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Comparative study of conventional, reactive-distillation and pervaporation integrated hybrid process for ethyl tert-butyl ether production

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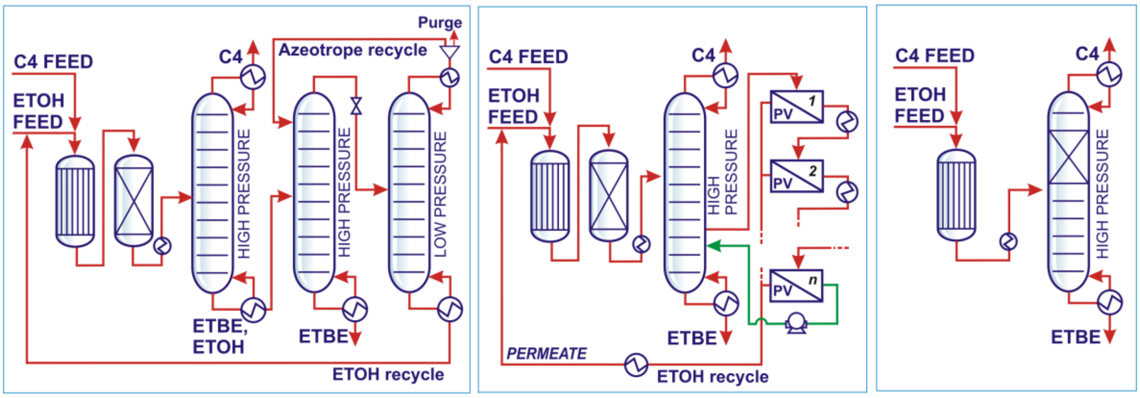
Graphical abstract



Highlights:

- Different processes for ETBE production are evaluated
- We propose the use of pervaporation to unload a distillation column.
- Alcohol-selective membranes are evaluated for removal of ethanol
- Reactive distillation allows a significant increase in the conversion of the reactants
- Process comparison was made based on energy consumption.

Abstract

Ethyl tert-butyl ether (ETBE) is widely used as an oxygenate additive to gasoline; however, a drawback in the conventional ETBE manufacture is the energy intensive product recovery process, making ETBE expensive. The purification process of ETBE involves the separation of ETBE, mixed C4 hydrocarbons and unreacted ethanol. The unreacted ethanol forms azeotropic mixtures with ETBE that are difficult to separate by distillation. In this work, a comparative study between the conventional process to produce ETBE and two alternative intensified processes is presented by means of process simulation in Aspen Plus. One of the alternative methods for improving the separation and purification section of ETBE is the use of a hybrid distillation-pervaporation process with alcohol-selective membranes, which allows to reach the target ETBE purity (95.2 wt%) with a lower energy consumption and at the same time the permeate stream, with a high ethanol content, is recycled back to the reaction section. Alternatively, the production of ETBE by means of reactive distillation is analyzed for the same basis of calculation. The results show that the reactive distillation allows a significant increase in the conversion of the reactants, but in contrast the energy consumption is higher than in the other processes evaluated.

Keywords: Membrane, Pervaporation, Reactive Distillation, Simulation, Purification

1. Introduction

The current concerns about sustainability of fossil fuels, in addition to the legislation aimed at reducing greenhouse gas emissions, have forced the industry to search for renewable fuels with smaller carbon footprints to replace (either completely or partially) the conventional fuels [1]. Oxygenate additives contain oxygen as part of their chemical structure and are usually employed as gasoline additives. These additives increment the octane rating and combustion quality and reduce particulate emission and carbon monoxide production [2]. Tertiary alkyl ethers, such as methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE), are commonly used as octane improvers for liquid fuels. As consequence of the negative impacts that MTBE has on the environment, ETBE has become a popular alternative oxygenate additive for gasoline. In addition, it has higher heating value and lower oxygen content, lower water solubility and faster degradation in soils [1].

ETBE is produced on industrial-scale by a reversible reaction of isobutene (IB) and ethanol (EtOH) with a strong acidic macroporous ion exchange resign in liquid phase at 10 bar. A drawback in the conventional ETBE manufacture is the energy intensive product recovery process, making ETBE expensive. The purification process of ETBE involves the separation of ETBE, mixed C4 hydrocarbons and unreacted ethanol. Unfortunately, the unreacted ethanol forms azeotropic mixtures with ETBE that are difficult to separate by distillation. For this reason, in this work we have evaluated two alternatives that are part of the tools for the process intensification, such as the production of ETBE by means of: i) a pervaporation integrated hybrid process, and ii) reactive distillation.

