially from loading and unloading of gasoline tanks in tank farms.

2.4.4.2 *Hydrophilic membrane*

The application of hydrophilic membrane pervaporation can be separated in three purposes as:

1. Solvent dehydration: such as the dehydration of alcohols.
2. Removal of water from reaction mixtures.
3. Organic-organic separation: such as removal of methyl alcohol from trimethyl borate

2.5 Aspen Plus

Aspen Plus is a component of the Aspen Engineering Suite. It is an integrated set of products designed specifically to promote best engineering practices and to optimize and automate the entire innovation and engineering workflow process throughout the plant and across the enterprise. It automatically integrates process models with engineering knowledge databases, investment analyses, production optimization and numerous other business processes. Aspen Plus contains data, properties, unit operation models, built-in defaults, reports and other features. Its capabilities develop for specific industrial applications, such as petroleum simulation.

Aspen Plus is easy to use, powerful, flexible, process engineering tool for the design and steady-state simulation and optimization of process plants. Process simulation with Aspen Plus can predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetic. Given reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Plus equipment models, actual plant behavior can be simulated. Aspen Plus can help to design better plants and to increase profitability in existing plants.

2.5.1 Features of Aspen Plus

- Utilize the latest software and engineering technology to maximize engineering productivity through its Microsoft Windows graphical interface and its interactive client-server simulation architecture.
- Contain the engineering power needed to accurately model the wide scope of real-world applications, ranging from petroleum refining to non-ideal chemical systems containing electrolytes and solids.
- Support scalable workflow based upon complexity of the model, from a simple, single user, process unit flowsheet to a large, multi-engineer developed, multi-engineer maintained, plant-wide flowsheet.
- Contain multiple solution techniques, including sequential modular, equation-oriented or a mixture of both, and allow as quick as possible solution times regardless of the application.

2.5.2 Benefits of Aspen Plus

- Proven track record of providing substantial economic benefits throughout the manufacturing life cycle of a process, from R&D through engineering and into production.
- Allow users to leverage and combine the power of sequential modular and equation-oriented techniques in a single product, potentially reducing computation times by an order of magnitude while at the same increasing the functionality and suability of the process model.
- Compete effectively in an exacting environment. To remain competitive in today's process industries it is necessary to do more, often with smaller staffs and more complex process.

CHAPTER 3

LITERATURE REVIEWS

In this chapter, reviews on the studies related to the synthesis of ethanol-based oxygenates with a close attention to a bio-ethanol are presented and discussed. The applications of various hybrid processes for octane enhancing ether production are also given. The hybrid processes include a reactive distillation and a pervaporation integrated with distillations and reactive distillations.

3.1 Ethanol-based oxygenate production

The phasing-out of MTBE and predicted lower prices of ethanol will likely lead to production of ethanol-based ethers as major gasoline oxygenates. Among the various oxygenates, ethanol and TAEE are expected to be widespread used. The fermented ethanols are currently produced by the conventional fermentation process of glucose contained in carbon-hydrated feedstock such as corn and beet. The potential rapid growth of the process from biomass during this decade would come from the enzymatic hydrolysis of cellulose to sugars ready for fermentation. Then, actual ethanol costs from cellulose are expected to be reduced by 1/3 to 1/4 times. The worldwide potential of bioethanol is estimated to be around 2 millions ton per year by 2020. The 25 percent of bioethanol production would be originated from the mature sugar and starch crops process and the remaining ratio from lingo-cellulosic biomass process (Evaluation of biomass-to-ethanol fuel potential in California, 1999).

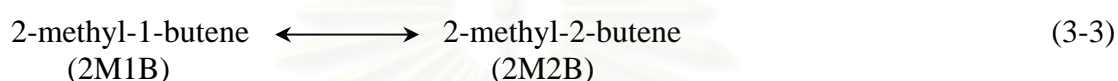
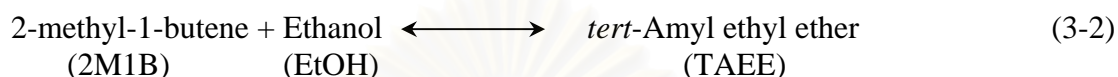
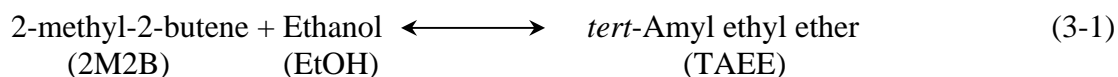
Despite the fact that TAEE has low oxygen content, it presents a real possibility to contribute to the oxygenate supply after MTBE phase-out. Indeed, it may be partially or totally produced from renewable resources.

3.1.1 TAEЕ synthesis from isoamylenes (IA)

The large availability of C₅ olefins in FCC cuts (10-15 wt%), readily used for *tert*-amyl methyl ether (TAME) production, can be advantageous for TAEЕ synthesis. TAEЕ might be preferred to other alcohols for hot places because of its lower bRvp. Despite the growing interest in higher ethanol-based ethers, few studies have been reported regarding the formation of TAEЕ. Kraus group from Helsinki University of Technology (Rihko *et al.*, 1994) largely contributed in TAEЕ synthesis. The reactivity of IA with ethanol in ion-exchange resin was reported by Rihko *et al.* (1993). A side reaction of isomerization was observed for 2M1B compared with less reactive isomer 2M2B. The kinetic mechanism presented by Linnekoski *et al.* (1997) followed the classical L-H model with separate surface acid sites for each reaction component. The classical equilibrium was studied by Kichaiya *et al.* (1995) and Rihko *et al.* (1994). The obtained chemical equilibrium constants were in good agreements with thermodynamic values. In aqueous ethanol which is an azeotropic mixture of water and ethanol, Jayadeokar *et al.* (1992) and Linnekoski *et al.* (1998) noticed that the hydration of IA to *tert*-amyl alcohol is a major side reaction. Compared to pure ethanol, a decrease of 50% in IA conversion was observed.

Besides fuel cracking, IA may be obtained from several other biomass which are considered as renewable resources derived from agriculture products such as sugar cane, corn and potato. IA can serve as heavy tertiary olefins for many applications. A particular attention towards isoamylenes (IA) for fuels oxygenates production has been observed as a consequence of the severe legislation in many countries under consideration on MTBE phasing-out (Linnekoski *et al.*, 1997). Generally, IA can be produced from the dehydration of amyl alcohols (C₅H₁₁OH) such as 2-methyl-1-butanol (2M1BOH), 2-methyl-2-butanol (2M2BOH) and *tert*-amyl alcohol (TAA), which are largely available in fusel oil. Fusel oil is a by-product of the alcoholic fermentation process, and is obtained during distillation of crude ethanol. Fusel oil dehydration in vapor phase has been studied by using gamma alumina as a catalyst. The study was oriented to maximum synthesis of 3M1B. The yield of 77% of 3M1B was obtained from initial 2M1BOH:3M1BOH ratio of 1:4 in the fusel oil.

The main reactions of TAEE synthesis from IA (2M1B and 2M2B) are represented by the following equations:



3.1.2 TAEE synthesis from *tert*-amyl alcohol (TAA)

Tert-amyl alcohol (TAA), one of the major products of fusel oil obtained from biomass fermentation, can be used to synthesize the ether product. Aiouache and Goto (2003a) studied the use of TAA as an alternative reactant instead of IA to produce the TAEE. With this route, the direct etherification of TAA and ethanol, the dehydration of TAA to IA, and the reaction of IA and EtOH are simultaneously occurred during the TAEE synthesis. The reaction involved can be represented by the following equations:



However, this method has been studied only in a few papers. Aiouache and Goto (2003a) studied the kinetic model of etherification of TAE from TAA and ethanol which was catalyzed by Amberlyst 15 with focus on a sorption effect. The results showed that the L-H model is suitable for describing the kinetic of the etherification. Furthermore, they had further studied the effect of feed location and reflux ratio on the performance of the reactive distillation inserted with a zeolite NaA membrane (Aiouache and Goto, 2003b).

3.2 Hybrid processes of reaction and separation

Hybrid processes applied to in-situ liquid phase reaction and separation processes have been recently recognized as an emerging new technology with a rapid growth. Among numerous potential combinations, a reactive distillation (RD) and a pervaporative membrane reactor (PVMR) have been the most cited in the recent advances of industrial applications. The merit of this popularity is attributed to their contribution to better energy and material utilization, and lower space-volume ratio. This can lead to more efficient chemical production and less pollution. The integration of reaction and separation process in a single unit improves the conversion of chemical reactants and the selectivity of the desired products, by shifting the chemical equilibrium boundaries, accelerating reactions, reducing by-products, and overcoming azeotropic limitations. Despite the rich literature in scientific papers and technical patents, a few hybrid processes of reaction and separation reach the maturity level to be industrialized. The existing industrial application using the concept of hybrid processes is found in the production of methyl acetate and methyl *tert*-butyl ether through a reactive distillation (Taylor and Krishna, 2000) and in the ETBE purification through a hybrid distillation-pervaporation unit. An overview of the hybrid processes, i.e., reactive distillation and pervaporation combined with distillation and reactive distillation, is presented in the next subsections.

3.2.1 Application of reactive distillation for octane enhancing ether production

The design and operation issues for reactive distillation systems in which the catalyst section is located inside the column, are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in-situ separation function within the reaction zone leads to complex interactions between vapor-liquid equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes), and chemical kinetics. Successful commercialization of RD technology requires careful attention to the modeling aspects, including column dynamics, even at the conceptual design stage (Doherty and Buzad, 1992).

The first simple reactive distillation was developed in 1921 for the production of methyl acetate. Presently, the synthesis of methyl acetate in a reactive distillation column is often used to study basic phenomena of the reactive distillation (Bessling *et al.*, 1998). It is noted that in conventional methyl acetate processes, liquid methanol reacts with liquid acetic acid in the presence of an acidic catalyst to form methyl acetate and water.

Reactive distillations can be further applied to other reactions such as etherification and esterification. The esterification of palmitic acid with isobutyl alcohol was studied by Goto *et al.* (1991). They found that the use of a solid ion-exchange resin as a catalyst has some advantages over a homogeneous catalyst, sulfuric acid (Goto *et al.*, 1992). Other esterifications have also been studied, such as the esterification of benzyl alcohol with acetic acid on Amberlyst-15 and the esterification of acetic acid with butyl alcohol to produce butyl acetate by using a sulfuric acid as a catalyst.

In recent years, reactive distillation is increasingly realized as a process for liquid phase synthesis of octane-enhancing ethers. Methyl tertiary butyl ether

(MTBE), the most widely used octane booster for reformulated gasoline, is produced in liquid phase over sulfuric acid resins (e.g., Amberlyst-15) at temperatures in the range of 323-343 K, pressure between 1.0 and 1.5 MPa, and methanol/isobutene (MeOH/IB) molar ratio higher than 1:1. Di-isobutenes (2,4,4 trimethyl-1-and-2-pentenes), *tert*-butyl alcohol, and dimethyl ether are the main by-products. The reaction is exothermic ($\Delta H = -37$ kJ/mol), and, therefore, careful control of temperature is required in order to avoid local overheating and releasing of sulfonic group and sulfuric acid from the catalyst, causing a loss of activity and giving rise to corrosion problems. The MeOH/IB molar ratios above stoichiometry were employed in order to ensure complete conversion of the isobutene (Collignon *et al.*, 1999).

Apart from the production of MTBE, the reactive distillation is implemented for the production of other octane enhancing compounds like ethyl tertiary butyl ether (ETBE). ETBE is an important oxygenate with better blending properties than methyl tert-butyl ether (MTBE). Various catalysts such as Amberlyst-15 (Quitain *et al.*, 1999a), Amberlyst 35, ZSM-5 and a supported fluorocarbonsulfonic acid polymer catalyst, heteropoly acid (Yin *et al.*, 1995), were investigated for the synthesis of ETBE in reactive distillations. A zeolitic catalyst is more attractive than resin-based catalysts in terms of higher thermal stability and no acid fume emission (Audshoorn *et al.*, 1999). However, the major side reaction of this system is the dehydration of TBA to IB (Yin *et al.*, 1995). It was shown recently that beta zeolite catalyst provides superior selectivity compared to the commercial Amberlyst-15 (Assabumrungrat *et al.*, 2002).

