Process Simulation of Ethyl tert-Butyl Ether (ETBE) Production from Naphtha Cracking Wastes

Pakorn Traiprasertpong, Apichit Svang-Ariyaskul

Abstract—The production of ethyl tert-butyl ether (ETBE) was simulated through Aspen Plus. The objective of this work was to use the simulation results to be an alternative platform for ETBE production from naphtha cracking wastes for the industry to develop. ETBE is produced from isobutylene which is one of the wastes in naphtha cracking process. The content of isobutylene in the waste is less than 30% weight. The main part of this work was to propose a process to save the environment and to increase the product value by converting a great majority of the wastes into ETBE. Various processes were considered to determine the optimal production of ETBE. The proposed process increased ETBE production yield by 100% from conventional process with the purity of 96% weight. The results showed a great promise for developing this proposed process in an industrial scale.

Keywords—ETBE, process simulation, naphtha cracking, Aspen Plus

TABLE I
COMPONENT AND COMPOSITION OF THE PRODUCTS FROM NAPHTHA CRACKING PROCESS

Component	Weight percent (Based on 100 kg ethylene)
Ethylene	100.00
Propylene	0.30
n-butane	5.20
i-butane	1.30
1-butene	16.00
cis-2-butene	5.30
trans-2-butene	6.60
isobutylene	27.40
1,3-butadiene	37.00
Methyl acetylene	1 ppm
Vinyl acetylene	0.30
Ethyl acetylene	0.10
n-pentane	0.50

I. INTRODUCTION

NAPHTHA cracking is one of the major processes in a petrochemical processing industry in which naphtha is cracked into shorter chain hydrocarbons. The major product is ethylene, which had the world production of 109 million tons in year 2006. The ethylene production yield is roughly a half and the rest is byproducts. The key byproducts are isobutylene, 1-butene, and 1,3-butadiene as shown in Table I.

This work was aimed to design a process to save the environment and to increase the production value by upgrading most of the key byproducts into one higher valued product. The industry can adopt this work to develop the ETBE production from naphtha cracking wastes. Ethyl *tert*-butyl ether (ETBE) is one of the most promising products that can be produced from isobutylene. Other byproducts, 1-butene and 1,3- butadiene, can be converted to isobutylene to produce ETBE as well.

ETBE is an anti-knocking additive to petro-oils and the production of ETBE is environmental friendly. ETBE is fast-degradable in water and soil. ETBE is also produced from ethanol which can be produced from biomass fermentation. ETBE is a competitive additive with MTBE (methyl *tert*-butyl ether) which is a former popular anti-knocking additive. Even though the production of MTBE is cheaper, ETBE is preferable as it is higher in octane rating but lower in BRvp, oxygen content, and water solubility and more environmental friendly.

The objective of this work was to design an ETBE production process from naphtha cracking byproducts by converting the majority of byproducts into ETBE. This work provided the detail information for the industry to use as example to develop ETBE production process from naphtha cracking byproducts. The majority of published ETBE production focused on only the reaction of isobutylene and ethanol. However, in this work, several processes were studied including the conversion of isobutylene to ETBE, conversion of other byproducts to isobutylene, separation of each byproduct, and purification of the final products. The design was optimized so that the product yield and purity were maximized.

II. PROCESS DESIGN

The overall process is illustrated in Fig. 1. Ethylene, a desirable product, was separated from byproducts by distillation tower T-101. Then, byproducts were separated in order to produce ETBE.