Pervaporation (PV) is a separation technology where a liquid mixture (feed) is placed in contact with one side of a membrane and the permeated product (permeate) is removed as a low-pressure vapor from the other side [3]. The affinity between the permeant and the polymer membrane material, as well as its mobility through the membrane matrix, are the main factors for the transport of the permeating compounds. The separation of organic-organic mixtures is possibly the most challenging application in pervaporation, and for this reason the development of new membranes has been addressed in numerous studies in the last two decades [4-6].

Hybrid separations integrate two different unit operations that complement each other to solve a defined separation task [7]. This arrangement enables the use of each unit operation in the operating window in which it outperforms all others. While distillation provides large capacities and simple operation, membranes potentially offer a high selectivity and low energy consumption, as well as a compact and modular design [8]. For this reason, we have done an analysis of a hybrid process combining PV with alcohol-selective membranes with distillation for ETBE production. Detailed reviews on pervaporation-based hybrid processes were presented by Lipnizki et al. [9] and recently by Holtbrügge [10].

On the other hand, the option of producing ETBE by means of reactive distillation (RD) has also been considered. The development of the catalytic or reactive distillation that unites in the same equipment catalyst and distillation devices finds its main applications for reversible reactions, such as ETBE synthesis, so as to shift an unfavorable equilibrium by continuous reaction product withdrawal [11,12].

Some recently published technical reports show that in Europe the projected gasoline consumption is expected to further decrease towards 2020 in favour of the use of diesel vehicles [13]. However the demand of gasoline ether oxygenates is expected to decrease less, as the biofuels directive mandates that the amount of fuels originating from renewable biological resources has to increase over time, up to 10%. The shift from MTBE to ETBE is expected to continue as ETBE derived from bio-ethanol is considered a biofuel. At present, there are approximately 30 ETBE plants located in Europe [13,14]. In 2013, Europe was the major ETBE consumer, accounting for 76.5% of the global demand. It was followed by the APAC region (17.5%) and North America (2.5%). Particularly, global ETBE market is expected to grow at 4% annually; Japan and EU countries will be the main contributors to this growth [14]. Taking into account that in the manufacture of ETBE the energy cost required by the purification stages represents a high percentage of the operating cost, it is relevant to make a comparative study of the different available technologies that would allow to make a revamping of existing facilities making them more competitive.

In the last years several studies have been published, in which are reported comparative analyzes between conventional processes and alternative processes that incorporate modifications that seek the process intensification. Luo et al. [15] reported the behavior of a cellulose acetate membrane that was selective towards ethanol. Based on these results the authors proposed a simplified PV model and performed an analysis of a PV-distillation hybrid process in Aspen Plus showing the potential of the hybrid process to separate the azeotropic mixture and increase ETBE recovery in the column. Among the simplifications of the PV model, the feed was assumed to be a binary mixture containing only ethanol and ETBE and also constant temperature in the membrane module was specified. However, the approximations of considering a binary mixture and isothermal conditions in the membrane module might bring errors on the evaluation of the membrane area. Thus, in our study we have considered multicomponent mixtures (including C4 compounds) and adiabatic operation in the membrane module.

In a previous work by our research group, Gonzalez and Ortiz [16] analyzed several flowsheets that combined distillation and PV for the purification process in MTBE production. Simulation tasks were carried out with the process modelling system gPROMS and the results of alternative process configurations that result from the relative location of the separation technologies were compared on the basis of the required membrane area. As another precedent to our work we can highlight the studies published by Arpornwichanop et al. [17,18]. These authors proposed a hybrid process of reactive distillation and PV for the production of tert-amyl ethyl ether (TAEE) [17]. A user-defined Fortran subroutine of a PV unit was developed, allowing the simulation of the hybrid process of in Aspen Plus simulator. Simulation results shown that the integrated process allows to increase the conversion of reactants and the purity of TAEE product, compared with the conventional reactive distillation.

Thus, the objective of this work is to present a comparative study between the conventional process to produce ETBE and two alternative intensified processes by means of process simulation in Aspen Plus. The results of conventional and alternative processes have been compared on the basis of their technical and energy performance.