Quitain *et al.* (1999a) investigated the synthesis of ethyl tert-butyl ether (ETBE) from bioethanol and tert-butyl alcohol (TBA) using Amberlyst 15 in the pellet form as a catalyst in reactive distillation. The results showed that the product ETBE at about 60 mol% was obtained in the distillate and almost pure water in the residue (Quitain *et al.*, 1999a). The same authors also simulated an industrial scale process for the synthesis of ETBE by using ASPEN PLUS, a sequential modular

simulation software package. The overall conversion of tert-butyl alcohol (TBA) and the overall ETBE selectivity are 98.9 and 99.9 % respectively (Quitain *et al.*, 1999b).

Recently, there is a pending legislation on the use of methyl *tert*-butyl ether (MTBE) in a number of states in the US due to its tendency to pollute underground water, and ETBE is predicted to face the same problem of MTBE as it has a similar molecule structure. *Tert*-amyl ethyl ether (TAEE) can be a potential alternative as it has been found to outperform MTBE and ETBE. TAEE has lower bRvp (0.21 psi) than ETBE (4 psi), which allows TAEE to be used successfully in obtaining gasoline with less bRvp than 7.8 psi as required in some hot places during summer (Mohammud and Halim, 2004). Although TAEE has better properties than other oxygenates, there are limited studies in the synthesis of TAEE. Aiouache and Goto (2003b) studied the etherification of TAEE from ethanol and TAA in a reactive distillation column inserted by a zeolite NaA membrane tube. Experimental tests were carried out in both of a pervaporation module and a reactive distillation column. Under suitable conditions, the pervaporation tests have shown higher than 99.9 % H₂O mole fraction in the permeate. The experimental study at standard conditions has shown a gain of 10% TAEE yield when the zeolite membrane tube was inserted inside the distillation column.

Apart from a large number of experimental works on reactive distillation with various reaction systems as mentioned above, modeling and simulation of reactive distillations are a topic of interest over the past years. Many studies have been carried out using a commercial simulation package, e.g., Aspen Plus, Pro/II, HYSYS and SpeedUp. Venkataraman *et al.* (1990) described an inside-out algorithm for calculation in the RADFRAC module of Aspen Plus program. The inside-out method involves the introduction of new parameters into the model equations and these parameters are used as primary iteration variables. Four case studies reported in their work demonstrate that the RADFRAC can be applied to a wide variety of reactive separation processes with either equilibrium reactions or kinetic-limited reactions. The RADFRAC module has been used to simulate the behavior of a reactive

distillation by many authors. For examples, Quitain *et al.* (1999a) simulated a small-scale reactive distillation column in the ETBE production from bioethanol. Later, Quitian *et al.* (1999b) used RADFRAC module to model the reactive distillation in the industrial-scale production of the same process. In addition, Hanika *et al.* (1998) carried out a simulation work on a butylacetate synthesis via catalytic distillation. Furthermore, Smejkal *et al.*, (2001) studied the simulation of 2 – Methylpropylacetate synthesis in a system of equilibrium reactor and reactive distillation column. It is noted that all of these studies compared the simulation results computed using Aspen Plus against experimental results and good agreement between experiment and the simulation results was observed.

3.2.2 Hybrid process of distillation-pervaporation

Pervaporation (PV) is a potential energy saving and efficient separation technique, especially for separation of azeotrope that is difficult to be separated by traditional distillation. In recent years, pervaporation has established itself as one of the most promising membrane technologies. Pervaporation offers potential solutions in a wide range of applications from the well-established dehydration of organic compounds to the recovery of organic compounds from water and the separation of organic mixtures. Within these applications, PV as a single process has often to compete with conventional processes like distillation, liquid-liquid extraction, adsorption, and stripping. Generally, in many cases PV alone may not supply products suitable for further processing or waste disposal in accordance with environmental standards (Frank *et al.* 1999). Thus, hybrid processes are regarded as one means of overcoming these limitations. The pervaporation-distillation hybrid process was the first pervaporation-based hybrid process as an attractive alternative among several separation processes. The use of a pervaporation-distillation hybrid process might seem advantageous. This could be accomplished in one of three ways:

- The PV process is integrated into the distillation process to reduce the number of trays by processing a side stream of the distillation column.

- The PV process is in front of the distillation process to split the azeotropes before distillation.
- The PV process is used as a polishing step of either the top or bottom product of the distillation column. This can be combined with splitting the azeotrope.

Uwe *et al.* (1998) designed and optimized the combination of pervaporation-distillation processes for the production of MTBE by using ASPEN PLUS with a compatible FORTRAN routine. The design and optimization was compared with the Huels process and economical benefits can be derived from both pervaporation at the side draw in the rectifying section and vapor permeation at a side draw in the stripping section.

Yin *et al.* (2002) designed and simulated a special hybrid process of distillation with side-connected pervaporation for separation of methanol, MTBE and C₄ mixture. The qualified product of C₄ and MTBE with methanol mole fraction less than 1×10^{-4} can be obtained only by this hybrid separating process, and the pervaporation permeate stream with methanol concentration greater than 0.92 could be recycled to reactor. The two important factors to achieve satisfactory separation are the capacity of pervaporation with distillation and the reflux ratio of distillation tower.

3.2.3 Hybrid process of Reactive distillation (RD)-pervaporation

Information on RD-pervaporation unit is unlikely inexistent in open literature. Hybrid process of a pervaporation and RD column would increase the reaction rate by lowering water inhibition influence, circumvent boundary azeotropic conditions between water and reaction mixture, and reduce the consumption energy.

Yang *et al.* (1997) carried out the etherification of TBA with MeOH and EtOH in combined process of RD with pervaporation in order to separate water from reaction mixture. The pervaporation cell unit was added to the bottom part of the

column to remove water. Higher reaction rates were observed, when the mole fraction of water in the bottom was lowered in significant amount during the pervaporation process.

Besides the production of ether, the esterification process is also interesting. Sven *et al.* (2004) used the hybrid processes by combining a reactive distillation and pervaporation for the production of *n*-butyl acetate by tranesterification of methyl acetate with *n*-butanol. The reaction catalyzed by a strongly acidic ion-exchange resin (Amberlyst 15) was investigated to find the kinetic parameters for a pseudohomogeneous reaction model. The experimental results were presented in comparison with simulation results. It has been shown that the combination of reactive distillation with pervaporation is favorable since conversions close to 100% can be obtained with a reasonable size of the reactive section.



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CHAPTER 4

SIMULATION OF TAAE PRODUCTION IN CONVENTIONAL REACTIVE DISTILLATION

In this chapter, the synthesis of TAAE from TAA and ethanol in reactive distillation was investigated. Emphasis is placed on the determination of an appropriate configuration of the reactive distillation column for the TAAE production. In addition, an analysis of the effects of various key operating parameters is performed.

4.1 Reactive distillation model

Simulation of the synthesis of *tert*-amyl ethyl ether (TAAE) in a reactive distillation (RD) is carried out using the Aspen Plus simulation package. The RADFRAC model, which is a rigorous equilibrium-stage distillation model to describe a multistage vapor-liquid separation in the distillation column, is used in this study. The equilibrium stage model is often applied with great success for the simulation of distillation columns (Dirk-Faitakis and Chuang, 2003). Similar to the previous work (Assabumrungrat *et al.*, 2004), the property option set PSRK based on the predictive Soave-Redlich-Kwong equation of state is employed. This correlation has been widely used for the prediction of enthalpy and other thermodynamic properties. Interaction parameters for computing multi-component vapor-liquid and liquid-liquid equilibria are predicted using the UNIFAC activity coefficient model (Sneesby *et al.*, 1997).

A typical configuration of the RD column used in the simulation studies is shown in Fig. 4.1. The column contains a total of 14 stages counted down from the top. This includes a total condenser and a partial reboiler as respectively shown as

stages 1 and 14. The RD column is divided into three sections: rectifying, reaction and stripping sections. The chemical reactions are assumed to occur in the liquid phase in the reaction section represented by 4 reactive stages (stage 6-9). The feed is introduced at the top of the reaction section (stage 6). It is noted here that such a column configuration is determined as a preliminary simulation study; however, it can be adjusted to meet optimal performance of the RD column. Table 4.1 summarizes the column parameters and feed conditions under the standard operation. The mixed TAA-EtOH feed stream enters the RD column at 25°C. It should be reminded that two additional input parameters of the column configuration are needed to be specified for the simulation of the RADFRAC column. These can be chosen from the following parameters: heat duty at the reboiler (Q_r), condenser temperature (T_c), ratio of total distillate flow to feed (D/F) and reflux ratio (R). Here, the parameters, Q_r and R , are selected in the study as they can be practically manipulated in real operation.

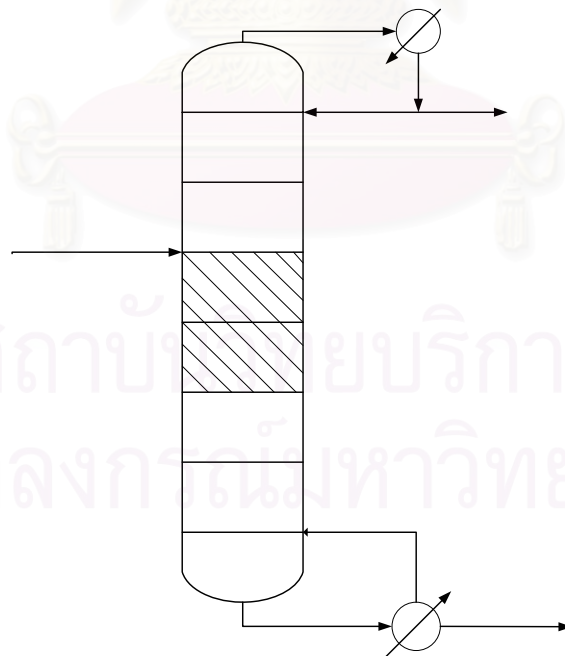


Fig. 4.1 The configuration of a reactive distillation column.

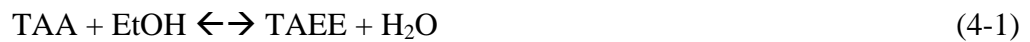
4.2 Kinetic model

In this work, a non-equilibrium kinetic model is used to describe the reactions occurring in the reaction stages. TAEE is produced by the direct etherification of TAA with EtOH in the liquid phase over Amberlyst 15, a commercial acid catalyst, and is inhibited by two undesired side reactions: the dehydration of TAA to IA and the etherification of the IA produced to TAEE. Although IA can be represented by two isomers: 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B), they are lumped together with the properties of the major isomer 2M2B (Rihko and Krause, 1993). The kinetic and thermodynamic studies have shown that the etherifications of EtOH with TAA and IA and the dehydration of TAA are reversible and equilibrium-limited. The etherifications in Eqs. (4-1) and (4-3) are exothermic while the dehydration in Eq. (4-2) is endothermic.

Table 4.1 Feed conditions and specification of reactive distillation column under the standard condition.