1,3-butadiene was first separated from other byproducts using extractive distillation tower T-201 before conversion to

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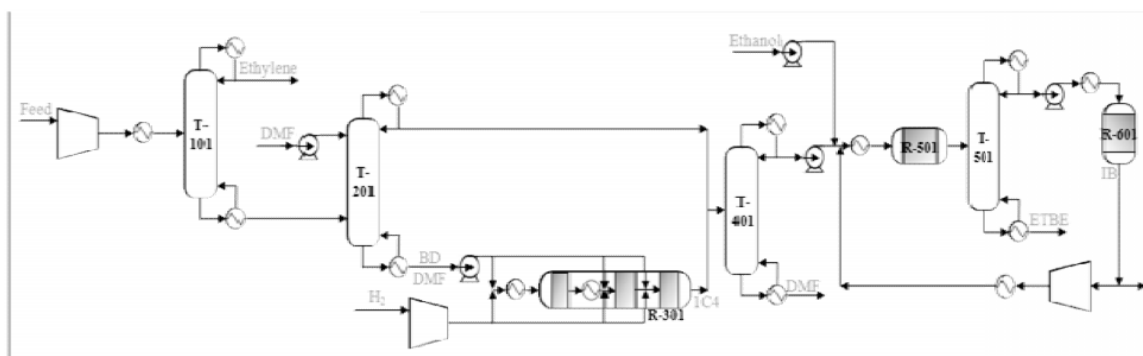
Fig. 1 Schematic diagram for ETBE production from naphtha cracking byproducts (DMF = dimethylformamide, BD = 1,3-Butadiene, 1C4 = 1-butene, IB = isobutylene, T-101/T-401/T-501 = distillation column, T-201 = extractive distillation column, R-301/R-501 = packed bed reactor)

TABLE II
REACTION AND RATE EXPRESSIONS OCCURRING OVER PD/AL$_2$O$_3$ CATALYST [6]

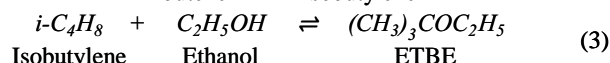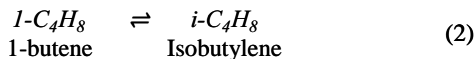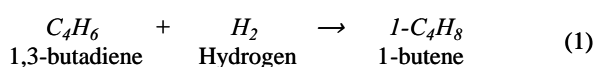| No.	Reaction	Rate expression	$k_{ref,i}$	E_a (J/kmol)
1	Butadiene + H$_2$ $\longrightarrow$ 1-butene	$r_1 = k_1 C_{BD} C_{H_2}^{0.5}$	$k_{ref,1} = 1.7361 \times 10^{-3}$	65.6×10^6
2	Butadiene + H$_2$ $\longrightarrow$ trans-2-butene	$r_2 = k_2 C_{BD} C_{H_2}^{0.5}$	$k_{ref,2} = 3.6176 \times 10^{-3}$	51.4×10^6
3	Butadiene + H$_2$ $\longrightarrow$ cis-2-butene	$r_3 = k_3 C_{BD} C_{H_2}^{0.5}$	$k_{ref,3} = 6.4830 \times 10^{-4}$	60.3×10^6
4	Butadiene + 2H$_2$ $\longrightarrow$ n-butane	$r_4 = k_4 C_{BD} C_{H_2}^{0.5}$	$k_{ref,4} = 1.7614 \times 10^{-3}$	48.3×10^6
5	1-butene $\longrightarrow$ trans-2-butene	$r_5 = k_5 C_{1C4} C_{H_2}^{0.5}$	$k_{ref,5} = 4.0509 \times 10^{-4}$	45.9×10^6
6	1-butene $\longrightarrow$ cis-2-butene	$r_6 = k_6 C_{1C4} C_{H_2}^{0.5}$	$k_{ref,6} = 4.8130 \times 10^{-4}$	40.2×10^6
7	1-butene + H$_2$ $\longrightarrow$ n-butane	$r_7 = k_7 C_{1C4} C_{H_2}^{0.5}$	$k_{ref,7} = 4.6865 \times 10^{-4}$	34.9×10^6
8	Isobutylene + H$_2$ $\longrightarrow$ Isobutylene	$r_8 = k_8 C_{IB} C_{H_2}^{0.5} \cdot \exp(-k_9 C_{BD})^a$	$k_{ref,8} = 6.6275 \times 10^{-5}$	39.1×10^6