2. Chemical reactions in the production of ETBE

ETBE is formed in an exothermic, reversible and highly selective reaction between isobutene and ethanol in liquid phase, catalyzed by an ion exchange resin [2]. Due to the light hydrocarbon content, the reaction mixture should be kept under pressure (10 bar) to be in the liquid phase. As is the case with MTBE, also the side reactions leading to the formation of di-isobutene (DIB) and tert-butyl alcohol (TBA) may take place. The overall scheme of conversion in the synthesis of ETBE can be represented as:

$$C_4H_8 + C_2H_6O \leftrightarrow C_6H_{14}O \qquad \text{(Eq. 1)}$$

$$C_4H_8 + H_2O \leftrightarrow C_4H_{10}O \qquad \text{(Eq. 2)}$$

$$2\,C_4H_8 \rightarrow C_8H_{16} \qquad \text{(Eq. 3)}$$

where Eq. 1 represents the etherification reaction, Eq. 2 represents the hydration of isobutene to form tert-butyl alcohol, and Eq. 3 represents the dimerization reaction of isobutene to form di-isobutene.

The etherification reaction is limited by the thermodynamic equilibrium in the range of temperatures typically used in the industrial field. Thus, the equilibrium conversion at 343 K for a stoichiometric mixture of reactants is only 84.7% [19,20]. Several experimental studies on the chemical equilibrium in ETBE formation reaction have been reported in the literature [19,21,22]. Izquierdo et al. [22] reported a study where equilibrium constants for the liquid-phase synthesis of ETBE were determined experimentally in the temperature range 313 -353 K and at 1.6 MPa, using as source of isobutylene a C4 olefinic cut proceeding from a steam cracking unit. The UNIFAC estimates of activity coefficients were used to describe the liquid-phase nonideality. As a result of that study the authors proposed the following expression to describe the dependence of the activity-based equilibrium constant with temperature:

$$K = 7.40\times10^{-5}\ \exp\left[4262.21/T\right] \qquad \text{(Eq. 4)}$$

The secondary reaction of isobutene dimerization (Eq. 3) is favored at low concentration of ethanol and at high temperature and is also equilibrium limited [23]. For this reason, a slight excess of ethanol is usually used in the reaction mixture to inhibit the isobutene dimerization reaction. Sneesby et al. [20] proposed an expression for the equilibrium constant of the dimerization, which had previously been estimated from the free energies of formation, as follows:

$$\ln K = 95.2633 + 5819.8644/T - 17.2\ \ln T - 0.0356T \qquad \text{(Eq. 5)}$$

Abufares and Douglas [24] verified that this correlation predicts well the formation of di-isobutene in a column reactive for the production of MTBE, and later this equation was used by Sneesby et al. [20] to simulate the ETBE process.

Both the reactive mixture and other process streams have a highly non-ideal behavior, so a careful selection of an appropriate thermodynamic method is a fundamental step in our study. The ETBE system is susceptible to form azeotropes due to nonidealities in the liquid phase. Several experimental studies have reported the characteristics of the binary azeotropes formed between ethanol and ETBE [25-28] and between ethanol and isobutene [29]. In the case of ethanol/ETBE mixtures, these compounds form an azeotropic mixture containing 20.4 wt% ethanol at 94.7 kPa and 65 ºC [28]. The UNIFAC model predicts the presence of these azeotropes and also suggests an azeotrope between ethanol and 1-butene at high pressure. As consequence of the presence of azeotropes, these mixtures cannot be separated by simple distillation and more advanced alternatives such as pressure-swing distillation or hybrid processes that combine distillation and pervaporation are required. In this work we have chosen the UNIFAC-Dortmund group contribution method considering that this thermodynamic method is able to predict the non-ideal behavior of the C4/ETBE/ethanol mixtures at moderate pressures [25,26]. The vapor phase properties are calculated using the Soave-Redlich-Kwong equation of state.

3. Methodology and description of alternative processes for the production of ETBE

In this work, a comparative study between the conventional process to produce ETBE and two alternative intensified processes is presented by means of process simulation in Aspen Plus. One of the alternative methods for improving the separation and purification section of ETBE is the use of a hybrid distillation-pervaporation process with alcohol-selective membranes. The other alternative process is one that incorporates reactive distillation technology. Both alternative processes are considered as options for revamping existing facilities.

We have adopted as reference process the one in operation at “Petróleos del Norte SA” (a petrochemical Spanish company) which employs a C4 hydrocarbon stream as feedstock, with 19 % molar content of isobutene as well as the provision of ethanol in excess (~10 %), as it has been reported by García-Echevarría [30]. Accordingly, the production target was to achieve a productivity of 6400 kg h^{-1} of ETBE with a minimum purity of 95.2 wt%.