Feed conditions		Column specification	
Temperature [K]	298	Rectification stages	4
Flow rate [mol/s]	2.71×10^{-3}	Reaction stages	4
Mole fraction [-]		Stripping stages	4
1) EtOH	0.5	Total stages	14
2) TAA	0.5	Catalyst weight per stage [kg]	0.125
Pressure [kPa]	101.3	Pressure [kPa]	101.3
		Reflux ratio (R) [-]	2
		Reboiler duty (Q_r) [W]	52

The reaction scheme for the liquid phase synthesis of TAEE from TAA and EtOH taking place in the reaction section can be summarized as follows:



The kinetic models of the above reactions on Amberlyst 15 are taken from Aiouache and Goto (2003a). In their work, the rate equations expressed in activity form are based on the power law model of which the validity was verified with the experimental data. However, the expressions for the rate equations in mole fraction form are required in Aspen Plus. For this reason, the kinetic parameters for the liquid phase synthesis of TAE reported by Aiouache and Goto (2003a) are multiplied with the average activity coefficients of each component (see Appendix A for details). The new sets of the kinetic parameters and the equilibrium constants shown in Table 4.2 are derived from the Arrhenius and Van't Hoff plots for various temperatures. Therefore, the rate equations of the reactions (4-1) to (4-3) can be expressed in terms of mole fractions as follows.

$$r_{\text{EtOH}} = -m_r Q \left[k_1 \left(x_{\text{EtOH}} x_{\text{TAA}} - \frac{x_{\text{TAE}} x_{\text{H}_2\text{O}}}{K_{\text{eq1}}} \right) + k_3 \left(x_{\text{IA}} x_{\text{EtOH}} - \frac{x_{\text{TAE}}}{K_{\text{eq3}}} \right) \right] \quad (4-4)$$

$$r_{\text{TAA}} = -m_r Q \left[k_1 \left(x_{\text{EtOH}} x_{\text{TAA}} - \frac{x_{\text{TAE}} x_{\text{H}_2\text{O}}}{K_{\text{eq1}}} \right) + k_2 \left(x_{\text{TAA}} - \frac{x_{\text{IA}} x_{\text{H}_2\text{O}}}{K_{\text{eq2}}} \right) \right] \quad (4-5)$$

$$r_{\text{IA}} = r_{\text{EtOH}} - r_{\text{TAA}} \quad (4-6)$$

$$r_{\text{TAE}} = -r_{\text{EtOH}} \quad (4-7)$$

$$r_{\text{H}_2\text{O}} = -r_{\text{TAA}} \quad (4-8)$$

where Q is ion-exchange capacity of Amberlyst 15 ($Q = 4.9 \text{ mol-H}^+/\text{kg}$).

Table 4.2 Expressions of the parameters used in the kinetic model.

Parameters	Activation energy, E_a (kJ/mol)
$k_1 = \exp (15.189 - 6597.3/T)$	54.9
$k_2 = \exp (14.490 - 6372.9/T)$	53.0
$k_3 = \exp (22.540 - 9184.6/T)$	76.4
$K_{eq1} = \exp (-0.471 + 524/T)$	
$K_{eq2} = \exp (5.16 - 1824.3/T)$	
$K_{eq3} = \exp (-5.64 + 2349/T)$	

4.3 Model validation

In order to use the RADFRAC model from Aspen Plus for simulating a reactive distillation with confidence, the reliability of the model is tested by comparing the simulated results obtained on this study with the experimental data from Aiouache and Goto (2003b). With the same standard experimental conditions from Table 2 in their paper, results of the simulation run in comparison to the experimental data are shown in Table 4.3. It can be seen that the compositions in the distillate and the residue, calculated by Aspen Plus are in good agreement with the experimental data. The small difference may be due to the modified kinetic parameters that are based on the mole fraction rate expression

Table 4.3 Comparison of simulated results and experimental data from Aiouache and Goto (2003b).

Components	Distillate (mole fraction)		Residue (mole fraction)	
	experimental	simulation	experimental	simulation
TAAE	0.04	0.04	0.19	0.167
TAA	0.04	0.042	0.23	0.231
EtOH	0.14	0.103	0.31	0.345
IA	0.72	0.812	0	0
H ₂ O	0.04	0.051	0.28	0.282
T (K)	313.1	313.6	351.2	355.2

4.4 Results and Discussions

In this section, the results of reactive distillation (RD) for the production of TAAE are obtained at many conditions. First, the mole fraction and temperature profiles in the reactive distillation are simulated at standard condition and the column efficiency is considered in terms of conversion and selectivity. Second, the effect of design variables are studied to find the suitable column specification. Finally, the effects of operating variables on the performance of reactive distillation are discussed below.

4.4.1 Standard condition

The reactive distillation and kinetic model mentioned in the previous section are used in the simulation of the RD column. Under the standard conditions given in Table 4.1, the simulated results of mole fraction profiles of each component with the column stage number are shown in Fig. 4.2. It can be seen that 27.93 mol% of TAAE can be obtained in the liquid residue of the RD while the distillate comprises mostly IA (87.67 mol%) and a little amount of EtOH and H₂O. Fig. 4.2 also presents the

temperature profile inside the column. The temperature at the reboiler and the condenser are 353 and 309 K, respectively. It is noticed that the temperature profile is rather smooth in the reaction section due to a mild reaction heat released.

To operate the RD column efficiently, it is important to convert TAA into the desired product (TAEE) and to obtain TAEE in the liquid residue as high as possible. Thus, the conversion of TAA and the selectivity of TAEE defined below are considered to compare the performance of the reactive distillation.

$$\text{Conversion of TAA} = \frac{\text{difference in molar flowrate of inlet and outlet of TAA}}{\text{feed molar flowrate of TAA}} \times 100\% \quad (4-9)$$

$$\text{Selectivity of TAEE} = \frac{\text{molar flowrate of TAEE in residue}}{\text{total molar flowrate of TAEE and IA in distillate and residue}} \times 100\% \quad (4-10)$$

The conversion of TAA and the selectivity of TAEE at the standard condition are 71.29% and 77.87%, respectively. In the following sections, key design and operating variables are varied to study their effects on the conversion of TAA and the selectivity of TAEE.

4.4.2 Effects of design variables

As stated earlier, the specification of the reactive distillation column given in Table 4.1 for the synthesis of TAEE is a preliminary configuration. To find optimal design variables for the operation of the RD, simulations are carried out to study the effects of these variables on the RD performance. The important design variables considered here include the number of rectifying, reaction and stripping stages.

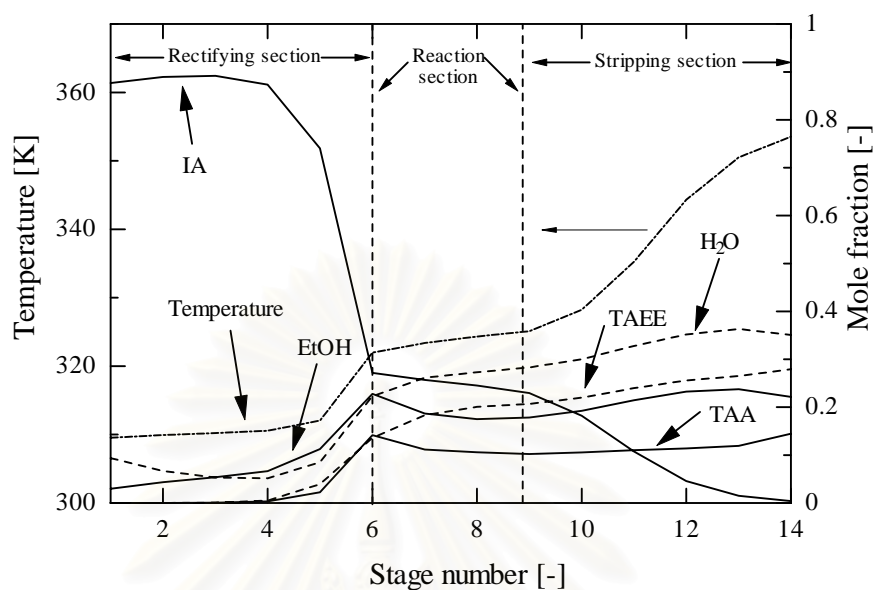


Fig. 4.2 Mole fraction and temperature profiles inside the column at the standard operating condition (Feed molar flowrate = 2.71×10^{-3} mol/s, Reflux ratio = 2, Catalyst = 0.5 kg, Feed TAA:EtOH = 1:1).

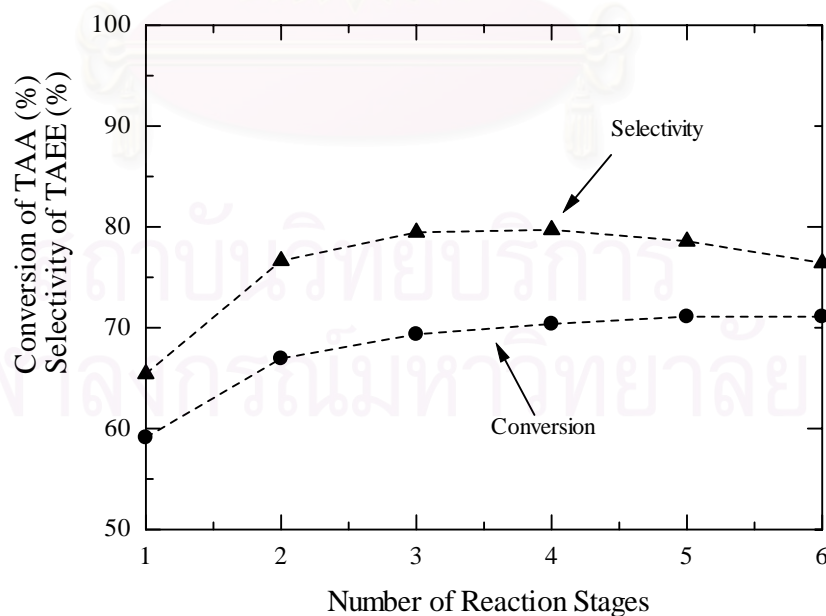


Fig. 4.3 Effect of the number of reaction stages on the reactive distillation performance.

4.4.2.1 Number of reaction stages

The function of a reaction section within the RD column is to provide a location where the reactions occur. Fig. 4.3 shows the effect of the number of reaction stages (1-6 stages) on the RD column performance. It is noted that all other design and operating variables such as the number of rectifying and stripping stages, reflux ratio, reboiler duty and feed conditions are kept at the values of the standard condition and the feed is still introduced at the top of the reaction section. The simulated results show that by using more reaction stages the conversion of TAA increases but the selectivity of TAEE decreases. According to Fig. 4.3, it can be seen that 4 reaction stages give a better performance in terms of the selectivity. Increasing a number of reaction stages above the optimal value results in more IA production, leading to the decrease in the selectivity of TAEE. This is to be expected as the excess number of reaction stages can promote undesired dehydration of TAA to IA (Eq. 4-2). Although IA can further react with EtOH to form TAEE according to Eq. (4-3), most of IA is in gas phase and its solubility in the liquid mixture is low under the standard operating pressure (0.1 MPa). As a consequence, the slight amount of TAEE is produced from the liquid phase etherification of IA (Eq. 4-3). For this reason, the number of reaction stages of 4 is used in the column configuration for the next simulations.

4.4.2.2 Number of rectifying stages

The purposes of a rectification section are to remove light components from the reaction zone, to prevent loss of TAEE in the distillate and to recycle the unreacted reactants back to the reaction section in the RD column. The effect of the number of the rectifying stages on the selectivity of TAEE and the conversion of TAA is demonstrated in Fig. 4.4. It is found that even though the TAA conversion increases with the increase of the number of rectification stages, the selectivity of TAEE decreases. This can be explained by the fact that with the increased number of the rectifying stages, IA, the lightest component, is more removed from the reaction section, decreasing the concentration of IA in the reaction zone. This causes the equilibrium equation of Eq. (4-2) shifting in the forward reaction and thus, the

conversion of TAA becomes higher whereas the selectivity of TAEE becomes lower. From the simulated results shown in Fig. 4.4, it seems that the increase of the number of rectifying stages has no significant effects on the performance of the reactive distillation. Therefore, no rectification stage is recommended for this system.

