

# Study on Coupling Separation Process of ETBE and Absolute Ethanol

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The coupling separation process of ETBE production can be combined with the ethanol dehydration to save energy consumption. A new idea of introducing the dilute ethanol feedstock made from biomass material into the coupling separation process was proposed to enhance the sustainability of ETBE production. The ethanol concentrate is optimized in terms of minimizing the cost of energy consumption and maximizing the gross annual profit (GAP), respectively. The GAP is discussed at different prices of dilute ethanol feedstock and compared with those of conventional ETBE production process and process based on reactive distillation (RD). Meanwhile, the impact of ethanol-to-olefin ratio and conversion of isobutene on the optimal mass fraction is also explored. The result shows that the minimum feasible mass fraction of ethanol concentration is optimal when minimizing the energy consumption cost. The ethanol-to-olefin ratio and conversion of isobutene would affect the optimal mass fraction by affecting the minimum feasible mass fraction. Besides, to make the GAP maximum, the optimal mass fraction of ethanol concentration would take minimum or maximum feasible mass fraction at different prices of dilute ethanol feedstock. And the coupling separation process would have economic advantages compared to conventional ETBE process and RD-based process to some extent when the price of dilute ethanol feedstock is less than 7.372 €/t and the optimal mass fraction of ethanol concentration is 95 wt% in this case.

## 1. Introduction

The carbon monoxide and unburned hydrocarbons discharged by vehicles is one of the main source of air pollution; their emission can be reduced by increasing the octane number of the fuel through adding oxygenate additives, and Methyl tert-butyl ether (MTBE) was initially chosen by most refiners. However, a ban on MTBE is announced in 1999 as trace amount of this substance is found in drinking water. Thereafter, ethyl tert-butyl ether (ETBE) emerged as a suitable replacement. Compared with MTBE and other competitor compounds, ETBE has higher octane rating, lower oxygen contents, low water solubility and low blending Reid vapor pressure, and hence better blending and environmental characteristics.

ETBE can be synthesized from isobutene (IB) and absolute ethanol (EtOH) using two different processes, the conventional ETBE production process and reactive distillation (RD) based process. The former involves a reaction section composed by two reactors in series, and a separation section comprised by two distillation columns and a liquid-liquid extraction column. The latter is simpler than the former, as RD column is used. In these two processes, large amount of energy is consumed by distillation columns.

In the synthesis of ETBE, large amount of ethanol is consumed. It is mainly produced in two ways, one is hydration method with ethylene and water as raw materials, the other is the fermentation method with biomass as raw materials. Biomass is a renewable, sustainable, and environmentally friendly energy. It will be very significant if the absolute ethanol produced from biomass can be used to produce ETBE. To achieve this, a large amount of energy will be consumed to concentrate the biomass-based dilute ethanol, which contains ethanol 5 % -10 % by mass.

Since both production processes of ETBE and absolute ethanol includes multiple distillation columns, there is the possibility of saving energy with these two separation processes coupled. Zhang et al. (2011) proposed a distillation-extraction coupling separation to produce ether fuel and alcohol, and shows that the energy consumption can be saved by 52 %. Liu (2012) optimized the distillation and extraction column, and showed that the energy consumption can be reduced by 30 %, and 0.94 kg 92.5 wt% ethanol could be dehydrated while

1 kg ETBE was produced. Khaledi et al. (2005) investigated the nonlinearity of an ETBE reactive distillation column, and developed a predictive control scheme. Menezes et al. (2008) explored the isobutene conversion in the synthesis of ETBE, and concluded that the highest isobutene conversion was obtained at reaction temperatures ranging from 61 to 67 °C. Domingues et al. (2014) studied the reactive distillation columns producing ETBE, and compared genetic algorithms and particle swarm optimization algorithm. Domingues et al. (2017) compared the economic performance of a process based on reactive distillation with that of the conventional ETBE production process, and showed that the RD-based process has higher yield of ETBE product, as well as lower costs of ethanol and steam. Although many researchers studied the ETBE production process, there is no study on the optimization of the coupling separation process.