Based on previous studies by the PAS research group, experimental information on the separation process of ethanol/ETBE mixtures was used to develop a new mathematical model that reliably describes the pervaporation process using commercial membranes according to the operating conditions. In the next stage this model together with the material and energy balance equations were used to develop a user model in the *Aspen Custom Modeler* simulator. After validation, this model was exported to the *Aspen Plus* environment, in order to be able to implement in this simulation environment the different flowsheets that describe the alternative hybrid processes that have been proposed. To broaden the scope of this work, a comparative study with the production process based on reactive distillation was also included. Thus, using tools such as the *Activated Energy Analysis*, the energy consumptions of the different alternatives were evaluated. Finally, we analyzed the options of performing energy integration using Pinch Analysis with the *Aspen Energy Analyzer* tool, proposing different scenarios to generate the heat exchange networks.

3.1. The conventional process for the production of ETBE

A typical configuration of a conventional process is that shown in Fig. 1. This process consists of two reactors connected in series in order to ensure high conversions. The first reactor is used to carry out most of the reaction. Due to the exothermic characteristics of the ETBE forming reaction, the use of a multitubular reactor is preferred, which allows the removal of part of the heat generated. This type of reactor consists of a set of small diameter tubes filled with catalyst, arranged in a housing through which cooling water is circulated [31]. The second reactor can mostly be operated adiabatically as much less heat is liberated and a packed-bed reactor is more economical [20]. The packed bed allows more catalyst to be used so that the reactor can be operated at lower temperatures to improve the reaction equilibrium and maximize conversion. The first reactor operates up to 90 °C, while the second reactor operates at 40-50 °C [32].

<Figure 1 near here>

Although conventional processes typically include two reactors in series, for simulation purposes we have used a single equilibrium reactor as a simplified model which can represent the overall performance of the reaction system. Two parallel reactions, the formation of ETBE and dimerization were considered and for the hydration reaction it was assumed that practically all the water is converted to TBA [33,34]. Thus, a REquil reactor model (Aspen Plus) with chemical equilibrium constants from literature [20,22] was used to calculate the products composition and the total molar flow-rate. The REquil reactor does not take into account reaction kinetics, even though the results provide a useful reference to be compared with experimental results, since this equilibrium reactor model can adequately describe conversion changes based on the amount of recycled ethanol. We have assumed that the equilibrium reactor operates at 10 bar and 46 ºC, so that water can be used as coolant utility.

The output stream from the reaction zone is fed to a distillation column (debutanizer column) to obtain a bottom stream where ETBE is the main component. The distillate stream from this column may contain an appreciable amount of unreacted ethanol and must be recovered.

The bottom ETBE product from the debutanizer always contains significant amounts of ethanol (typically between 5 and 15 wt%). Ethanol and ETBE form azeotropes (e.g. at 22.4 wt % ethanol under atmospheric pressure) so that they cannot be separated by simple distillation [35]. Between the possible separation schemes for this azeotropic mixture, we have adopted for the conventional process that scheme based on pressure-swing distillation, that is to say, a separation scheme that includes two distillation columns and that is based on the change of ethanol/ETBE azeotropic composition with pressure [36]. The ethanol/ETBE mixture is thus separated using two distillation columns operating at two different pressures. Pure ETBE is thus obtained from the bottom of the first column operating at high pressure (7.5 bar) and purified ethanol is obtained from the bottom of the second column operating at low pressure (1 bar). The azeotropic mixtures obtained overhead from each column are recycled to the other column. This process, however, require the use of two distillation columns which renders these processes relatively expensive as regards both investment and energy consumption.

3.2. Pervaporation integrated hybrid process for ETBE production

In this section we report an analysis of a hybrid process that integrates the pervaporation process coupled to the debutanizer column, replacing the pressure-swing distillation system to improve the separation and purification efficiency of ETBE. The reaction system and debutanizer column used in the conventional process constitute the first part of the hybrid process.

The different types of separation units can be combined in various ways; the pervaporation unit can be positioned before the distillation column, after the column on a side stream or directly to the distillate stream of the column. In a previous study the authors have reported a comparative analysis of alternative hybrid process flowsheets based on the combination of distillation and PV operations for the production of ETBE [37]. That study showed that the hybrid process, in which the pervaporation modules are located on a side-stream withdrawn from the distillation column, is more favorable in energy consumption and it shows lower content of ethanol in distillate stream than other membrane integrated hybrid processes. Therefore, that configuration has been adopted in our study (Fig. 2).