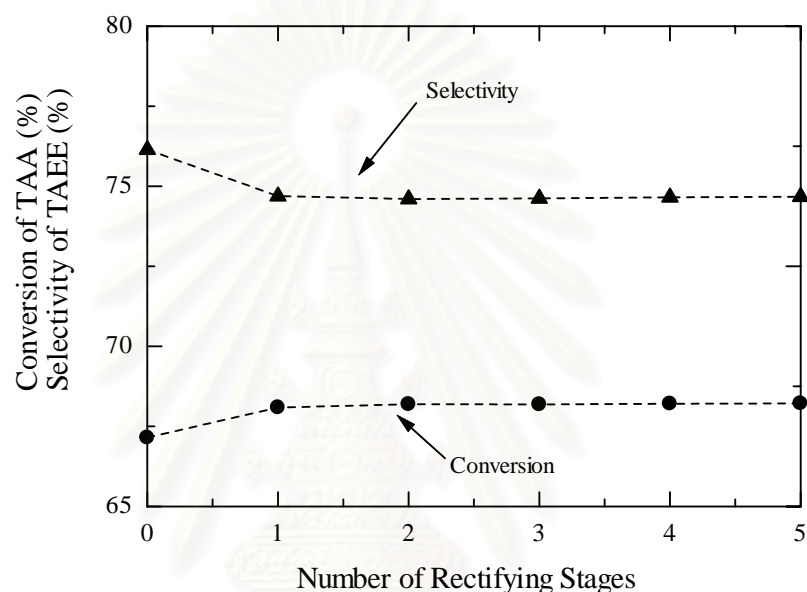


Fig. 4.4 Effect of the number of rectifying stages on the reactive distillation performance.

4.4.2.3 Number of stripping stages

In a reactive distillation, a number of stripping stages is adjusted to ensure that a satisfactory separation is achieved. The main function of the stripping section is to purify the TAEE product in the residue. It can be seen from Fig. 4.5 that the TAA conversion slightly decreases as the number of stripping stages are increased from 4 to 10 stages; however, the selectivity of TAEE shows a contrary trend. Increasing the stripping stages causes more TAA contents removed from the reaction section to the residue and therefore, the TAA conversion is decreased. In addition, the increased stripping stages decreases the concentration of TAEE in the reaction zone shifting the equilibrium of the etherification of TAA in the forward direction. As a result, the

selectivity of TAAE becomes higher. Fig. 4.5 also shows the mole fraction of TAAE in the residue. The TAAE purity in the residue exhibits a similar response to the change in the selectivity; it gradually increases to 26% mole fraction of TAAE as more stages are added. The results for the studied system indicate that both the two parameters: the selectivity and purity of TAAE, earn benefits from the increase in the number of stripping stages. Therefore, the optimum configuration would be 8 stripping stages.

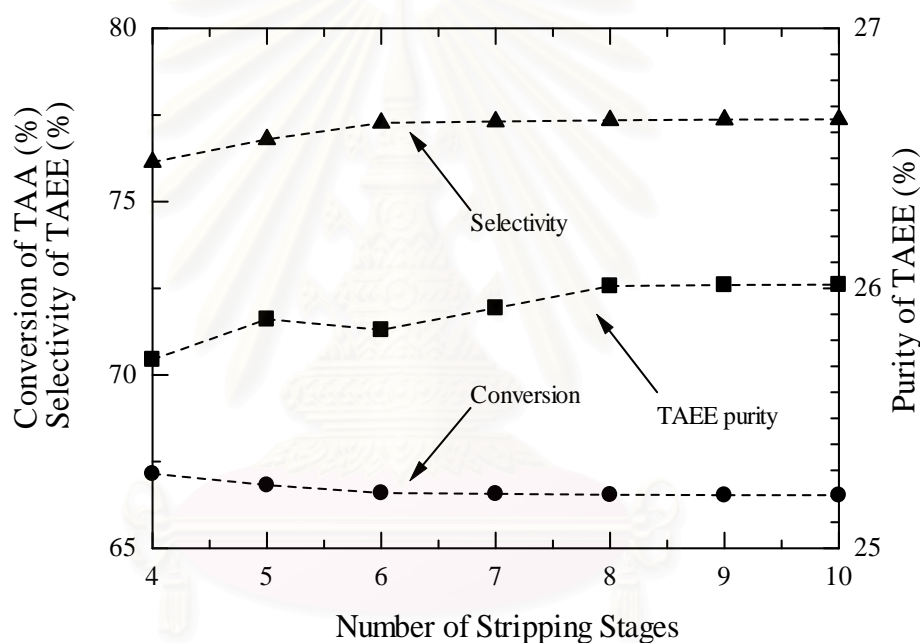


Fig. 4.5 Effect of the number of stripping stages on the reactive distillation performance.

At this stage, the optimal design variables for the reactive distillation are no rectifying, 4 reaction and 8 stripping stages. It should be noted that the location of feed consisting of TAA and EtOH is still fixed at the top tray of the reaction section. This suitable configuration will be further used in order to examine the effects of operating variables: reflux ratio, catalyst weight, operating pressure and location of feed. This provides beneficial information for improving an operation of the reactive distillation.

4.4.3 Effects of operating variables

4.4.3.1 Reflux ratio

Fig. 4.6 presents the effect of the reflux ratio on the performance of the reactive distillation. It can be seen from this figure that an increase in the reflux ratio from 2 to 16 causes a decrease in the conversion of TAA; however, it has a positive effect on the selectivity of the desired TAAE product in residue as the selectivity increases from 81.59% to 94.22%. This is because the increase of the reflux ratio increases the concentration of IA in the reaction section where it can react with EtOH to produce more TAAE. It is noticed that IA is a major component in the distillate. Moreover, some contents of unreacted reactants: EtOH and TAA in the distillate are recycled back to the reaction section, leading to higher selectivity of TAAE. However, it should be noted that some extents of the reflux IA can react with H₂O (reverse reaction of Eq. 4-2) generating more TAA. This is probably a reason for a slight decrease of the TAA conversion.

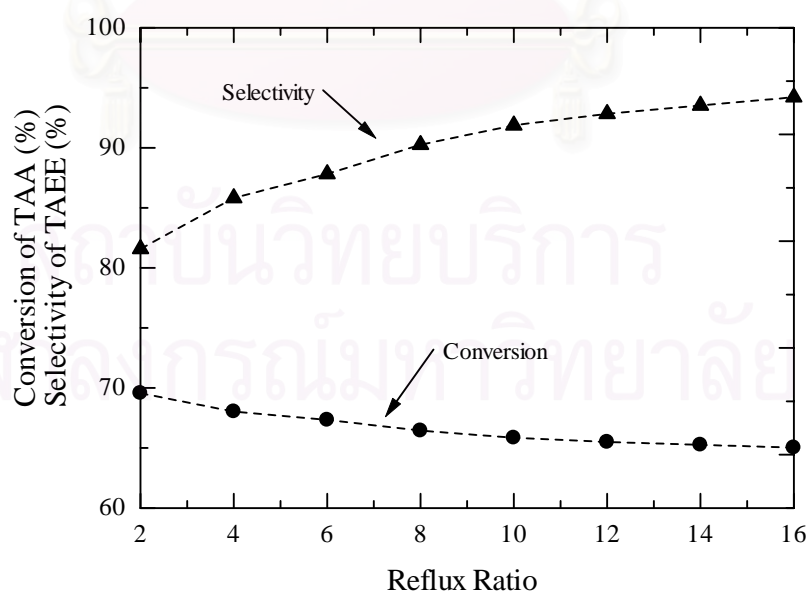


Fig. 4.6 Effect of the reflux ratio on the reactive distillation performance.

4.4.3.2 Catalyst weight

Since the catalyst is used to accelerate the reaction rate and to influence the selectivity, the effect of the amount of total catalyst in the reaction section on the performance of RD column is studied. Fig. 4.7 shows that as the amount of catalyst on the reaction stage increases, the amount of TAA converted to TAEF as well as the selectivity of TAEF increases. However, it is observed that when the catalyst weight is more than 0.4 kg, the conversion of TAA and the selectivity of TAEF are slightly improved. This indicates that the reactions are approaching equilibrium-limited conditions. It should be noted that although the increase in the amount of catalyst has a positive effect on the performance of the reactive distillation, other factors, e.g., cost of catalyst and capacity of column should also be considered in selecting the appropriate amounts of catalyst in the reaction section.

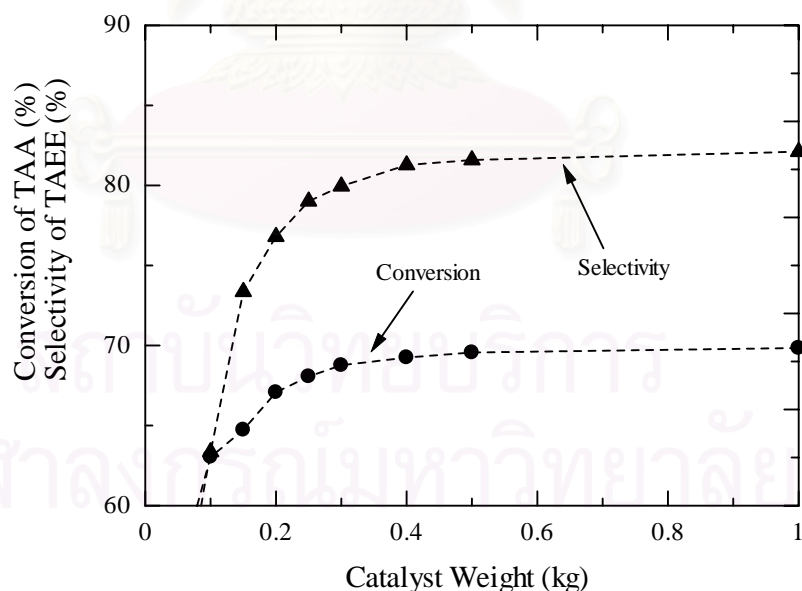


Fig. 4.7 Effect of the catalyst weight on the reactive distillation performance.

4.4.3.3 Operating pressure

The operating pressure is one of the key operating parameters of a distillation column. The choice of operating pressure for the reactive distillation column depends on many considerations such as overhead temperature, bottom temperature and reaction temperature in the system. Since chemical reactions take place in the liquid phase, the reaction temperature is close to the boiling point of the liquid phase flowing around the catalyst. Fig. 4.8 shows the influence of the column pressure on the TAA conversion and TAAE selectivity. It is found that as the pressure increases from 0.1 to 0.6 MPa, the reaction stage temperature increases linearly from 48 to 100°C (data not shown). From the kinetic parameters given in Table 4.2, one would expect that rate of the dehydration of TAA to IA, Eq. 4-2, is more pronounced when the reaction temperature increases, resulting in the lower selectivity of TAAE as can be seen from Fig. 4.8. However, the conversion of TAA is quite insensitive to the operating pressure. This suggests that the operating pressure of 0.1 MPa is suitable for the reactive distillation to synthesis TAAE.

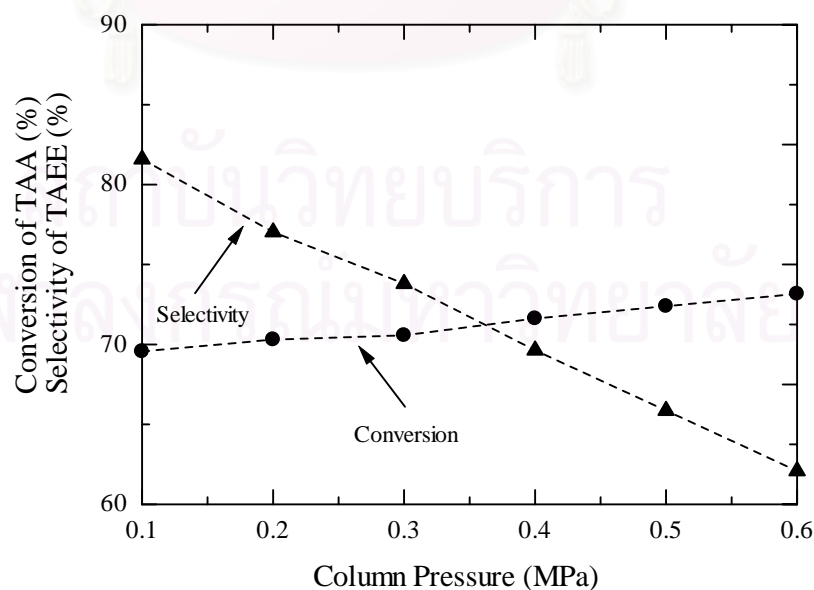


Fig. 4.8 Effect of the column pressure on the reactive distillation performance.