In this work, the dilute ethanol feedstock made from biomass material will be introduced into the coupling separation process to enhance the sustainability of ETBE production. The concentration of ethanol concentrate will be optimized; the impact of the ethanol-to-olefin ratio ( $b$ ) and the conversion of isobutene ( $\beta$ ) on the optimal mass fraction of ethanol concentrate will be explored. Furthermore, the effect of dilute ethanol's price ( $P_{DEtOH}$ ) is studied, and the appropriate price making the coupling separation process economically competitive is identified.

## 2. Coupling separation process

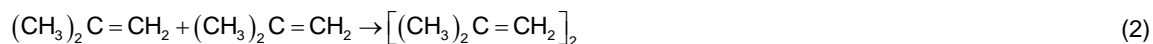
The coupling separation process involves one reactor, three distillation columns and two liquid–liquid extraction columns, as shown in Figure 1.

### 2.1 Reaction

Before entering the reactor, the C<sub>4</sub> feedstock are pre-treated in order to remove impurities (such as butadiene, nitrogen-containing compounds and metal ions), which deactivate the catalyst. Most of the feed is converted in the reactor, and ETBE is produced according to Eq(1), which is reversible and exothermic.



Besides, many side reactions exist in the reactor (Badia et al. 2013), and two main side reactions are commonly considered, as shown by Eq(2) and Eq(3). Other side reactions are negligible as the amount of generated byproducts is quite small.



### 2.2 Coupling separation

The separation of the reaction product starts in the RD column: the mixture of ETBE and ethanol is obtained as the bottom product; C<sub>4</sub>s raffinate and part of unreacted ethanol are obtained as the top product. Then, the mixture of ETBE and ethanol is mixed with the concentrated ethanol from ethanol concentration column by appropriate ratio, which will be illustrated in 3.2 Section. The distillate produced by the coupling separation column is a mixture with composition close to the ETBE-EtOH-H<sub>2</sub>O ternary azeotropic, and the bottom product is absolute ethanol. The feasibility of the coupling separation can be proved by boundary value method.

### 2.3 Ethanol recovery

Since the ethanol has more affinity towards water than towards the organic phase, the ethanol in stream 5 can be extracted in liquid-liquid extraction column I with water, and the extract liquor, i.e. dilute ethanol solution, is feed into ethanol extraction column II to extract the ethanol in distillate produced by coupling separation column. In addition, pure water (stream 13) is also feed to the ethanol extraction column II. Then, ETBE with purity greater than 98 wt% can be obtained as raffinate, and extract liquor (stream 15) with almost all unreacted ethanol recovered, is concentrated in ethanol concentration column, which is used to concentrate the dilute ethanol solution made from biomass.

## 3. Models of main equipment and assumptions

### 3.1 Reactor model

Although kinetic model was commonly used, reaction conversation is used in this work in order to explore whether the conversion of isobutene affect the optimal mass fraction of ethanol concentrate conveniently. Moreover, the molar concentration of each component can be derived theoretically with the conversion rate specified. In most industrial plants, the conversion of isobutene is generally in interval 94–97 %, and the ETBE selectivity is approximately 98 % (Domingues et al. 2012).