<Figure 2 near here>

The PV performance is based on the experimental results with PERVAP 2256 commercial membranes reported by Ortiz et al. [38]. A mathematical model of the PV membrane modules was developed in Aspen Custom Modeler and integrated with Aspen Plus software. The mass transport rate of the components through the membrane is proportional to the activity gradient of permeant components as driving force. The UNIFAC-Dortmund model and SRK equation of state are used in the vapor-liquid equilibrium (VLE) and physical property calculations.

The permeance of component *i* in the membrane, Q_i, is defined with regard to the permeation flux J_i as:

$$J_i = Q_i \left(p_i^o \; x_i^{feed} \; \gamma_i - y_i \; P^{perm} \right) \qquad \text{(Eq. 6)}$$

where P_i^o is the saturation vapor pressure, γ_i is the activity coefficient and P^{perm} is the downstream pressure (permeate side).

The activities of the components in the liquid phase are calculated as:

$$a_i = x_i\ \gamma_i \qquad \text{(Eq. 7)}$$

As reported by Ortiz et al. [38], the partial fluxes are a nonlinear function of the activity of the components, i.e., permeances are not constant but depend on the activity of the components. The following equation, that depends only on the activity of ethanol, provide a close fit to the ethanol permeability data:

$$Q_{ethanol} = A_1 + B_1 * \left(a_{ethanol}\right)^{C_1} \qquad \text{(Eq. 8)}$$

With regard to ETBE, its permeance can be described as a function of the activities of both ethanol and ETBE, as follows:

$$Q_{ETBE} = A_2 + B_2 * \left(a_{ethanol}\right) + C_2 * \left(a_{ETBE}\right) \qquad \text{(Eq. 9)}$$

We have assumed that only two components (ethanol and ETBE) permeate through the membrane, while the rest of the components remain at the retentate side and do not permeate. This simplification was experimentally tested with the membrane PERVAP 2256 used to find the experimental data.

The temperature dependence of membrane permeance in the mathematical model was described trough the Arrhenius-type equation:

$$Q_{i,T} = Q_{i,To}\ \exp\left(\frac{-E_{act,i}}{R\,T}\right) \qquad \text{(Eq. 10)}$$

The parameters of the PV model are listed in Table 1.

<Table 1 near here>

In order to simulate the behavior of a pervaporation module at industrial scale, a mathematical model of a plate and frame membrane module was adapted from Luyben

[39] where the above membrane performance model was incorporated. Steady-state mass and energy balances were developed considering (i) plug-flow for the feed liquid stream, (ii) perfect mixing in the permeated vapor, (iii) negligible polarization effects and (iv) negligible heat losses. For calculation purposes a discretization technique has been applied: the membrane module has been divided into a set of cells; five cells have been considered in each membrane module. Thus the steady-state mass and energy balances are as follows:

$$\frac{dM_R}{dt} = 0 = F_{R,n-1} - F_{R,n} - F_{P,n} \qquad (\text{Eq.11})$$

$$M_R \frac{dh_{R,n}}{dt} = 0 = F_{R,n-1}\, h_{R,n-1} - F_{R,n}\, h_{R,n} - F_{P,n}\, H_{P,n} \qquad (\text{Eq.12})$$

$$M_R \frac{dz_{R,n,i}}{dt} = 0 = F_{R,n-1}\, z_{R,n-1,i} - F_{R,n}\, z_{R,n,i} - F_{P,n}\, z_{P,n,i} \qquad (\text{Eq.13})$$

where

$F_{R,n}$ = molar flowrate of the liquid retentate from cell *n* (kmol h^{-1})

$F_{P,n}$ = molar flowrate of vapor permeate from cell *n* (kmol h^{-1})

M_R = molar holdup in each retentate cell in the pervaporation module (kmol)

$h_{R,n}$ = molar enthalpy of liquid retentate in cell *n* (GJ $kmol^{-1}$)

$H_{P,n}$ = molar enthalpy of vapor permeate leaving cell *n* (GJ $kmol^{-1}$)

$z_{R,n,i}$ = mole fraction of component *i* in the liquid retentate in cell *n*.

$z_{P,n,i}$ = mole fraction of component *i* in the vapor permeate leaving cell *n*.