$r_1 - r_8$ in unit of (mol/s.kg cat) $k_1 - k_8$ in unit of (mol/s.kg cat)(m^3/kmol)$^{1.5}$ $k_9 = 41.9$ m^3/kmol, C in unit of kmol/m^3

1-butene in R-301. Solvent for 1,3-butadiene extraction was recovered in tower T-401. The rest of the mixture was mostly 1-butene and isobutylene and there was no efficient method to separate these two components. 1-butene and isobutylene were fed into reactor R-501 for converting isobutylene to ETBE before converting 1-butene to isobutylene in reactor R-601. Isobutylene produced from R-601 was recycled to R-501. The reason 1-butene was converted isobutylene afterwards because 1-butene conversion reaction was counter-productive if large amount of isobutylene was present.

The main processes were reaction and separation. In the reaction processes, the major byproducts—isobutylene, 1-butene, and 1,3-butadiene—had to be mostly converted to achieve maximum ETBE production. The separation processes involves with the purification of the product and the feed for each reaction unit.

III. REACTION PROCESS

Various reaction routes were searched. One possible route was conversion of 1,3-butadiene to 1-butene, then conversion of 1-butene to isobutylene and finally, conversion of isobutylene to ETBE. The series of reaction can be described as (1)-(3):

$$\underset{\text{1,3-butadiene}}{C_4H_6} + \underset{\text{Hydrogen}}{H_2} \rightarrow \underset{\text{1-butene}}{1\text{-}C_4H_8} \tag{1}$$

$$\underset{\text{1-butene}}{1\text{-}C_4H_8} \rightleftharpoons \underset{\text{Isobutylene}}{i\text{-}C_4H_8} \tag{2}$$

$$\underset{\text{Isobutylene}}{i\text{-}C_4H_8} + \underset{\text{Ethanol}}{C_2H_5OH} \rightleftharpoons \underset{\text{ETBE}}{(CH_3)_3COC_2H_5} \tag{3}$$

A. Conversion of 1,3-butadiene to 1-butene

There are various kinds of catalysts that can be used for conversion of 1,3-butadiene to 1-butene (1). The hydrogenation of 1,3-butadiene could result in various C4 products. Pt and Pd based catalysts could be used to hydrogenate 1,3-butadiene [1]. Pt-based catalysts produced a mixture of butane isomers and butanes while Pd-based catalysts produced higher selectivity towards butenes [1]-[3] and had good activity, stability and selectivity to 1-butene [4], [5]. Therefore Pd/α-Al$_2$O$_3$ catalyst was chosen. Pd/α-Al$_2$O$_3$ catalyst properties and the reaction kinetics were obtained from [6]. According to Seth's work [6], the large presence of 1-butene in butadiene hydrogenation resulted in 1-butene conversion to undesirable C4 products. Therefore, 1-butene must be separated during butadiene hydrogenation. The rates of reactions are shown in Table II.

B. Conversion of 1-butene to isobutylene

1-butene can be converted to isobutylene through isomerization reaction. Various kinds of catalysts were searched for the highest yield of isobutylene production. Alumino silicate was one of the catalysts that can be used;

however, it produces low yield of isobutylene compared to fluorinated alumina [7], [8]. The catalyst chosen for this study was fluorinated η-alumina [9], [10]. The reaction is shown in (2). It was assumed that the polymerization of isobutylene was negligible. The rate of reaction can be expressed as shown in (4) and (5) in kmol/s.kg cat.

$$r'_B = 6.10\, e^{\frac{8006\, cal/mol.K}{RT}} \left(p_A - \frac{p_B}{K} \right)^n \qquad (4)$$

$$ln\, K = -1.4507 + \frac{2018.76}{T} \qquad (5)$$

C. Conversion of isobutylene to ETBE

The kinetics studies of ETBE production from isobutylene and ethanol have been studied through several publications [11]-[21]. The chosen catalysts were Lewatit K2631 and Amberlyst-15. Table III shows the reaction rate kinetics and conditions for each catalyst.