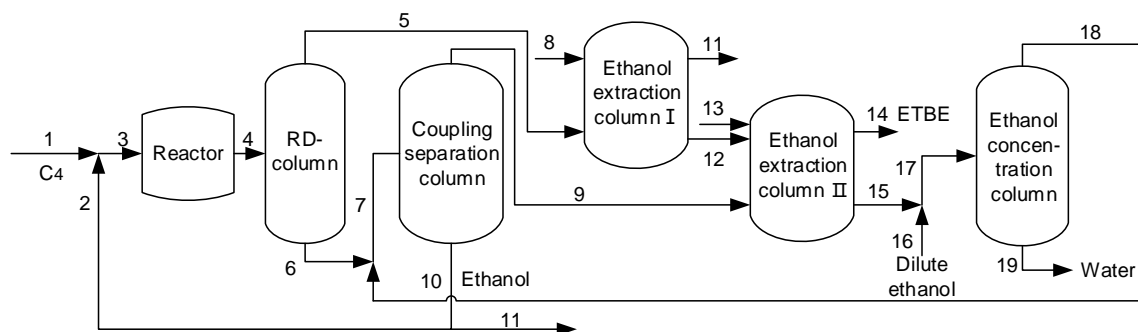


Figure 1: Coupling separation process for the production of ETBE

### 3.2 Vapor flow rate of distillation column

The vapor flow rate in rectifying section of distillation column could be calculated by Eq(4), and that in stripping section can be calculated by Eq(5) (Porter et al. 1991).

$$V = D \left[ 1 + \frac{R_F F}{\alpha - 1 D} \right] \quad (4)$$

$$V' = V - (1 - q)F \quad (5)$$

Where  $V$  is the vapor flow rate,  $D$  is the distillate flow rate,  $R_F$  is the ratio of actual reflux ratio to minimum reflux ratio,  $\alpha$  is relative volatility between the key components,  $F$  is the feed flow rate,  $q$  is the thermal condition of feed.

To calculate the relative volatility required in Eq(4), the azeotrope is treated as a pseudo component. The relative volatility between each pair of components is assumed to be constant in the distillation column and can be calculated according to Eq(6).

$$\alpha_{ik} = \frac{\gamma_i p_i^0}{\gamma_k p_k^0} \quad (6)$$

Where  $\gamma_i$  and  $\gamma_k$  are the activity coefficient,  $p_i^0$  and  $p_k^0$  are the vapor pressure of component/pseudo component, respectively (Vogelpohl, 2002).

### 3.3 Explanation and assumptions

In the reactive distillation column, ethanol is the middle-boiling component, while the inerts in  $C_4$  feedstock, such as n-butane and iso-butane, are the low-boiling components, and ETBE, DIB and TBA are the high-boiling species. Small amount of ethanol exists in the top product, while most ethanol stays in the bottom product. The fraction between ethanol contained in feed and that in the distillate is assumed to be constant, and it's assumed to be 0.9 in the calculation of minimum feasible mass fraction of ethanol concentration.

For the coupling separation column, ethanol, water and ETBE can form a ternary azeotrope, in which the molar ratio among ETBE, ethanol and water is 64 %:13 %:22 %. To guarantee absolute ethanol can be obtained at the bottom and reduce the ethanol to be recovered, the molar ratio of ETBE to water in stream 7 should approximately be 2.83:1, and the molar fraction of ethanol must be more than 13.04 %. Otherwise, the purity of absolute ethanol at bottom will be less than 99.5 wt%. For the ethanol concentration column, the mass fraction of ethanol concentrate is no more than 95 wt%, the azeotropic composition at 1 atm.

For extraction columns, the water consumption will vary along the ethanol-to-olefin ratio and the conversion of isobutene. But the water consumptions of both columns changed slightly. Therefore, it is assumed that the water consumptions are constants, and all water and ethanol go into extracts as the amount of water and ethanol existing in raffinate is very small.