The flux of component "*i*" in each cell is calculated using the following equation:

$$J_i = Q_i \left(z_{Ri}\, \gamma_i\, P_i^{sat} - z_{Pi}\, P_{permeate} \right) \qquad (\text{Eq. 14})$$

The permeate flowrate is the sum of the two components (ethanol and ETBE) fluxes times the membrane area (A_{mem}) as given by Eq. 15:

$$F_{P,n} = A_{mem} \left(J_{n,ethanol} + J_{n,ETBE} \right) \qquad (\text{Eq. 15})$$

The Aspen Custom Modeler (ACM) software is used to simulate the pervaporation process. Composition and temperature of retentate and permeate streams are variables distributed along the module, which are computed by simultaneously solving the material and energy balances (Eqs. 11-13). To do this, the thermodynamic properties that are a function of temperature and composition need to be computed in each cell using subroutines specific in ACM software. Since an adiabatic operation of the pervaporation module has been assumed, the energy balance is simplified to an enthalpy balance over the feed, retentate and permeate streams. The enthalpy of each stream depends on its temperature and composition, the enthalpies being evaluated by the UNIFAC-Dortmund method for the liquid phase and by the SRK equation of state for the vapor phase. In addition, the membrane permeances are also calculated in each cell using the equations of the model (Eqs. 8-10) as a function of the activities and temperature. The differential and algebraic equations (Eqs. 8-15) for each cell and each module are incorporated in the Aspen Custom Modeler program. The ACM model is then exported to Aspen Plus software as a standalone module to integrate the pervaporation membrane module into global flowsheets. Taking into account the commercially available pervaporation modules, a membrane area of 30 m^2 for each module was assumed. Permeating molecules are removed from the downstream surface of the membrane in the vapor phase, and the latent heat for the phase change is obtained from the sensible heat of the feed [40]. Thus, in PV cells a temperature drop is observed between the feed inlet and the retentate outlet streams.

3.3. Reactive distillation process for ETBE production

As a third alternative, we have analyzed the ETBE production by reactive distillation. Although several previous simulation studies in the literature have considered flowsheets where the fresh feed streams are fed into the RD column [41,42], virtually all commercial processes incorporate a pre-reactor where most of the isobutene conversion takes place [43]. For this reason we have adopted a process flowsheet including a single fixed bed catalytic reactor and its output stream is fed to a RD column where the conversion of isobutene is complete. The bottom product of this RD column is ETBE of purity suitable for addition to the gasoline and the distillate stream is composed of inerts and small amounts of unreacted ethanol and isobutene. The column is formed of non-reactive stages and a section with the packed catalyst bed, always within the area above the feed stage. The non-reactive steps above and below the reactive section are necessary to produce the separation among products and reactants.

The RadFrac model, a rigorous equilibrium stage distillation model in Aspen Plus, is used to represent the RD column. To carry out the simulation and because the reaction rate is fast enough compared to the mass transfer rate occurring in the distillation process, it can be assumed that at each theoretical stage of the RD column the reaction reaches the chemical equilibrium. This approach has also been assumed by the authors of other studies previously reported in the literature [44-46].

To check the validity of our approach, we have used the case reported by Sneesby et al. [20]. In that study the authors model the ETBE synthesis using two different approaches: 1) Rigorous reaction kinetics were used to model the ETBE reaction in SpeedUp (an equation-oriented simulator), and 2) An ETBE reaction equilibrium model was also built to test the assumption of chemical equilibrium using Pro/II (a sequential-modular simulator). We have simulated the RD column in Aspen Plus using the RadFrac model with the column parameters reported in the cited paper. The comparison between the results is shown in Figure 3, where an acceptable agreement can be observed.

<Figure 3 near here>

4. Results

4.1 Conventional process simulation results

Taking into account the above aspects, we have carried out the simulation of the conventional process using the Aspen Plus process simulator. As mentioned above, we have adopted as reference process one that employs a C4 hydrocarbon stream as feedstock, with 19 % molar content of isobutene as well as the provision of ethanol in excess (~10 %), as described by García-Echevarría [30]. Accordingly, the production target was to achieve a productivity of 6400 kg h^{-1} of ETBE with a minimum purity of 95.2 wt%. It is assumed that all C4-C6 hydrocarbons except isobutene are inert [20]. Therefore, all the inert C4 hydrocarbons are lumped, based on their similarities, and represented here by n-butene.

To carry out the simulation of the debutanizer distillation column for the recovery of C4 as distillate from C4/ETBE/ethanol mixtures, we have used the RadFrac model (Aspen Plus), which describes the full performance of the column through rigorous mathematical methods. The column operation is simulated at constant internal reflux ratio of 0.5 and pressure between 7 bar and 9 bar, with 26 separation stages, including condenser and reboiler.