4.4.3.4 Feed stage location

Since the location of the feed can be adjusted to make the best separation and the most favorable reaction conditions, simulations are performed to investigate the effects of the feed location of TAA and EtOH on the RD performance. The cases where the feed of reactants (TAA and EtOH) are separated in two streams on the reaction section (fixed at stage 2-5) are compared with the one that both TAA and EtOH are mixed in one feed stream as in the standard conditions. The results are summarized in Table 4.4. It has been known that when the feed components are separated in two different locations, the reactant with lower boiling point is normally introduced at the lower stage of the reaction section, compared to the higher boiling point. However, it is found here that feeding TAA and ethanol together at the top of the reaction section offers the highest conversion of TAA (69.64%) and selectivity of TAEE (81.71%). It is noticed that separating the feed components decreases both the TAA conversion and TAEE selectivity. This is probably due to the fact that the residence time of the reactants is decreased when the location of the EtOH feed in the reaction section is below, compared to that of the TAA feed; i.e., EtOH will travel down to the bottom part of the column without being reacted as shown in Table 4.4.

Table 4.4 Effect of feed separation on the TAA conversion and the TAEE selectivity.

Feed location		TAA	TAEE	Residue composition (%mole fraction)				
TAA	EtOH	Conversion	Selectivity	TAEE	TAA	EtOH	IA	H ₂ O
2	2	69.64	81.71	28.68	15.38	21.3	0	34.63
2	3	69.52	79.16	27.82	15.17	22.61	0	34.38
2	4	67.88	74.5	25.57	16.04	24.98	0	33.4
2	5	61.06	60.53	18.74	19.48	31.96	0	29.71

CHAPTER 5

REACTIVE DISTILLATION WITH PERVAPORATION

Pervaporation is a potential energy saving and efficient separation technique, especially for separation of azeotropic mixture that is difficult to be separated by traditional distillation. Generally, in many cases pervaporation alone may not supply the suitable products. Thus, reactive distillations combined with pervaporation are regarded as one means of overcoming these limitations. In this chapter, the production of TAAE is studied using a hybrid processes.

5.1 Hybrid process of reactive distillation and pervaporation

The kinetic and thermodynamic studies of TAA etherification with EtOH in the reactive distillation column has shown chemical equilibrium limitations and H₂O inhibition. Although it has been shown in the previous chapter that a reactive distillation is a favorable alternative process since conversions and selectivity beyond equilibrium conversions can be achieved, the combination of reactive distillation with another unit operation for H₂O removal should be considered to improve the performance of the reactive distillation. Pervaporation is a suitable unit operation for H₂O removal and will move TAA equilibrium conversion to completion according to Le Chatelier's principle. Pervaporation denotes a membrane process where a liquid feed is divided into a liquid retentate and vapor permeate, which is maintained by evacuation.

As in chapter 4, all simulations presented in this chapter are carried out using the commercial program ASPEN PLUS. This modular based software includes a number of conventional unit operations which can be combined into any flow scheme. It should be noted that membrane processes are not included in the standard version; however, ASPEN PLUS offers the possibility to include user-defined FORTRAN routines that allow the implementation of any additional unit operation. For

investigations regarding the optimal synthesis of a hybrid process for the TAAE production, the subroutine *usrpv* for a pervaporation unit has been developed for use in the ASPEN PLUS. In *usrpv*, the calculations are performed by solving the mass and energy balances associated with the data for flux and selectivity of the membrane. Details for mathematical models of a pervaporation process are given in the next section.

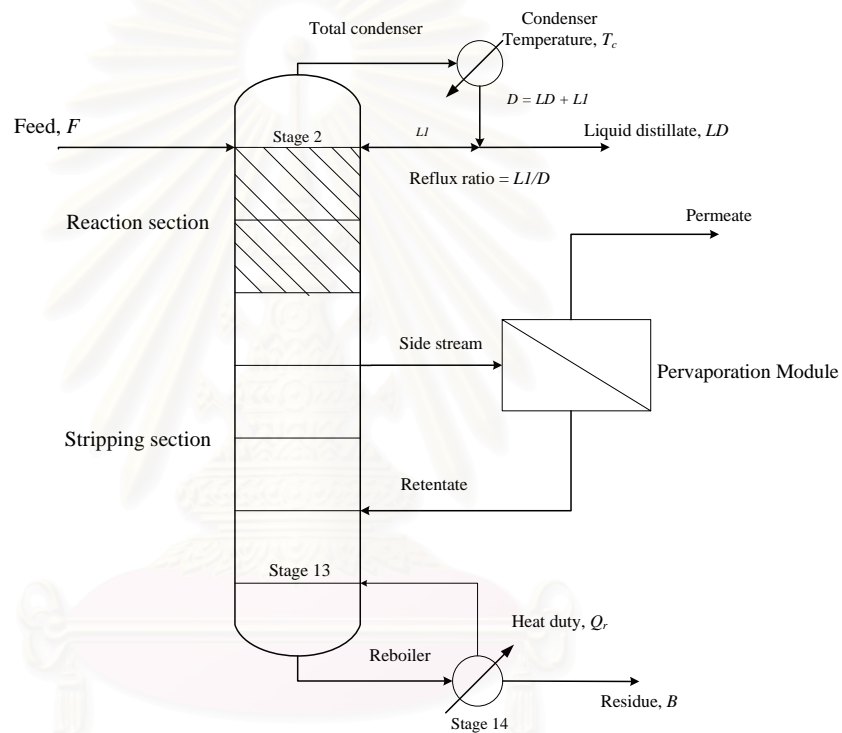


Fig. 5.1 The configuration of combined process consisting of a reactive distillation column and a pervaporation unit

A hybrid process of reactive distillation column and a pervaporation unit is shown in Fig. 5.1. In this study, the optimal configuration of the RD column for TAAE production as reported in Chapter 4 is used here for the hybrid process. Within the RD, it contains a total of 14 stages numbered from the top. This includes a total condenser being the first stage and a partial reboiler being the last stage. The RD column is divided into two sections: the reaction section represented by 4 reactive stages (2-5) and the stripping section represented by 8 stages (6-13). The feed is

introduced at the top of reaction stage (stage2). Table 5.1 summarizes the column parameters and feed condition of RD with pervaporation. The two additional input parameters of the column configuration specified for simulation of the RADFRAC are heat duty at the reboiler (Q_r) and reflux ratio (R).

Table 5.1 Feed conditions and specification of reactive distillation column with the pervaporation.

Feed conditions		Column specification	
Temperature [K]	298	Reaction stages	4
Flow rate [mol/s]	2.71×10^{-3}	Stripping stages	8
Mole fraction [-]		Total stages	14
1) EtOH	0.5	Side draw stage	2
2) TAA	0.5	Catalyst weight per stage [kg]	0.125
Pressure [kPa]	101.3	Pressure [kPa]	101.3
Flow rate to pervaporation [mol/s]	1.50×10^{-3}	Reflux ratio (R) [-]	2
		Reboiler duty (Q_r) [W]	52
		Membrane area [m ²]	0.01

5.2 Pervaporation model

Mathematical models of pervaporation process are developed to investigate the performance of a hybrid process of reactive distillation with pervaporation. It is assumed that there is no reaction occurring in the pervaporation; pressure drops and polarization effects is negligible; the partial pressure of component i in the permeation side is negligible and the components passing through the pervaporation membrane are ideal mixing (activity coefficient, $\gamma = 1$). Fig. 5.2 shows the schematic diagram of a pervaporation membrane process.

5.2.1 Mass balance

The activity can be calculated from the following relation:

$$a_i = \gamma_i x_i \quad (5-1)$$

where x_i is the mole fraction of species i in the liquid mixture and γ_i is the activity coefficient which is assumed to be an ideal mixture ($\gamma_i = 1$)

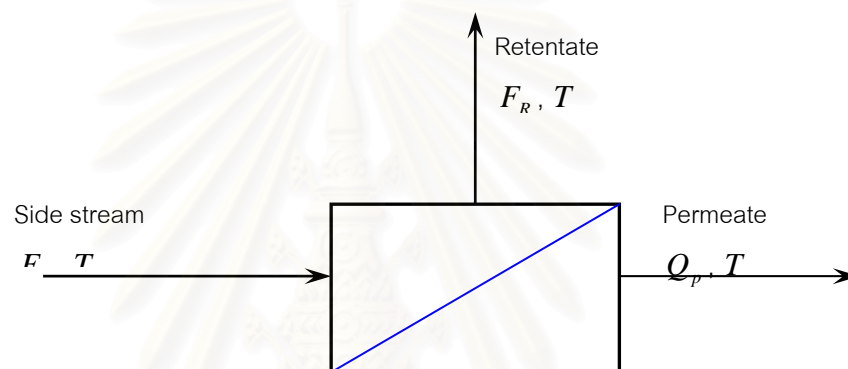


Figure 5.2 schematic diagram of pervaporation membrane

The permeation rate of species i through the zeolite NaA membrane which is adopted from Aiouache and Goto (2003b) can be expressed as follows:

$$Q_i = AP_i x_i \quad [\text{mol/s}] \quad (5-2)$$

$$P_{TAA} = \exp\left(-5.4 - \frac{1046}{T}\right) \quad [\text{mol}/(\text{s}\cdot\text{m}^2)] \quad (5-3)$$

$$P_{EtOH} = \exp\left(-5.4 - \frac{1247}{T}\right) \quad [\text{mol}/(\text{s}\cdot\text{m}^2)] \quad (5-4)$$

$$P_{IA} = \exp\left(-2.1 - \frac{2656}{T}\right) \quad [\text{mol}/(\text{s}\cdot\text{m}^2)] \quad (5-5)$$

$$P_{H_2O} = \exp\left(9.4 - \frac{3656}{T}\right) \quad [\text{mol}/(\text{s}\cdot\text{m}^2)] \quad (5-6)$$

It is noted that the permeation of TAEE is negligibly small so its permeation was not included. By performing mass balances around a pervaporation process at steady state conditions; the following equation is obtained:

$$F_{f,i} = F_{R,i} + AP_i x_i \quad (5-7)$$

5.2.2 Energy balance

The temperatures of retentate and permeate stream is calculated by using energy balance around the pervaporation module. It is assumed that pervaporation module is operated under adiabatic system; no heat lost occurs in the system. Therefore, the temperature in the retentate stream is the same as in permeate stream. The energy balance can be expressed as follow:

$$H_{f,i} = H_{R,i} + H_{P,i} \quad (5-8)$$

The enthalpy of component i in each stream (H_i) can be calculated by integrating the heat capacity (C_p) of each component. It is noted that the temperature of a side stream is used as the reference state for calculation; thus, the enthalpy in side stream is zero.

$$H_{R,i} = F_{R,i} \int_{T_f}^T c_{pl} dT \quad (5-9)$$

$$H_{P,i} = Q_i \left(\int_{T_f}^{T_r} c_{pl} dT + H^T_{vap,i} \right) \quad (5-10)$$

Substitute Eqs. (5-9) and (5-10) into Eq. (5-8) gives

$$F_{R,i} \int_{T_f}^T c_{pl} dT + Q_i \left(\int_{T_f}^{T_r} c_{pl} dT + H^T_{vap,i} \right) = 0 \quad (5-11)$$

From Eq. (5-11), the Newton method is applied to determine the temperature of retentate and permeate stream.