### 3.4 Cost of energy consumption ( $C_Q$ ) and gross annual profit (GAP)

Since the sensible heat of the stream is very smaller compared with the latent heat, it could be neglected. For the mixture, the molar latent heat can be calculated according the mixing rule, the molar fractions of components and their molar latent heat. Besides, with the energy loss in condensers and reboilers ignored, their energy consumption equals to the heat duty caused by liquefaction and vaporization, and can be calculated by vapor flow rate and latent heat. The cost of energy consumption ( $C_Q$ ) can be calculated according to the following equations:

$$Q_C = \sum V_j \Delta H_j \quad \text{where} \quad \Delta H = \sum x_i \Delta H_i \quad (7)$$

$$Q_H = \sum V'_j \Delta H_j \quad (9)$$

$$C_Q = F_{\text{steam}} P_{\text{steam}} + F_{\text{CW}} P_{\text{CW}} \quad \text{where} \quad F_{\text{steam}} = \frac{Q_H}{\Delta H_{\text{steam}}} \quad \text{and} \quad F_{\text{CW}} = \frac{Q_C}{c_p (T_{\text{out,CW}} - T_{\text{in,CW}})} \quad (10)$$

Where  $\Delta H_i$  is the mole latent heat of component  $i$ ,  $\Delta H$  and  $\Delta H_j$  are mixed mole latent heat,  $x_i$  is the mole fraction of component  $i$ ,  $Q_C$  and  $Q_H$  are the energy consumption of all condensers and all reboilers, respectively;  $C_Q$  is the cost of energy consumption, M€/y,  $F$  is the flowrate,  $P$  is the price,  $\Delta H_{\text{steam}}$  is the latent heat of medium pressure steam,  $c_p$  is the heat capacities at constant pressure of water;  $T_{\text{out,CW}}$  and  $T_{\text{in,CW}}$  are the outlet and inlet temperatures of cooling water,  $V_j$  and  $V'_j$  can be calculated according to Eq. (4) and Eq. (5), respectively.

In order to compare the coupling separation process with other processes, the GAP should be determined, and the economic parameters are taken from Domingues et al. (2017). The GAP is calculated by Eqs(11) - (13).

$$GAP = R_{S14} + R_{S10} + R_{S11} - (C_{S1} + C_{S2} + C_{S16} + C_{\text{steam}} + C_{\text{CW}}) \quad (11)$$

$$R_i = 86,400 F_i N_{\text{day}} \eta P \quad (12)$$

$$C_i = 86,400 F_i N_{\text{day}} \eta P \quad (13)$$

Where  $R_i$  is the revenue of product stream  $i$ ,  $C_i$  is the cost of stream  $i$ , steam or cooling water,  $F_i$  is the flowrate of stream  $i$ .  $N_{\text{day}}$  is the number of days per year,  $\eta$  is the conversion factor of kg to ton.

In the calculation, the mass flowrate of  $C_4$  is 1.81 kg/s with an isobutene content of 45 wt%, and the MP steam used in this process is 20.3 bar, 213.3 °C; the inlet and outlet cooling water temperatures are 26 °C and 40 °C, respectively. The economic parameters shown in Table 1 are used. The price of dilute ethanol feedstock has great impact on the GAP of coupling separation process, and will be discussed in the next section.

Other values specified in this work are as follows unless special instructions: for reactor, the ethanol-to-olefin ratio is 1.5, conversion of isobutene ( $\beta$ ) is 0.95; for RD column, the fraction that ethanol in feed enters the distillate is 0.1; for extraction columns, the flowrates of water stream 8 and 13 are 0.59 kg/s, 0.28 kg/s.

Table 1: Economic parameters used in the economic evaluation

Parameters	Value	Parameters	Value
$P_{\text{ETBE}}$	1,270 €/t	$P_{\text{C4s}}$	375 €/t
$P_{\text{EtOH}}$	750 €/t	$P_{\text{steam}}$	30 €/t
$P_{\text{C4}}$	500 €/t	$P_{\text{CW}}$	0.51 €/t