The following two distillation columns, which operate according to pressure-swing mode to achieve ETBE purification and ethanol recovery, have also been simulated by adopting the RadFrac model. Each of these columns has 16 ideal separation stages, while the operating pressure is 7.5 bar for the ETBE purification column (DC2) and 1 bar for the ethanol recovery column (DC3). The 3rd column distillate is partly supplied as reflux to the head of the DC3 column and is in part recycled to the head of the DC2 column. The purified ETBE is collected at the bottom of the DC2 column. As a bottom product from the DC3column, the purified ethanol is recycled to the reaction zone.

The material balances for the conventional process obtained from the simulation of the process are shown schematically in Figure 1 and more in detail in Table 2. The main product is the ETBE rich stream (95.2 wt%), with a production of 6343 kg h^{-1}, with an isobutene conversion of 94.3%.

<Table 2 near here>

4.2 Pervaporation integrated hybrid process results

The feed stream to the membrane modules is considered to be in liquid phase. The values adopted in this work were 70 ºC for the feed temperature and 20 mmHg (2.7 kPa) for the permeate pressure. Feed pressure was set to 4.8 bar so that the feed to the pervaporation module is in liquid phase at the operating temperature.

Taking into account that the debutanizer column has 26 separation stages, including condenser and reboiler, we have used the following configuration for the distillation-pervaporation integrated system: the fresh feed is located in stage 11, the liquid side withdrawal in stage 18, and the permeate from the membrane modules is recycled in stage 23. The sidestream flow rate can have considerable influence on the separation performance; we have found that a mass flow rate of 1260 kg h^{-1} is the most appropriate to achieve the required ETBE purity, while the content of ethanol and butenes in the bottom product is at a minimum value. A further increase in the sidestream flow rate does not result in an improved separation. Thus, 7 PV modules (210 m^2 membrane area) are required to obtain the specified composition of ETBE in the bottom stream. In these conditions about 6420 kg h^{-1} of ETBE with a purity of 95.2 wt% is obtained, this implies that 99.9 % of the produced ETBE leaving the reactor is recovered in the bottom of the column.

In pervaporation, the permeation fluxes increase appreciably with the operating temperature. As previously indicated, we have adopted a feed temperature to the PV modules of 70 °C to preserve the thermal stability of the membrane. In the hybrid process model, pervaporation operates in adiabatic mode, so interstage heaters are then required between membrane module stages to compensate for temperature drop due to latent heat of evaporation removed by the permeating vapor [16,40]. Thus, the retentate streams leaving each PV module need to be heated back up to 70 ºC, which means an additional consumption of low pressure steam.

The material balances for the PV integrated hybrid process obtained from the process simulation are shown schematically in Figure 2 and more in detail in Table 2. The main product is the ETBE rich stream (95.2 wt%), with a production of 6420 kg h^{-1}. The isobutene conversion is 94.3 %, as in the conventional process, because a molar stoichiometric excess of 10% ethanol is maintained in the reactor feed stream. Our results are in good agreement with those previously reported by Alonso [33], who simulated the hybrid process using a pervaporation model based on an empirical data fit for binary mixtures and found that 16 PV modules are required to obtain 6350 kg h^{-1} of a product stream containing 97.3 wt% of ETBE. The higher number of modules required is due to the higher target purity than in our case and because the allowed temperature drop for the retentate stream in each PV module was only 5 °C.

4.3 Reactive distillation process results

The process flowsheet consists of a single reactor whose operating pressure is set at 10 bar, as in the conventional process, which is coupled to the RD column (Fig. 4). The temperature at the exit of the reactor is 70 °C and an isobutene conversion of 80% is achieved.

<Figure 4 near here>

We have adopted a RD column taking as reference the column described in the study by Sneesby et al. [20], modifying some characteristics in order to achieve the required product purity with a high isobutene conversion. The RD column consists of 2 stages in the rectification section (including a total condenser), 3 reactive stages and 11 stages in the stripping section (including the reboiler). The feed to the column is done just below the reaction section (stage 6) to minimize the amount of product in this section and thus favor the shift of the reaction equilibrium towards ETBE formation. The pressure at the top of the RD column is 9.5 bar and the temperature in the reaction section is between 70 and 75 °C (Fig. 5), thereby avoiding the conditions favoring both the catalyst deactivation (high temperatures) and the formation of DIB (low reaction temperatures). The column produces a bottom stream with 95.2 wt% ETBE, for which a reflux ratio of 5 is required. Concentration of main components and temperature profile in the RD column is shown in Fig. 5.