5.3 Results and Discussions

In Chapter 4, the kinetic and thermodynamic studies of *tert*-amyl alcohol (TAA) etherification with ethanol (EtOH) has shown three equilibrium-limited reactions Eqs. (4-1) to (4-3), water as an inhibiting product and isoamylene (IA) as an undesired intermediate. The use of pervaporation membrane for H₂O removal should further move TAA equilibrium conversion to completion according to Le chatelier's principle. In this study, the concept of proper incorporation of a pervaporation module in a reactive distillation is suggested. The addition of incorporated membrane along the reactive distillation column leads to complex interactions between vapor-liquid equilibrium, vapor-liquid mass transfer, chemical kinetics and mass and energy transfer through the membrane. The impact of the pervaporation to RD will be investigated

5.3.1 Standard condition with pervaporation

In this section, the performance of RD and RD with pervaporation used in the synthesis of TAEE are compared to find out the improvement of the system performance by the use of the pervaporation module. From Table 5.1, the parameters used in the studies are the same as the ones in Table 4.1, except that there is the pervaporation connected with reactive distillation and the column consists of only two sections zone (reaction and stripping zone). The flowrate of side stream to pervaporation process is set to 0.0015 mol/s and is drawn from the second stage of reactive distillation. The area of membrane (0.01 m²) used for separation can be calculated from the capacity of water separated from the side stream. The comparison results between both cases are shown in Table 5.2. It shows that when pervaporation system is included, the values of yield and selectivity of TAEE and conversion of TAA increase since the pervaporation system can separate water occurred from the reaction and this causes the shift of the equilibrium reaction forward to the product

side. Therefore, it is obvious that use of the pervaporation module can improve the efficiency of system when it was connected with reactive distillation for separation of water that inhibits the TAAE reaction.

Table 5.2 Comparison of RD and RD connected with pervaporation under standard condition (Side stream flowrate = 0.0015 mol/s, membrane area = 0.01 m²).

Condition	TAA conversion	TAAE selectivity	TAAE yield	Mole fraction of TAAE in Bottom
RD	69.56	81.59	56.76	28.66
RD with Pervaporation	72.60	82.70	60.00	32.99

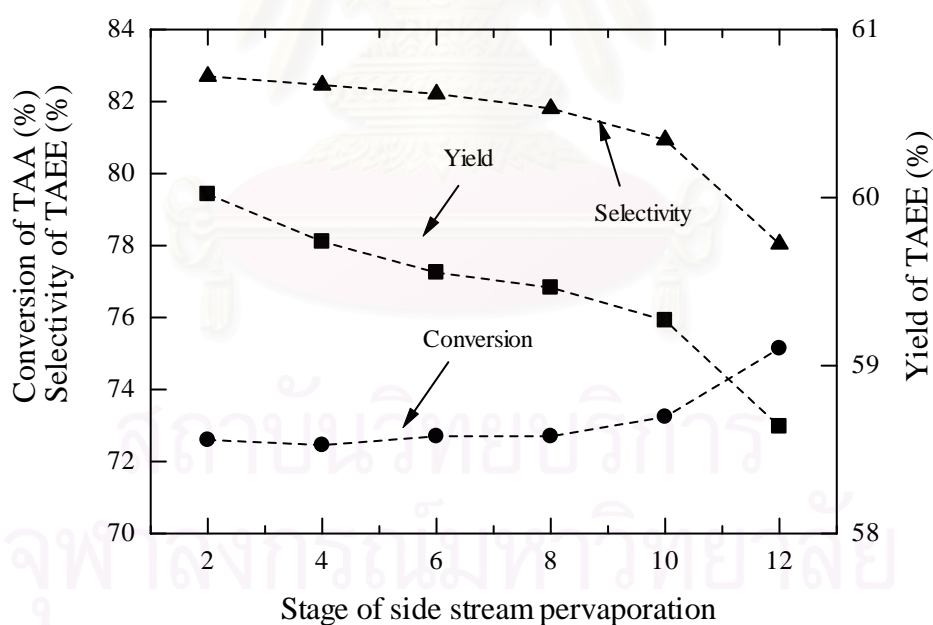


Fig 5.3 Effect of location of side stream pervaporation on the performance of reactive distillation.

5.3.2 Effect of location of side stream pervaporation module

Figure 5.3 presents the effect of side stream pervaporation module on conversion and selectivity. It is found that when the location of the pervaporation unit changes from the upper stage to the lower stage, the conversion increases while the selectivity decreases. This is particularly pronounced when the location is below the feed point. With the higher temperature of the stage close to the reboiler, more water permeates through the membrane and consequently moves the reaction forward to more complete conversion. The selectivity decreases because the forward reaction rate of side reaction, dehydration of TAA, is higher than the forward reaction rate of etherification reaction of TAAE, and this causes more side reaction. Therefore, the selectivity as well as the yield of TAAE decrease.

5.3.3 Effect of side stream flowrate

Figure 5.4 shows the result of side stream flowrate to the conversion and selectivity. It can be seen that these two values are rather constant, and they do not change according to the increasing flowrate of side stream because the mole fraction of water is constant, independent on the flow rate as shown in Figure 5.4. As a result, the permeation rate of water flowing through the pervaporation membrane, which depends on the mole fraction according to Eq. 5.2, is rather constant.

5.3.4 Reactive distillation with two pervaporation modules

The previous section shows the results of the RD with one pervaporation module. In this section, one more pervaporation will be added to find out whether or not it can increase the efficiency of RD. The results are given in Table 5.3. It is found that the use of two pervaporation modules increases the performance of RD with only one pervaporation module. Moreover, the location of the second pervaporation unit also slightly affected the conversion and selectivity. However, the suitable position for connecting pervaporation with RD and making these two values optimum is at the reaction zone (stage 2-5) because water is separated in the reaction stage packed with

catalyst. Therefore, the reaction can more directly forward to TAAE product increasingly.

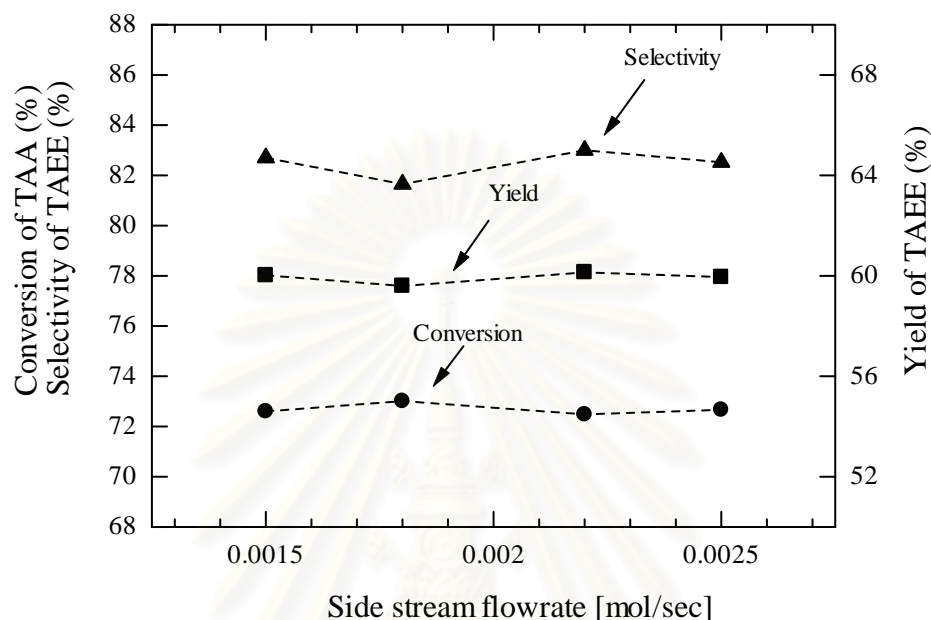


Fig 5.4 Effect of side stream flowrate to pervaporation on the performance of reactive distillation.

Table 5.3 Effect of two pervaporation on the performance of reactive distillation (Side stream flowrate = 0.0015 mol/s, membrane area 0.01 m², reflux ratio = 2, reboiler duty 52 watts).

Side draw stage of 2 pervaporation	TAA conversion	TAAE selectivity	TAAE yield	Mole fraction of TAAE in Bottom
2 (one pervap)	72.60	82.70	60.02	32.99
2,3	75.45	83.49	62.21	36.59
2,4	75.27	83.34	62.69	36.55
2,6	74.64	83.09	62.00	35.69
2,8	74.67	83.05	61.98	35.69
2,10	74.98	82.57	61.88	35.65
2,12	75.53	81.71	61.69	35.59

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The research studies the synthesis of TAEF from TAA and ethanol in reactive distillation by using Aspen Plus. Emphasis is placed on the determination of an appropriate configuration of the reactive distillation column for the TAEF production. An analysis of the effects of key operating parameters on the conversion of TAA conversion and the selectivity of TAEF is performed. In addition, the pervaporation, a membrane process for liquid mixture separations is incorporated in the reactive distillation for facilitating water removal from the system and improving the performance of reactive distillation. The following conclusions can be drawn from the investigations.

6.1.1 Reactive distillation

The liquid phase synthesis of tert-amyl ethyl ether (TAEF) from *tert*-amyl alcohol (TAA) and ethanol in a reactive distillation column has been studied in this thesis. The simulation of this process using a rate-based kinetic expression and an equilibrium stage model are performed via Aspen Plus. The influences of key design variables on the performance of the reactive distillation are investigated.

The results indicate that the optimal design of the column consists of no rectifying, 4 reaction, and 8 stripping stages.

In order to operate the reactive distillation column efficiently, the effects of various operating parameters on the reactive distillation performance are analyzed. It has been found that the reflux ratio and operating pressure are the most important factors affecting the conversion of TAA and the selectivity of TAEF.

6.1.2 Reactive distillation with pervaporation

The performances of the combined reactive distillation and pervaporation system have been calculated using the commercial software, ASPEN PLUS. This modular based software includes various conventional unit operations which can be combined to any flow scheme. Membrane processes are not available in the standard version, but ASPEN PLUS allows user-defined FORTRAN routines of any additional unit operation to be included in the program. The subroutine *usrpv* of a pervaporation unit has been developed for use in the ASPEN PLUS. The design calculations in *usrpv* are performed by solving the mass and energy balances including data for flux and selectivity of the membrane.

The reactive distillation connected with pervaporation can improve the performance of the system for the TAEE by removing water from the system.

The location of the pervaporation unit in the reactive distillation column is an important parameter determining the system performance. It has been found that an optimal location of the pervaporation unit for the TAEE production is placed in the reaction zone with packed catalyst.

It is found that the addition of more pervaporation unit slightly improve the efficiency of RD when compared with only one pervaporation unit.

6.2 Recommendations

In this work, the pervaporation unit is included in the reactive distillation column for improving the performance on the TAEE production. It is demonstrated under the standard condition the benefit of the presence of the pervaporation unit.

It is recommended that the effects of various operating variable such as reflux ratio, operating pressure, and feed stage location, and system configurations on the TAA conversion and TAEE selectivity should be further investigated.

In addition, experimental works should be carried out using the obtained appropriate configuration and operating condition to verify the simulation results.



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APPENDIX A

MODIFIED KINETIC PARAMETERS OF TAAE SYNTHESIS

The kinetic parameters determined by Aiouache and Goto (2003a) are modified for use in the study. As reported from their paper, the kinetic parameters are based on the activity (Table A.1); however, it is not allowed to use the activity-base parameters in the ASPEN PLUS simulator. Therefore the kinetic parameters based on activity are converted to mole fraction forms by multiplying with average activity coefficient which estimated from UNICFAC method (see Appendix D for details). Table A.2 shows the average activity coefficients that are calculated by using MATLAB. The modified kinetic parameters are obtained by calculating the rate parameters at several temperature levels.