TABLE III
RATE OF REACTION FOR CONVERSION OF ISOBUTYLENE TO ETBE

Catalyst: Lewatit K2631 [11]	Temperature: 40 – 90 °C

$$r'_{ETBE} = \frac{k'_{ETBE}\left(a_{IB}a_{EtOH} - \frac{a_{ETBE}}{K} \right)}{a^3_{EtOH}}$$

$$k'_{ETBE} = 1{,}305{,}555{,}556\, exp\left(-\frac{86{,}133{,}040\, J/kmol}{RT} \right)$$

Catalyst: Amberlyst-15 [15]	Temperature: 40 – 80 °C

$$r'_{ETBE} = \frac{k_{si}\left(a^2_{EtOH}a_{IB} - \frac{a_{EtOH}a_{ETBE}}{K} \right)}{\left(1 + K_{EtOH}a_{EtOH} \right)^3}$$

$$ln\, K = 10.387 + \frac{4069.59}{T} - 2.89055\, ln\, T - 1.91544 \times 10^{-2}T$$
$$+ \left(5.28586 \times 10^{-5} \right)T^2 - (5.32977 \times 10^{-8})T^3$$

$$ln\, K_{EtOH} = -1.707 + \frac{1{,}323.07}{T}$$

$$k_{si} = 2{,}060{,}555{,}556\, exp\left(-\frac{60.4 \times 10^6\, J/kmol}{RT} \right)$$

Catalyst: Amberlyst-15 [17]	Temperature: 40 – 80 °C

$$r'_{ETBE} = \frac{k_{r1}\left(a_{EtOH}a_{IB} - \frac{a_{ETBE}}{K_1} \right)}{(a_{EtOH})^2}$$

$$ln\, K_1 = 10.387 + \frac{4069.59}{T} - 2.89055\, ln\, T - 0.01915T$$
$$+ \left(5.28586 \times 10^{-5} \right)T^2 - (5.32977 \times 10^{-8})T^3$$

$$k' = 4{,}383{,}333{,}333\, exp\left(-\frac{87.2 \times 10^6\, J/kmol}{RT} \right)$$

r′ in unit of kmol/s.kg catalyst. T in unit of Kelvin. R = 8,314 J/kmol.K

IV. SEPARATION PROCESS

From Table I, the main components that needed to be considered for separations were ethylene, byproducts (1,3-butadiene, 1-butene, and isobutylene), and ETBE. Ethylene and ETBE could be separated easily because their boiling points are very different. It is wise to separate isobutylene (feedstock for ETBE production) from 1,3- butadiene and 1-butene which could not be separated by conventional distillation due to their close boiling points. There was an efficient way to separate 1,3-butadiene from 1-butene and isobutylene but not for 1-butene and isobutylene.

It is important to separate 1-butene for the conversion of 1,3-butadiene because the excess of 1-butene led to undesirable products according to [6]. 1,3-butadiene could be purified using extractive distillation as a simple and cost efficient method even though it required high amount of solvent compared to feed amount [22]-[25]. Acetonitrile (ACN), *N*-methyl-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) could be used because solvent as they have higher affinity towards 1,3-butadiene compared with other C4 byproducts. ACN was undesirable because ACN causes complications in solvent recovery and environmental pollution. NMP has a good solubility even in water [22], [25]. DMF is well-compatible without forming azeotrope with C4 mixture. DMF was chosen over NMP for the simulation as its lower cost.

V. RESULTS AND DISCUSSION

Aspen Plus was used to simulate and to design the process. The thermodynamic model was NRTL. All distillation towers were RADFRAC model. The results and discussions were carried on in two sections—unit operations and overall process as illustrated in Fig. 1. The basis of the work had feed mass of 206,000 kg/hr with 50% ethylene and 50% byproducts. Byproduct compositions are shown in Table I.

