

## Process simulation of reactive distillation in dividing wall column for ETBE synthesis process

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Process intensification and energy integration represent ways of economical efficiency, as well as environmental friendly operating conditions.

In this paper, the process of reactive distillation in dividing wall column for ethyl-tert-butyl-ether (ETBE) synthesis is presented. Process integration and process simulation methodology was applied for the above mentioned process creation.

The aim of this process was to operate in a single apparatus the synthesis of ETBE from isobutene and ethanol and to separate the resulting ETBE as a product and the excess of ethanol in order to recycle it in the process.

In this paper are presented the results of the simulation, emphasizing the energy implications in this process, as well as the column main characteristics.

### 1. Introduction

Despite its high energy consumption, distillation is the widest used separation technique in petrochemical and chemical plants. It contributes about 40% to the total energy consumption of these industries. Multiple mixture separation is generally performed in a sequence of distillation columns. It has been demonstrated that thermal coupling can be very successfully by reducing energy demands up to 30-40% compared to direct or indirect separation sequences (Triantafyllou and Smith, 1992; Wolff and Skogestad, 1995; Emtir et al., 2001, Isopescu et al, 2005). The total integrated structure, the Petlyuk distillation column, built in a single shell (figure 1) represents the dividing wall distillation column (DWC) which can bring also important capital cost savings. On the other hand, in chemical and petrochemical industry there is a lot of potential to use synergy between processes, especially combining chemical reactions and distillation. Performances of systems combining reaction and separation depend on more factors as level of heat integration, level of exploitation of synergy potential. These factors are determined by the combined topological structure of the process.

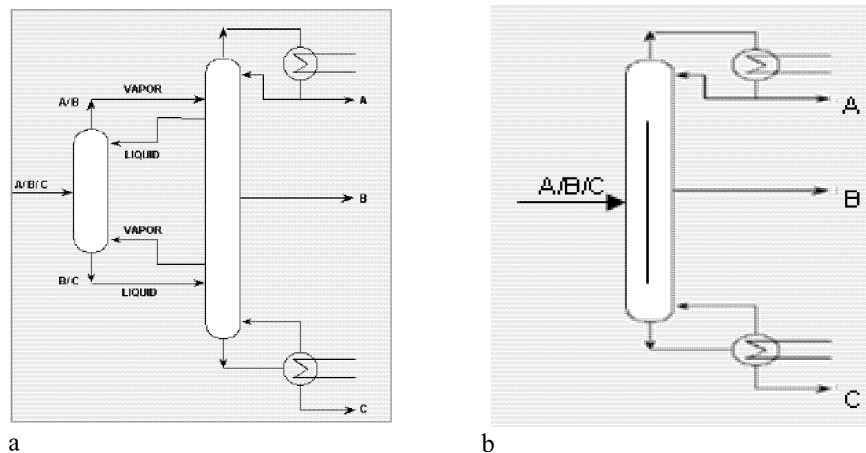


Figure 1. Petlyuk distillation column (a) and DWC (b)

The advantages of reactive distillation, such as increased conversion due to overcoming equilibrium limitation and less energy consumption, are well known (Muller and Kening, 2005). If reactive distillation and DWC are further integrated, a reactive divided wall distillation column will be generated (RDWDC). This unit is a highly integrated configuration as it contains a reactive part placed in a certain zone of the DWC, generally in the prefractionator. The following reactive systems can be considered suitable for this type of integration: reactive systems with more than two products (e.g. with consecutive and side reactions), system containing both reactive and non-reactive components, reactive systems with an excess of a reagent. The RDWDC seems to be a very attractive and challenging process and some theoretical studies have been focused on modeling and control of a RDWDC (Hernandez et al., 2009, Bumbac et al., 2006).

## 2. Kinetic and thermodynamic study

An ecologically alternative to increase the octane index simultaneously with reduction of unsaturated components of gasoline is to generate tertiary ethers compounds from reaction between isobutene components, which exist in the raw gasoline produced in FCC (fuel catalytic cracking) plant of a refinery site, and alcohols. ETBE (ethyl-tert-butyl-ether) is an important oxygenated compound which can be obtained by the direct treating of the raw light gasoline with ethanol, in specific reaction conditions of temperature and pressure in the presence of acidic ion exchange resin catalyst as Amberlyst type. These etherification reactions are chemical equilibrium limited, and face challenges with product purification. The chemical reaction between iso-butene (IB), ethanol (EtOH) is:



An EtOH excess is used in the reaction system (molar ratio EtOH/i-C<sub>4</sub>= is of 1.15). Due to higher polarity of ethanol compared to the other components, the reaction mixture

presents a strong non-ideal behavior and consequently the kinetic expressions have to be formulated in activities. Also, more realistic rate expressions are possible using LHHW model, which is considered closer to real mechanism of catalyst surface transformations. The activities are calculated using UNIFAC model to predict the behavior of a homogeneous mixture of ethanol and C<sub>4</sub> hydrocarbons over the whole concentration range, also at boiling temperature. The residue curves maps (figure 2) suggest the separation (by distillation) possibilities in a very concise way.