Table A.1. Kinetic constant and activation energy reported by Aiouache and Goto (2003a)

Kinetic constant in paper Goto	Ea (KJ/mol)
$k_1 = \exp(14.2 - 6324/T)$	52.578
$k_2 = \exp(14.0 - 6240/T)$	51.879
$k_3 = \exp(21.5 - 9214/T)$	76.605
$k_{-1} = \exp(15.59 - 7634/T)$	63.469
$k_{-2} = \exp(8.25 - 4864/T)$	40.439
$k_{-3} = \exp(28.64 - 11900/T)$	98.937
$Keq_1 = \exp(-1.39 + 1310/T)$	
$Keq_2 = \exp(5.75 - 1376/T)$	
$Keq_3 = \exp(-7.14 + 2686/T)$	

Table A.2. Activity coefficient calculated by MATLAB

Temperature °C	Activity coefficient (average)				
	H2O	EtOH	TAA	TAE E	IA
50	2.70200	1.06613	1.07699	1.96923	2.90471
60	2.63750	1.08531	1.09623	1.87370	2.84595
70	2.61300	1.09930	1.10726	1.81571	2.79859
80	2.59850	1.10578	1.11569	1.78896	2.78035

The input rate expressions for Aspen Plus are in the following equations:

$$r_{\text{EtOH}} = -m_r Q \left[k_1 \left(x_{\text{EtOH}} x_{\text{TAA}} - \frac{x_{\text{TAE E}} x_{\text{H}_2\text{O}}}{K_{\text{eq1}}} \right) + k_3 \left(x_{\text{IA}} x_{\text{EtOH}} - \frac{x_{\text{TAE E}}}{K_{\text{eq3}}} \right) \right] \quad (\text{A-1})$$

$$r_{\text{TAA}} = -m_r Q \left[k_1 \left(x_{\text{EtOH}} x_{\text{TAA}} - \frac{x_{\text{TAE E}} x_{\text{H}_2\text{O}}}{K_{\text{eq1}}} \right) + k_2 \left(x_{\text{TAA}} - \frac{x_{\text{IA}} x_{\text{H}_2\text{O}}}{K_{\text{eq2}}} \right) \right] \quad (\text{A-2})$$

$$r_{\text{IA}} = r_{\text{EtOH}} - r_{\text{TAA}} \quad (\text{A-3})$$

$$r_{\text{TAE E}} = -r_{\text{EtOH}} \quad (\text{A-4})$$

$$r_{\text{H}_2\text{O}} = -r_{\text{TAA}} \quad (\text{A-5})$$

The following example shows how to converse the kinetic parameters based on activity form to mole fraction form. For the reaction rate of EtOH in activity form, as given in Eq. (A-6),

$$r_{\text{EtOH}} = -m_r Q \left[k_1 \left(a_{\text{EtOH}} a_{\text{TAA}} - \frac{a_{\text{TAE E}} a_{\text{H}_2\text{O}}}{K_{\text{eq1}}} \right) + k_3 \left(a_{\text{IA}} a_{\text{EtOH}} - \frac{a_{\text{TAE E}}}{K_{\text{eq3}}} \right) \right] \quad (\text{A-6})$$

substituting the activity of each component (a_i), as shown in Eq. (A-7), in Eq. (A-6)

$$a_i = \gamma_i x_i \quad (\text{A-7})$$

and rearranging the kinetic parameters, we obtain

$$k_1(new) = k_1 * (\gamma_{EtOH} \gamma_{TAA}) \quad (A-8)$$

$$k_{-1}(new) = k_{-1} * (\gamma_{TAAE} \gamma_{H_2O}) \quad (A-9)$$

$$k_3(new) = k_3 * (\gamma_{IA} \gamma_{EtOH}) \quad (A-10)$$

$$k_{-3}(new) = k_{-3} * (\gamma_{TAAE}) \quad (A-11)$$

Next, the new value of the modified kinetic parameters based on average activity coefficients (Table A.2) is calculated at several temperature levels as follows.

$$\begin{aligned} \text{At } T = 323.15 \text{ K, } \quad k_1(new) &= k_1 * (\gamma_{EtOH} \gamma_{TAA}) \\ k_1(new) &= \exp(14.2 - 6324/323.15) * (1.066 * 1.077) \\ k_1(new) &= 0.005345 \end{aligned}$$

With the same method of calculation as shown above, the new value of the kinetic parameter, $k_I(new)$, at various temperature is obtained:

$$\begin{aligned} \text{At } T = 333.15 \quad k_1(new) &= 0.009965 \\ \text{At } T = 343.15 \quad k_1(new) &= 0.017726 \\ \text{At } T = 353.15 \quad k_1(new) &= 0.030276 \end{aligned}$$

Then, the Arrhenius plot ($\ln k_1$ versus $1/T$) as shown in Figure A.1 is made to find the new rate expression of the kinetic constant, $k_I(new)$.

From Figure A.1, we obtain the rate expression of $k_1(new)$ as follows,

$$k_1(new) = \exp(15.189 - 6597/T)$$

and the activation energy is

$$E_a = 6597.3 * 8.314 = 54.85 \text{ (kJ/mol)}$$

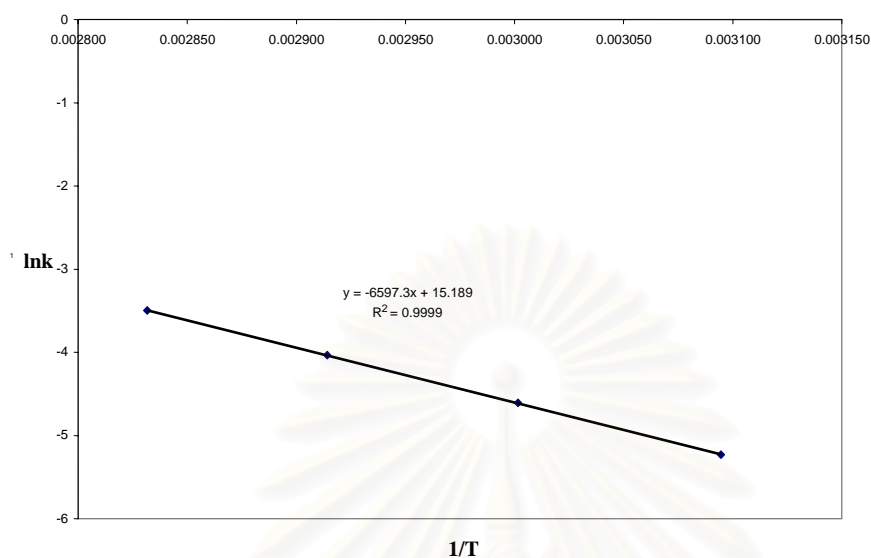


Figure A.1 Arrhenius plot of $k_1(\text{new})$

Table A.3 summarizes other modified kinetic parameters which are based on rate expression in mole fraction form and used in ASPEN Plus.

Table A.3. Modified kinetic constant and activation energy for this study

Kinetic constant in my calculate	Ea (KJ/mol)
$k_1 = \exp (15.189 - 6597.3/T)$	54.850
$k_2 = \exp (14.49 - 6372.9/T)$	52.984
$k_3 = \exp (22.54 - 9184.6/T)$	76.361
$k_{-1} = \exp (15.66 - 7121.7/T)$	59.210
$k_{-2} = \exp (9.33 - 4548.6/T)$	37.812
$k_{-3} = \exp (28.18 - 11533/T)$	95.885
$Keq_1 = \exp (-0.471 + 524/T)$	
$Keq_2 = \exp (5.16 - 1824.3/T)$	
$Keq_3 = \exp (-5.64 + 2349/T)$	

APPENDIX B

PARAMETERS USED IN PERVAPORATION

The temperature in retentate and permeate stream of the pervaporation system is calculated by the energy balance equation that required the heat capacity and heat of vaporization of each component. These parameters are shown in Table B.1 and B.2.

Table B.1 Heat capacity of liquid (J/mol.K) $c_{pl} = A + BT + CT^2$

Cpl (J/mol.K)	A	B	C
TAAE*	250.55		
TAA	-38.513	2.2919	-6.5955E-03
Ethanol	59.342	3.6358E-01	-1.2164E-03
IA	74.305	5.8380E-01	-2.1386E-03
H ₂ O	92.053	-3.9953E-02	2.1103E-04

* estimate by functional group

Since there is no information on the heat capacity of TAAE, the heat capacity of TAAE is estimated by using its functional groups as shown below (Perry's Chemical Engineer's Hand Book, Seventh edition).

Calculation of heat capacity of TAAE

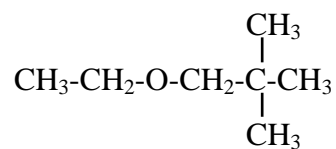
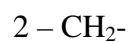
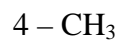


Fig B.1 Molecular structure of TAAE

The atomic groups are:



Therefore, the estimate heat capacity of TAEE is

$$\begin{aligned} c_{TAEE} &= (4)(36.82) + (2)(30.38) + (1)(7.36) + (1)(35.15) \\ &= 250.55 \text{ J/mol.K} \end{aligned}$$

Table B.2 Heat of vaporization (kJ/mol) $H_{vap} = A\left(1 - \frac{T}{T_c}\right)^n$

H_{vap} (kJ/mol)	A	T_c	n	T_{boil} (K)
TAEE				374.57
TAA	78.205	545.15	0.573	375.15
Ethanol	43.122	516.25	0.079	351.44
IA	39.38	471	0.365	311.71
H ₂ O	52.053	647.13	0.321	373.15

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APPENDIX C

FORTRAN USER MODEL

Aspen Plus, a modulus based software, generally the commercial program includes various conventional unit operations which can be combined to any flow scheme. However, pervaporation are not included in the standard version, but Aspen plus offers a Fortran user-subroutine thus allowing the implementation of any additional unit operation. This section describes the procedure to write and compile Fortran user model, and to specify the location of the Fortran user models during Aspen Plus runs.

1. Program requirement

There are two essential programs to be installed, as shown below, in computer before writing and compiling the Fortran user models.

- Aspen Plus 10.2 or higher
- Fortran language program (eg., Compaq Visual Fortran 6.6)

An Aspen Plus Fortran user model generally consists of one or more subroutines written to extend the capabilities of Aspen Plus. There are six kinds of Fortran user models for use in Aspen Plus:

- User unit operation models
- User physical property models for the calculation of various major, subordinate and intermediate physical properties
- User models for sizing and costing
- User models for special stream properties
- User stream reports
- User models for performing various types of calculations within Aspen Plus unit operation models

2. Writing Fortran user models

User models written in Fortran should follow these rules:

- **Filename:** Files may be given any name, but should end with a “.f” file extension.
- **Subroutine Names:** The name of all Fortran user model should contain no more than six characters.
- **Double Precision:** All real variables must be declared as double precision (REAL*8).
- **Units:** All variables in the argument list are in SI units, unless the variable description states otherwise.

3. Compiling Fortran user models

All Fortran user models must be compiled before beginning an Aspen Plus run. In order to insure consistent compiler options, use the “aspcmp” command for compiling:

Command used to compile: `aspcmp *.f`

4. Supplying Fortran user models to Aspen Plus

The simplest method of supplying Fortran user models to Aspen Plus is by putting the user model’s object module files (the results of the “aspcmp” command) in the run directory that a project file is saved. By default, whenever Aspen Plus spawns a subprocess to link a run-specific Fortran user model, it includes all object module files from the run directory.