A. Ethylene Separation (T-101)

Ethylene separation was carried out by using normal distillation as it had very different boiling point from other components. T-101 was optimized so that ethylene recovery and purity were over 99% while the energy consumption was the least by changing the reflux ratio, number of stage, feed stage, and feed temperature. The design equations were based on Fenske-Underwood-Gilland equation. The optimizal design column had 22 stages, feed stage of 10, condenser pressure and temperature of 28.6 bar and -15.3 °C, reboiler pressure and temperature of 29.3 bar and 124.1 °C, reflux ratio of 2.95, and distillate to feed ratio of 0.49.

B. Butadiene Extraction (T-201) and Solvent Recovery (T-401)

1,3-butadiene could be separated through extractive distillation using DMF as a solvent as discussed in section IV. The extractive distillation column in this study was adapted from [25] which used the column of 78 stages, reflux ratio of 1.4 kg/kg, and solvent to feed ratio of 7.5 kg/kg at ambient pressure. As can be seen from [25], the solvent amount was 7.5 times larger than the feed amount resulting in a requirement of extremely large column. In this work, the optimization parameters were solvent to feed ratio, distillate to feed ratio, and the reflux ratio in order to reduce the amount of solvent usage.

Fig. 2 shows weight fraction of 1,3-butadiene for 1,3-butadiene recovery in T-201 and for 1,3-butadiene in bottom stream of T-201 compared to key byproducts (1,3-butadiene, 1-butene, and isobutylene) versus weight ratio of DMF to feed of T-201 at reflux ratio of 1.4 kg/kg and 78 stages with the ratio of outlet DMF in distillate to bottom of 0.4. As shown in Fig. 2, the recovery of 1,3-butadiene was maximum at the

ratio of 4 kg solvent (DMF)/kg feed. This could come from the fact that the larger amount of DMF that came out of the distillate stream of T-201 was significant enough to bring larger amount of 1,3-butadiene with. However, the weight fraction of 1,3-butadien in the extract compared to key C4 components reached over 99% at 5 kg solvent (DMF)/kg feed. In this work, 4 kg solvent (DMF)/kg feed was selected to do further simulation because it had the highest potential with maximum 1,3-butadiene recovery with high purity. Further optimization was carried out by varying the reflux ratio and distillate to feed ratio to achieve 1,3-butadiene recovery of 99%. The corresponding reflux ratio and distillate to feed ratio were 2.5 and 0.34 kg/kg respectively. In conclusion, column T-201 had 78 stages, DMF feed stage of 1, feed stage of 55, condenser pressure and temperature of 1 bar and -8.3 ^{o}C, reboiler pressure and temperature of 1.7 bar and 45.5 ^{o}C, reflux ratio of 2.5, and distillate to feed ratio of 0.34.

After the extraction, DMF was extracted through a normal distillation column (T-401) due to its different boiling point from others. The recovery and purity were over 99%. The optimizal design column had 22 stages, feed stage of 7, condenser pressure and temperature of 6.4 bar and 42.6 ^{o}C, reboiler pressure and temperature of 7.1 bar and 241.2 ^{o}C, and reflux ratio of 1.
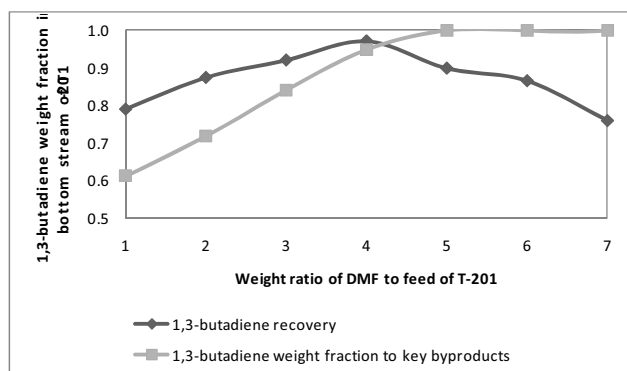