According to previous study (Bumbac G. et al., 2006) the kinetic parameters in the ETBE synthesis were obtained by the model fit to experimental data corresponding to conversion interval 0.01-0.40. Table 1 presents the kinetic model used in the present work.

Table 1 Kinetic model

| Reaction rate expression  | Arrhenius parameters   |
|---|--|
| $r_{\text{ETBE}} = \frac{k_1 \cdot (a_{\text{EtOH}} \cdot a_{\text{IB}} - a_{\text{ETBE}} / K_e)}{(1 + K_{\text{EtOH}} \cdot a_{\text{EtOH}})^2}$ | $k_1 = k_0 \cdot e^{-E/z}$                                       |
| $K_{\text{EtOH}} = 27 \cdot \exp\left(\frac{11000}{R} \cdot \left[\frac{1}{T} - \frac{1}{303}\right]\right)$                                      | $z = \frac{1}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_m}\right)$ |

The ethanol adsorption constant is given by Zang et al. (1997) and T<sub>m</sub> is 325 K. The kinetic parameters, as estimated by Bumbac et al (2004) are:

k<sub>0</sub>=103.2743 mole/(gcat.dry.h) and E=35474 J/mol.

The equilibrium constant K<sub>e</sub> is calculated with the relation (Vila et al., 1993):

$$\ln K_e = 1140.912 - \frac{14580}{T} - 232.9 \cdot \ln T + 1.087 \cdot T - 1.114 \cdot 10^{-3} \cdot T^2 + 5.538 \cdot 10^{-7} \cdot T^3 \quad (2)$$

### 3. Case study

The synthesis and separation of ETBE was studied in two alternatives. The first alternative denoted by “base case” consists in a sequence of two columns: the first column is an integrated reaction-separation unit (RDC) and the second column is a conventional distillation column.

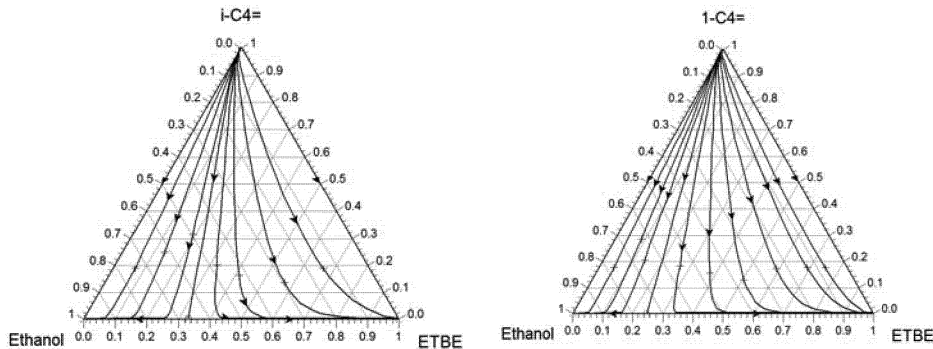


Figure 2. Residue curve maps for butene-EtOH-ETBE mixture

The first unit, a RDC, is used to perform the ETBE synthesis and to separate it at very high concentration at the bottom of the column, while the second distillation column separate EtOH from 1-butene in order to recycle EtOH in the process. The second alternative uses a RDWC that include both columns previously defined.

### 3.1 Base case

The flowsheet for the base case (a pilot plant case) is represented in figure 3. The distillation column has a catalytic reactive part simulated in ASPEN-HYSYS by means of a series of well mixed reactors, while the separation is realized on the trays above and below the reactive zone.

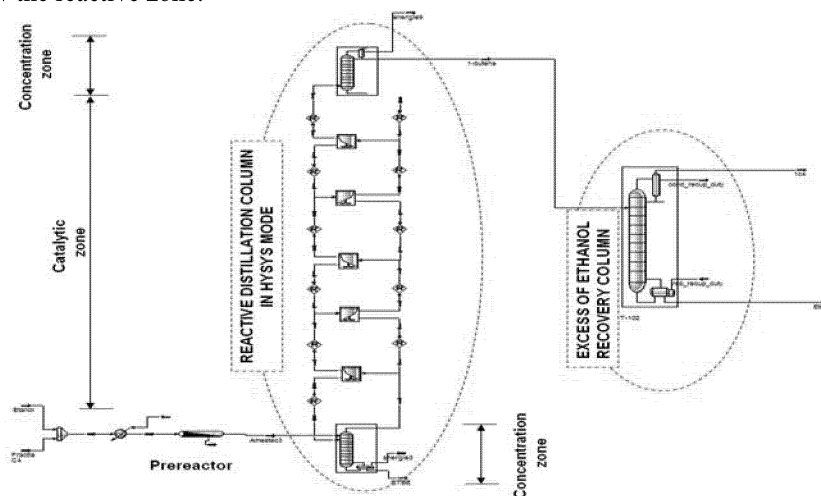


Figure. 3 Base Case (RD with external excess of EtOH recovery)

The main characteristic of the feed are presented in figure 4. As can be seen the outlet from pre-reactor (see figure 3 for details) contains ETBE 35 % mol corresponding to a thermodynamic chemical equilibrium. A convergent solution is obtained corresponding to a conversion of i-butene to ETBE of over 98% and purity of ETBE of 90 % (wt).