APPENDIX D

UNIFAC METHOD

The UNIFAC method for estimation of activity coefficient depends on the concept that a liquid mixture may be considered as a solution of the structural units from which the molecules are formed rather than a solution of the molecules themselves. These structural units are called subgroups, and some of them are listed in the second column of Table D-1. A number, designated k , identifies each subgroup. The relative volume R_k and relative surface area Q_k are properties of the subgroups, and values are listed in column 4 and 5 of Table D.1. When it is possible to construct a molecule from more than one set of subgroups, the set containing the least member of different subgroups is the correct set. The great advantage of the UNIFAC method is that a relatively small number of subgroups combine to form a very large number of molecules.

Activity coefficients depend not only on the subgroup properties R_k and Q_k , but also on interactions between subgroups. Here, similar subgroups are assigned to a main group, as shown in the first two columns of Table D.1. The designations of main groups, such as “CH₂”, “ACH”, etc., are descriptive only. All subgroups belonging to the same main group are considered identical with respect to group interactions. Therefore parameters characterizing group interactions are identified with pairs of main groups. Parameter value a_{mk} for a few such pairs are given in Table D.2.

The UNIFAC method is based on the UNIQUAC equation which treats $g \equiv G^E / RT$ as comprised of two additive parts, a *combinatorial* term g^C to account for molecular size and shape differences, and a *residual* term g^R to account for molecular interactions:

$$g = g^C + g^R \quad (\text{D-1})$$

Function g^C contains pure-species parameters only, whereas function g^R incorporates two binary parameters for each pair of molecules. For a multi-component system,

$$g^C = \sum x_i \ln \frac{\phi_i}{x_i} + 5 \sum q_i x_i \ln \frac{\theta_i}{\phi_i} \quad (\text{D-2})$$

and

$$g^R = - \sum q_i x_i \ln (\sum \theta_j \tau_{ji}) \quad (\text{D-3})$$

where

$$\phi_i = \frac{x_i r_i}{x_j r_{j i}} \quad (\text{D-4})$$

and

$$\theta_i = \frac{x_i q_i}{x_j q_{j i}} \quad (\text{D-5})$$

Subscript i identifies species, and j is a dummy index; all summations are over all species. Note that $\tau_{ji} \neq \tau_{ii}$; however, when $i = j$, then $\tau_{ji} = \tau_{ii} = 1$. In these equations r_i (a relative molecular volume) and q_i (a relative molecular surface area) are pure-species parameters. The influence of temperature on g enters through the interaction parameters τ_{ji} of Eq. (D-3), which are temperature dependent:

$$\tau_{ji} = \exp \frac{-(u_{ji} - u_{ii})}{RT} \quad (\text{D-6})$$

Parameters for the UNIQUAC equation are therefore values of $(u_{ji} - u_{ii})$.

An expression for $\ln \gamma_i$ is applied to the UNIQUAC equation for g [Eqs. (D-1) to (D-3)]. The result is given by the following equations:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (\text{D-7})$$

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \quad (\text{D-8})$$

and

$$\ln \gamma_i^R = q_i \left(1 - \ln s_i - \sum \theta_j \frac{\tau_{ij}}{s_j}\right) \quad (\text{D-9})$$

where in addition to Eqs (D-5) and (D-6)

$$J_i = \frac{r_i}{\sum x_j r_j} S \quad (\text{D-10})$$

$$L_i = \frac{q_i}{\sum x_j q_j} S \quad (\text{D-11})$$

$$s_i = \sum \theta_l \tau_{li} \quad (\text{D-12})$$

Again subscript i identifies species, and j and l are dummy indices. All summations are over all species, and $\tau_{ij}=1$ for $i=j$. Values for the parameters ($u_{ij} - u_{jj}$) are found by regression of binary VLE data.

When applied to a solution of groups, the activity coefficients are calculated by:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (\text{D-13})$$

when

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \quad (\text{D-14})$$

and

$$\ln \gamma_i^R = q_i \left[1 - \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k}\right)\right] \quad (\text{D-15})$$

The quantities J_i and L_i are given by:

$$J_i = \frac{r_i}{x_j r_j} \quad (\text{D-16})$$

$$L_i = \frac{q_i}{x_j q_j} \quad (\text{D-17})$$

In addition, the following definition of parameters in Eqs. D-14 and D-15 apply:

$$r_i = v_k^{(i)} R_k \quad (\text{D-18})$$

$$q_i = v_k^{(i)} Q_k \quad (\text{D-19})$$

$$e_{ki} = \frac{v_k^{(i)} Q_k}{q_i} \quad (\text{D-20})$$

$$\beta_{ik} = e_{mi} \tau_{mk} \quad (\text{D-21})$$

$$\theta_{ik} = \frac{x_i q_i e_{ki}}{x_j q_j} \quad (\text{D-22})$$

$$s_k = \theta_m \tau_{mk} \quad (\text{D-23})$$

$$\tau_{mk} = \exp\left(\frac{-a_{mk}}{T}\right) \quad (\text{D-24})$$

Subscript i identifies species, and j is a dummy index running over all species. Subscript k identifies subgroups, and m is a dummy index running over all subgroups. The quantity $v_k^{(i)}$ is the number of subgroups of type k in a molecule of species i . Values of the subgroup parameters R_k and Q_k and of the group interaction parameters, a_{mk} come from tabulation in the literature. Tables D.1 and D.2 show some parameter values.

TABLE D.1: UNIFAC-VLE subgroup parameters[†]

Main group	Subgroup	Group name	Rk	Qk
1	1	CH ₃	0.9011	0.848
1	2	CH ₂	0.6744	0.540
1	3	CH	0.4469	0.228
1	4	C	0.2195	0.000
2	5	CH ₂ =CH	1.3454	1.176
2	6	CH=CH	1.1167	0.867
2	7	CH ₂ =C	1.1173	0.988
2	8	CH=C	0.8886	0.676
2	9	C=C	0.6605	0.485
3	10	ACH	0.5313	0.400
3	11	AC	0.3652	0.120
4	12	ACCH ₃	1.2663	0.968
4	13	ACCH ₂	1.0396	0.660
4	14	ACCH	0.8121	0.348
5	15	OH	1.0000	1.200
6	16	CH ₃ OH	1.4311	1.432
7	17	H ₂ O	0.9200	1.400
8	18	ACOH	0.8952	0.680
9	19	CH ₃ CO	1.6724	1.488
9	20	CH ₂ CO	1.4457	1.180
10	21	CHO	0.9980	0.948
11	22	CH ₃ COO	1.9031	1.728
11	23	CH ₂ COO	1.6764	1.420
12	24	HCOO	1.2420	1.188
13	25	CH ₃ O	1.1450	1.088
13	26	CH ₂ O	0.9183	0.780
13	27	CH-O	0.6908	0.468
13	28	FCH ₂ O	0.9183	1.100
14	29	CH ₃ NH ₂	1.5959	1.544
14	30	CH ₂ NH ₂	1.3692	1.236
14	31	CHNH ₂	1.1417	0.924
15	32	CH ₃ NH	1.4337	1.244
15	33	CH ₂ NH	1.2070	0.936
15	34	CHNH	0.9795	0.624
16	35	CH ₃ N	1.1865	0.940
16	36	CH ₂ N	0.9597	0.632
17	37	ACNH ₂	1.0600	0.816
18	38	C ₅ H ₅ N	2.9993	2.113
18	39	C ₅ H ₄ N	2.8332	1.833
18	40	C ₅ H ₃ N	2.6670	1.553
19	41	CH ₃ CN	1.8701	1.724
19	42	CH ₂ CN	1.6434	1.416
20	43	COOH	1.3013	1.224
20	44	HCOOH	1.5280	1.532
21	45	CH ₂ Cl	1.4654	1.264
21	46	CHCl	1.2380	0.952
21	47	CCl	1.0060	0.724

TABLE D.2: UNIFAC-VLE Group Interaction Parameters, a_{mk} , in kelvins[†]

a_{mk}	k	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
m	Name	CH ₂	C=C	ACH	ACCH ₂	OH	CH ₃ OH	H ₂ O	ACOH	CH ₂ CO	CHO	CCOO	HCOO	CH ₂ O	CNH ₂	CNH ₂	(C) ₃ N	ACNH ₂	PYRIDINE	CCN	COOH
1	CH ₂	0	86.02	61.13	76.5	986.5	697.2	1318	1333	476.4	677	232.1	741.4	251.5	391.5	225.7	206.6	920.7	287.7	597	663.5
2	C=C	-35.36	0	38.81	74.15	524.1	787.6	270.6	526.1	182.6	448.8	37.85	449.1	214.5	240.9	163.9	61.11	749.3	0	336.9	318.9
3	ACH	-11.12	3.446	0	167	636.1	637.3	903.8	1329	25.77	347.3	5.994	-92.55	32.14	161.7	122.8	90.49	648.2	-4.449	212.5	537.4
4	ACCH ₂	-69.7	-113.6	-146.8	0	803.2	603.2	5695	884.9	-52.1	586.6	5688	115.2	213.1	0	-49.29	23.5	664.2	52.8	6096	603.8
5	OH	156.4	457	89.6	25.82	0	-137.1	353.5	-259.7	84	441.8	101.1	193.1	28.06	83.02	42.7	-323	-52.39	170	6.712	199
6	CH ₃ OH	16.51	-12.52	-50	-44.5	249.1	0	-181	-101.7	23.39	306.4	-10.72	193.4	-128.6	359.3	266	53.9	489.7	580.5	36.23	-289.5
7	H ₂ O	300	496.1	362.3	377.6	-229.1	289.6	0	324.5	-195.4	-257.3	72.87	0	540.5	48.89	168	304	-52.29	459	112.6	-14.09
8	ACOH	275.8	217.5	25.34	244.2	-451.6	-265.2	-601.8	0	-356.1	0	-449.4	0	0	0	0	0	119.9	-305.5	0	0
9	CH ₂ CO	26.76	42.92	140.1	365.8	164.5	108.7	472.5	-133.1	0	-37.36	-213.7	-38.47	-103.6	0	0	-169	6201	165.1	481.7	669.4
10	CHO	505.7	56.3	23.39	106	-404.8	-340.2	232.7	0	128	0	-110.3	11.31	304.1	0	0	0	0	0	0	0
11	CCOO	114.8	132.1	85.84	-170	245.4	249.6	200.8	-36.72	372.2	185.1	0	372.9	-235.7	0	-73.5	0	475.5	0	494.6	660.2
12	HCOO	90.49	-62.55	1967	2347	191.2	155.7	0	0	70.42	35.35	-261.1	0	0	0	0	0	0	0	0	-356.3
13	CH ₂ O	83.36	26.51	52.13	65.69	237.7	238.4	-314.7	0	191.1	-7.838	461.3	0	0	0	141.7	0	0	0	-18.51	664.6
14	CNH ₂	-30.48	1.163	-44.85	0	-164	-481.7	-330.4	0	0	0	0	0	0	0	63.72	-41.11	-200.7	0	0	0
15	CNH ₂	65.33	-28.7	-22.31	223	-150	-500.4	-448.2	0	0	0	136	0	-49.3	108.8	0	-189.2	0	0	0	0
16	(C) ₃ N	-83.98	-25.38	-223.9	109.9	28.6	-406.8	-598.8	0	225.3	0	0	0	0	38.89	865.9	0	0	0	0	0
17	ACNH ₂	1139	2000	247.5	762.8	-17.4	-118.1	-367.8	-253.1	-450.3	0	-294.8	0	0	-15.07	0	0	0	0	-281.6	0
18	PYRIDINE	-101.6	0	31.87	49.8	-132.3	-378.2	-332.9	-341.6	-51.54	0	0	0	0	0	0	0	0	0	-169.7	-153.7
19	CCN	24.82	-40.62	-22.97	-138.4	-185.4	157.8	242.8	0	-287.5	0	-266.6	0	38.81	0	0	0	777.4	134.3	0	0
20	COOH	315.3	1264	62.32	268.2	-151	1020	-66.17	0	-297.8	0	-256.3	312.5	-338.5	0	0	0	0	-313.5	0	0

VITA

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