Fig. 2 weight fraction of 1,3-butadiene for 1,3-butadiene recovery in T-201 and for 1,3-butadiene in bottom stream of T-201 compared to key byproducts (1,3-butadiene, 1-butene, and isobutylene) versus weight ratio of DMF to feed of T-201 at reflux ratio of 1.4 kg/kg and 78 stages with the ratio of outlet DMF in distillate to bottom of 0.4

C. Conversion of 1,3-butadiene (R-301)

1,3-butadiene conversion process was established in order to produce 1-butene to produce isobutylene for ETBE production. 1,3-butadiene converted to 1-butene through hydrogenation process. In Table II, various C4 products were produced from Pd/α-Al$_2$O$_3$ [6]. The concentrations of 1-butene and hydrogen must be minimized to prevent undesirable products to occur. 1-butene came from 2 sources: the feed and butadiene conversion process. To achieve low concentrations of 1-butene and hydrogen, a packed bed reactor was simulated with partial feed to enter small amount of feed along the reactor. In Fig. 1, the feed entered PBR at 3 different points

along the reactor. The feed fraction to each point was equal for both C4 feed and hydrogen. The reactor temperature range was from 200-280 ^{o}C. The acceptable feed temperature was 250 ^{o}C because the utility was not too high while the conversion reached 100%. Fig. 3 shows the effects of ratio of hydrogen feed to C4 feed on the ratio of outlet 1-butene and 1,3-butadiene to the inlet 1,3-butadiene at 250 ^{o}C. Fig. 3 shows that at hydrogen feed ratio of 1.03, 1-butene ratio was maximum and 1,3-butadiene ratio was almost zero. When 1,3-butadiene was completely consumed at hydrogen feed ratio of 1.06, 1-butene started to drop and dropped drastically at hydrogen feed ratio of 1.1. An explanation was that as there was no 1,3-butadiene present, hydrogen reacted with 1-butene to form undesirable byproducts resulting in a diminish of 1-butene. Therefore, the hydrogen feed ratio was selected to be 1.03 each section of the reactor.
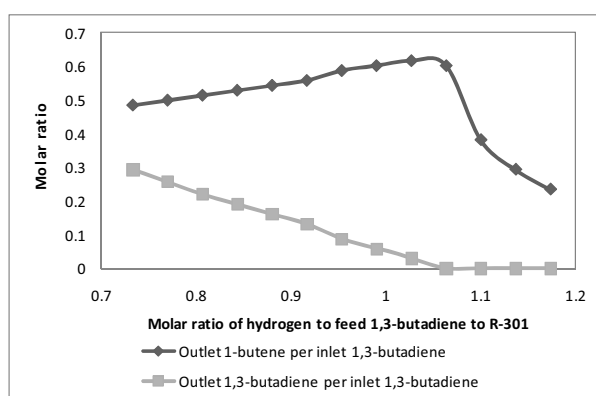

Fig. 3 Molar ratio of outlet 1-butene and 1,3-butadiene per inlet 1,3-butadiene versus molar ratio of feed hydrogen to feed 1,3-butadiene to reactor R-301

D. ETBE Production (R-501) and ETBE purification (T-501)

This unit consisted of a packed-bed reactor (R-501) and a distillation column (T-501) for purification. Isobutylene, 1-butene and ethanol were feed into R-501 reactor. There was no efficient way to separate isobutylene and 1-butene. As the conversion of 1-butene to isobutylene was reversible, the presence of isobutylene was counter-productive for 1-butene conversion. Therefore, 1-butene was converted into isobutylene after the ETBE production stage. Aspen Plus simulations were performed to determine the most desirable catalysts and operating conditions. The simulations were performed with Lewatit K2631 and Amberlyst-15 catalysts with packed bed reactor (PBR) at the operating condition range shown in Table IV. The molar ratio of ethanol to isobutylene was varied from 1.1:1 to 1.5:1. The simulation was based on constant catalyst weight (100 kg) and constant void fraction (0.4). Table IV shows that the highest isobutylene conversion was obtained from Lewatit K263 with the molar ratio of ethanol to isobutylene of 1.1:1 at feed temperature of 90 ^{o}C with adiabatic condition. It was logical