| Name                             | Feed in process |
|----------------------------------|-----------------|
| Vapour Fraction                  | 0.0000          |
| Temperature (C)                  | 20.00           |
| Pressure (atm)                   | 10.86           |
| Molar Flow (kgmole/h)            | 0.5428          |
| Mass Flow (kg/h)                 | 28.82           |
| Liquid Volume Flow (m3/h)        | 4.535e-002      |
| Heat Flow (kJ/h)                 | -5.611e+004     |
| Master Comp Mole Frac (1-Butene) | 0.4200          |
| Master Comp Mole Frac (Ethanol)  | 0.2999          |
| Master Comp Mole Frac (i-Butene) | 0.2800          |
| Master Comp Mole Frac (ETBE)     | 0.0000          |

a.

| Name                             | RDC_feed    |
|----------------------------------|-------------|
| Vapour Fraction                  | 0.0000      |
| Temperature (C)                  | 60.00 *     |
| Pressure (atm)                   | 10.66       |
| Molar Flow (kgmole/h)            | 0.4086      |
| Mass Flow (kg/h)                 | 28.82       |
| Liquid Volume Flow (m3/h)        | 4.287e-002  |
| Heat Flow (kJ/h)                 | -5.672e+004 |
| Master Comp Mole Frac (1-Butene) | 0.5580      |
| Master Comp Mole Frac (Ethanol)  | 0.0700      |
| Master Comp Mole Frac (i-Butene) | 0.0436      |
| Master Comp Mole Frac (ETBE)     | 0.3284      |

b.

Figure 4 Feed characteristics at inlet in the process (a), and at inlet of the RDC (b)

### 3.2 Reactive divided wall distillation column

The best topology found for the RDWDC is presented in figure 5. As it can be noticed, the side draw is very close to the lower border of the wall. This structure led to a good solution in terms of ETBE purity and EtOH recovery (figure 6).

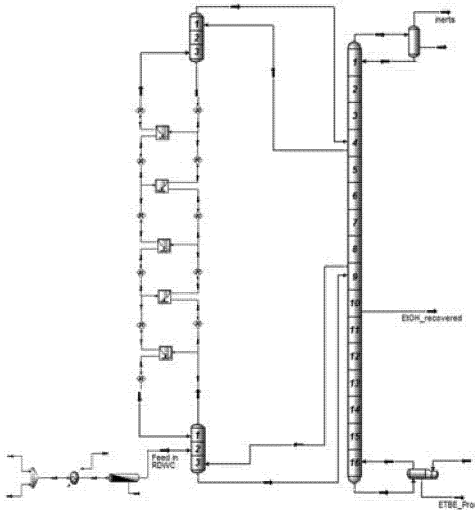


Figure 5. RDWDC for ETBE synthesis and separation

| Name                            | ETBE_Prod  | Name                              | EtOH_recovere |
|---------------------------------|------------|-----------------------------------|---------------|
| Vapour Fraction                 | 0.0000     | Vapour Fraction                   | 1.0000        |
| Temperature [C]                 | 140.3      | Temperature [C]                   | 109.3         |
| Pressure [atm]                  | 11.35      | Pressure [atm]                    | 11.15         |
| Molar Flow [kgmole/h]           | 0.1303     | Molar Flow [kgmole/h]             | 8.655e-002    |
| Mass Flow [kg/h]                | 12.06      | Mass Flow [kg/h]                  | 5.039         |
| Liquid Volume Flow [m3/h]       | 1.599e-002 | Liquid Volume Flow [m3/h]         | 7.723e-003    |
| Heat Flow [kW]                  | 2.364      | Heat Flow [kW]                    | -2.046        |
| Master Comp Mole Frac (1-Buten  | 0.0722     | Master Comp Mole Frac (1-Buten    | 0.5853        |
| Master Comp Mole Frac (Ethanol  | 0.1072     | Master Comp Mole Frac (Ethanol    | 0.2526        |
| Master Comp Mole Frac (i-Butene | 0.0057     | Master Comp Mole Frac (i-Butene   | 0.0613        |
| Master Comp Mole Frac (ETBE)    | 0.8148     | Master Comp Mole Frac (ETBE)      | 0.1008        |
| The bottom product in figure 5  |            | The side draw product in figure 5 |               |

Figure 6. Results for RDWDC obtained in the frame of ASPEN-HYSYS simulation

The side draw (EtOH\_recovered in figure 5) is recycled to the RDWDC above the reactive zone on the feed side of the wall. The results obtained in the frame of ASPEN-HYSYS simulator show that ethanol has a good recover ratio as side draw fraction in vapor phase. The total energy consumption in the RDWC is 3.004 kW which represents an energy reduction with 36 % compared with the base case (4.70 kW).

#### 4. Conclusion

The use of a RDWC in ETBE synthesis and separation provides important energy savings. The purity of ETBE obtained as bottom product is high, and the excess of EtOH can be recirculated to the prefractionating zone allowing a good overall yield of the process.

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