## 4. Results

### 4.1 Optimization by minimizing the cost of energy consumption

For different ethanol-to-olefin ratio ( $b$ ) and conversion of isobutene ( $\beta$ ), the cost of energy consumption ( $C_Q$ ) versus  $x$  curves are shown in Figure 2a. This figure shows the cost increases along the purity of ethanol concentration. In addition, with  $b$  kept unchanged (e.g.  $b = 1.5$ ), the variation of the energy cost along ethanol concentrate under different  $\beta$  is very small. Similar situation exists when  $\beta$  is kept unchanged and  $b$  changes. Hence,  $b$  and  $\beta$  do not affect the monotonicity of energy cost, and the optimal mass fraction corresponding the minimum energy cost must be the minimum feasible value ( $x_{\text{min}}$ ). However,  $b$  and  $\beta$  affect the optimal ethanol concentration, as shown by Eq(14), which is derived based on the material balance and composition ratio mentioned in section 3.3. It should be noted that the corresponding flowrate of the dilute ethanol in this case is zero, the ethanol concentration column is more like a recovery column for recycling unreacted ethanol.

$$x_{\text{min}} = 1 - \frac{b}{0.7225b + 1.7442\beta} \quad (14)$$

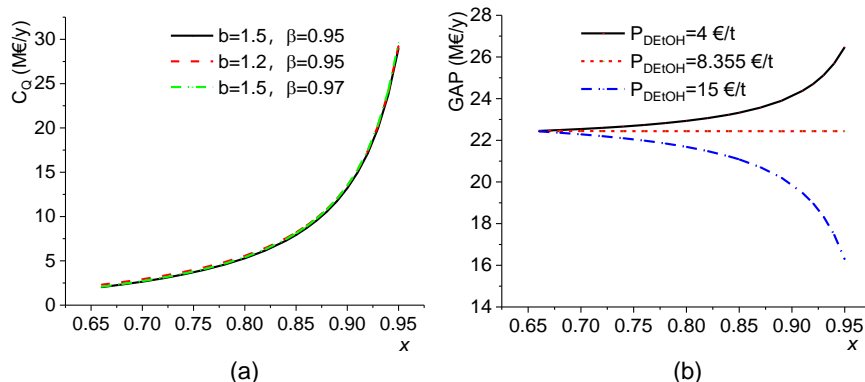


Figure 2: (a) The cost of energy consumption ( $C_0$ ) at different  $b$  and  $\beta$ . (b) Variation trends of GAP along ethanol concentrate at different  $P_{DEIOH}$

#### 4.2 Optimization by maximizing GAP

The optimal mass fraction of ethanol concentrate can also be explored by maximizing the GAP, and it is better than by minimizing the cost of energy consumption, as the manufacturers are more interested in profit. The variation trend of GAP along the mass fraction of ethanol concentrate is different at different prices of dilute ethanol, and three circumstances are identified.

(1)  $P_{DEIOH} > 8.355$  €/t. The GAP of coupling separation process decreases as the mass fraction increases, the reason is that the cost of raw material and energy increases faster than the product value, as shown by the GAP versus  $x$  curve ( $P_{DEIOH} = 4$  €/t) in Figure 2b. The optimal mass fraction of ethanol concentrate is 66 wt%, only the recovered ethanol is concentrated in this case.

(2)  $P_{DEIOH} = 8.355$  €/t. When the mass fraction of ethanol concentrate increases from 66% to 95%, the GAP of the coupling separation process is almost the same, as shown in Figure 2b. The reason is that the cost of raw material and energy increases as fast as the product value. However, when the mass fraction of ethanol concentrate is 66 wt% (i.e. the flowrate of dilute ethanol is zero), it is more convenient to operate and the labor cost will be smaller. Therefore, the optimal mass fraction of ethanol concentrate is 66 wt%.

(3)  $P_{DEIOH} < 8.355$  €/t, the GAP of coupling separation process increases along ethanol concentrate, as the cost of raw material and energy increases slower than the product value. The optimal mass fraction of ethanol concentrate is 95 wt% (azeotropic composition at 1 atm).