TABLE IV
MAXIMUM CONVERSION OBTAINED FROM EACH CATALYST AT ITS HIGHEST FEED TEMPERATURE FROM THE REFERENCES

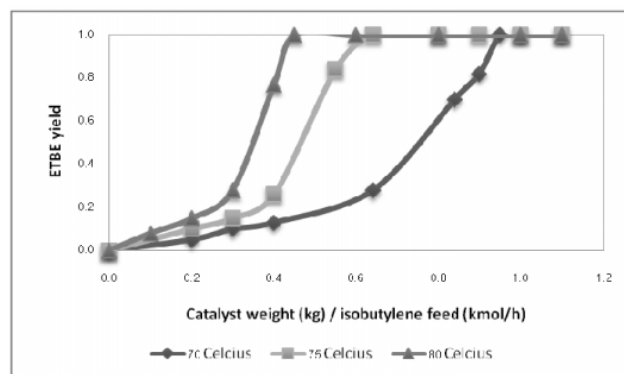| Feed Temp (°C)	Catalyst	Maximum conversion at certain molar ratio of feed (%)				
		1.5:1	1.4:1	1.3:1	1.2:1	1.1:1
90	Lewatit K2631 [11]	97.50	98.36	99.20	99.84	100.00
80	Amberlyst-11 [15]	28.54	23.47	23.47	23.46	23.41
80	Amberlyst-15 [17]	23.00	23.05	23.07	23.08	23.09

Fig. 4 ETBE yield versus catalyst weight (kg)/isobutylene feed (kmol/h) at various feed temperature of 70, 75, and 80 °C
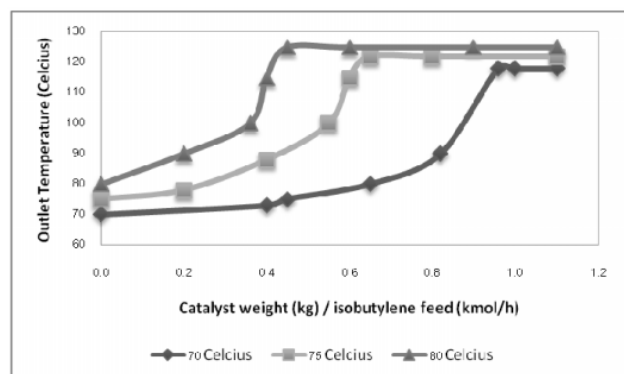

Fig. 5 Outlet temperature versus catalyst weight (kg)/isobutylene feed (kmol/h) at various feed temperature of 70, 75, and 80°C

that the conversion decreased with the increase of ethanol concentration from the rates of reaction in Table III. The amount of ethanol still needed to be larger than isobutylene to convert all isobutylene. Lewatit K2631 was chosen for isobutylene conversion. The maximum temperature that Lewatit K2631 could tolerate was 120 °C [11]. Fig. 4 and 5 show the effects of catalyst weight and inlet temperature on the highest ETBE yield and outlet temperature. Fig. 4 shows that ETBE yield reached unity early if the feed temperature was high. The reaction was exothermic; hence, the equilibrium was reached faster at high temperature. The inlet temperature and the catalyst weight were chosen in the manner that ETBE yield was unity and the outlet temperature was less than 120 °C. Fig. 5 shows that the only condition meeting the requirement was inlet feed temperature of 70 °C and catalyst weight per isobutylene feed of 0.96 kg (cat) / kmol/h (isobutylene) and this condition was chosen for reactor R-501. The operating pressure was 20 bar and the packed bed was 1.20 m³ with 0.42 void fraction.

Purification of ETBE was simulated in distillation tower T-501. The separation was quite simple as ETBE, ethanol, and other C4 components have very different boiling points. The normal distillation technique was applied here. The purity of ETBE was 96% weight for the product stream. Column T-501 had the configuration of number stage of 18, feed stage of 13, condenser pressure and temperature of 6.7 bar and 57.1 °C, reboiler pressure and temperature of 7.4 bar and 139.1 °C, and reflux ratio of 1.4.
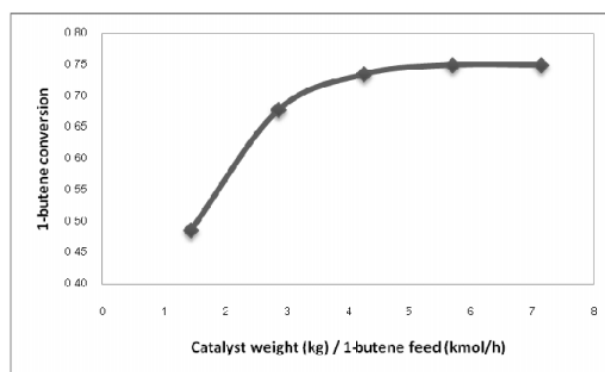
E. Conversion of 1-butene (R-601)

Fig. 6 Conversion of 1-butene versus catalyst weight (kg) per feed 1-butene (kmol/h) at 435°C

Reactor R-601 converted 1-butene to isobutylene; then, isobutylene was recycled to packed-bed reactor R-501 to produce ETBE. The conversion of 1-butene was a very slow reaction even though the temperature was at the maximum tolerance for the catalyst (435 °C). Fig. 6 shows the conversion of 1-butene at 435 °C with the catalyst weight ranged from 1.-7.2 kg catalyst per feed 1-butene (kmol/h). It shows that the amount of produced isobutylene had no change (0.75) after the catalyst weight of 5.7 kg/feed 1-butene (kmol/h). However, the catalyst weight of 2.9 kg/feed 1-butene (kmol/h) was chosen because the conversion was little smaller (0.68) while the amount of catalyst was much lower. The configuration of reactor R-601 was 4.26 m³ with a void volume of 0.42 at 40 bar and 435 °C.

F. Overall Process

The major objective was to design the process that can upgrade the majority of wastes from naphtha cracking process. From Table I, the mole fractions in the key byproducts were 0.34, 0.20, and 0.36 for isobutylene, 1-butene, and 1,3-butadiene respectively. In this proposed process, 1-butene and 1,3-butadiene were mostly converted to isobutylene. The proposed process increased the mole fraction of isobutylene to 0.68 or doubled the original amount. The conventional process can use only isobutylene to produce ETBE. The

maximum conversion for conventional process was 1 mole of ETBE/mole of isobutylene. The simulated conversion for the proposed process was 2 mole of ETBE/mole of isobutylene which was twice higher than the conventional process. The purity of ETBE final product was 96% weight.

VI. Conclusion

Process design of ETBE production from naphtha cracking wastes was simulated using Aspen Plus. The proposed process converted 1-butene and 1,3-butadiene to isobutylene which is the feedstock for ETBE production. The proposed process doubled amount of ETBE produced per isobutylene feed from conventional process with purity of 96% weight. This process was promising for the industry to develop further as it could double the conversion of wastes to product to save the environment and to increase the profitability of naphtha cracking process.

Nomenclature

C	Molar concentration
E_a	Activation energy
k	Rate constant
K	Equilibrium constant
n	Order of reaction
p	Partial pressure
r	Rate of reaction
R	Gas constant
T	Temperature

Acknowledgment

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