#### 4.3 Analysis and comparison of the GAP

For the conventional ETBE process and the RD-based process, their GAPs are 23.350 M€/y and 23.587 M€/y, respectively (Domingues et al., 2017). For the coupling separation process studied in this work, by using the same parameters, its GAP can be compared with those of the former two processes. From the previous section, it can be seen that the price of dilute ethanol solution made from biomass raw materials has a great impact on the GAP. The relationship between GAP and  $P_{DEIOH}$  is shown in Figure 3. Similarly, the variation of GAP along the price of dilute ethanol is discussed in four intervals.

(1)  $P_{DEIOH} \geq 8.355$  €/t. In this interval, the GAP of the coupling separation process reaches the maximum value when the ethanol concentration is 66%, and the maximum GAP is 22.440 M€/y, smaller than those of conventional ETBE process and RD-based process. Hence, the coupling separation process is not competitive economically, and its sustainability is not enhanced since the dilute ethanol made from biomass

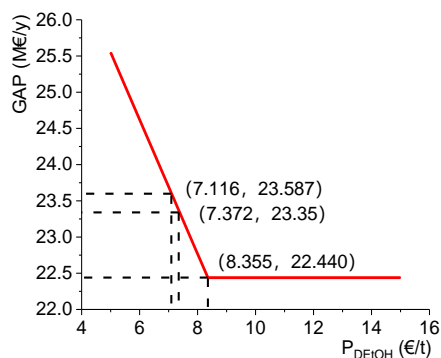


Figure 3: The relationship between GAP of the coupling separation process and  $P_{DEIOH}$

raw material is not used. Besides, the investment cost of the coupling separation process is greater than the other two processes, as there are more columns in the coupling separation process. Therefore, the coupling separation process is not a better choice in this interval.

(2)  $7.372 \text{ €/t} < P_{DEIOH} < 8.355 \text{ €/t}$ . In this interval, the GAP of the coupling separation process will reach the maximum when the mass fraction of ethanol concentration is 95 wt%. However, the GAP of the coupling separation process is still smaller than those of the other two processes, as shown in Figure 4. Hence, it has no economic advantages. However, its sustainability of production is better as dilute ethanol feedstock is used.

(3)  $7.116 \text{ €/t} < P_{DEIOH} < 7.372 \text{ €/t}$ . In this interval, the GAP of the coupling separation process reaches the maximum when the mass fraction of ethanol concentration is 95 wt%. And the GAP of the coupling separation process is greater than that of the conventional ETBE process but smaller than that of RD-based process. Hence, the coupling separation process has economic advantages and better sustainability.

(4)  $P_{DEIOH} < 7.116 \text{ €/t}$ . In this interval, the GAP of the coupling separation process reaches the maximum when the ethanol concentration is 95 wt%. And the GAP of the coupling separation process is greater than those of the other two processes, i.e.  $\text{GAP} > 23.587 \text{ M€/y}$ . The coupling separation process has obvious advantages in economic benefit and sustainability.

## 5. Conclusions

The analysis of optimal mass fraction of ethanol concentrate revealed that the cost of energy consumption is monotone increasing along the feasible mass fraction, so the energy consumption cost takes minimum at the minimum feasible mass fraction. The ethanol-to-olefin ratio and conversion of isobutene affect the optimal mass fraction of ethanol concentration by affecting the minimum feasible mass fraction, and the mathematical equation was derived. Besides, the monotonicity of GAP along the feasible mass fraction varies at different price intervals of dilute ethanol feedstock, then the optimal mass fraction of ethanol concentrate varies along the price of dilute ethanol feedstock. When  $P_{DEIOH} \geq 8.355 \text{ €/t}$  and  $P_{DEIOH} < 8.355 \text{ €/t}$ , it is 66 wt% and 95 wt%, respectively. In addition, the coupling separation process has economic advantages compared to conventional ETBE process and RD-based process only when the price of dilute ethanol feedstock is less than 7.372 €/t, and its sustainability is better.

## Acknowledgments

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