<Figure 5 near here>

The justification for the number of stages in the column is shown below. First we have evaluated the effect of the number of reactive stages on the conversion of isobutene and on the content of ETBE in the bottom stream. A reflux ratio of 5 was specified, keeping the number of trays in the rectification section and in the stripping section, so that only the number of stages in the reactive section varies. In all cases the feed stage is located just below the reactive section. As can be seen in Fig. 6, both the isobutene conversion and ETBE purity show a maximum when 3 reactive stages are used. In agreement with the study reported by Sneesby et al. [20], increasing the number of reactive stages above the optimum produced a detrimental interaction between the phase and chemical equilibrium which led to the decomposition of product on the lower reactive stages.

<Figure 6 near here>

In the same way we have proceeded to evaluate the effect of the number of trays in the separation stages. Fig. 7 shows simulation results for an ETBE column where the number of rectification stages was varied. These results indicate that increasing the number of stages reduces ETBE and ethanol losses with the distillate stream, but at the same time the isobutene conversion decreases slightly. For this reason two stages have been adopted in the rectification section, as a trade-off solution.

<Figure 7 near here>

In order to evaluate the number of trays in the stripping section required to achieve the target product purity, we have carried out a sensitivity analysis, as shown in Fig. 8. A reflux ratio of 5 was specified, keeping the number of stages in the rectification section and in the reactive section, so that only the number of trays in the stripping section varies. As can be seen in Fig. 8, 11 trays are required to reach 95.2 wt% ETBE in the bottom stream, but adding more trays in the stripping section does not imply an additional improvement in product purity.

<Figure 8 near here>

In a reactive distillation column, reflux not only enhances separation but recycles unreacted reactants to the reaction zone and increases conversion [20]. The effect of reflux ratio on ETBE purity in bottom stream and ETBE losses with distillate stream is shown in Fig. 9, where it is evident that an increase in the reflux ratio favors an increase of the ETBE content in bottom stream and, at the same time, a decrease of ETBE losses with the distillate stream.

<Figure 9 near here>

As Sneesby [20] has highlighted, in reactive distillation the reboiler duty must be set to ensure sufficient recycle of unreacted, heavy reactant to the reaction zone without excluding the light reactant from the reaction zone. As shown in Fig 10, there is an optimal reboiler duty value for which the ETBE purity is maximal while the ETBE losses in the distillate stream increase monotonically with the reboiler duty.

<Figure 10 near here>

The material balances for the conventional process obtained from the simulation of the process are shown schematically in Figure 4 and more in detail in Table 2. The main product is the ETBE rich stream (95.2 wt%), with a production of 6860 kg h^{-1}.

4.4. Heat integration analysis

In this work, pinch analysis has been applied to evaluate various heat integration options for the ETBE production. The simulation program Aspen Energy Analyzer has been used to create heat exchanger networks from process models generated in Aspen Plus. We have adopted as base case the one that corresponds to each of the three alternative processes described above, with all the energy requirements provided by utilities. The utilities used are cooling water (20 °C), low pressure steam (125 °C) and medium pressure steam (175 °C).

First we have analyzed the case corresponding to the conventional process with pressure swing distillation (PSD) for product purification. Heat exchanger network (HEN) design for the heat integrated PDS process, using a global minimum ΔT of 10ºC is shown in Fig. 11. Thus, for the preheating of the incoming feed mixture to the reactor from 35 °C to 73 °C, part of the energy required is provided by the stream to be condensed in the condenser located in atmospheric pressure column (DC3), using an additional heat exchanger (E100). Second, the reaction product stream is at 46 °C and requires to be heated to 72 °C to be fed to the distillation column. The energy demand is provided by the bottoms product stream from the second distillation column (DC2) by modifying the heat exchanger before the debutanizer column (E101). Thus, heat integration with pinch analysis shows that it is possible to achieve savings of up to 11% in utilities consumption.

<Figure 11 near here>

Table 3 gives detailed information about the expected utility consumption in the different alternatives, both for the base cases (without heat integration) and for the scenarios resulting from energy integration. Energy consumptions are expressed per ton of product (ETBE with a purity of 95.2 wt %). The amount of refrigerant and electricity consumed is not significant in relation to the total energy consumption.

<Table 3 near here>

In the case of the PV-integrated hybrid process, from the flowsheet analysis we have found that there are several process streams that have potential to be used in the heat integration, namely: 1) the ETBE product stream is obtained as a bottom stream in the distillation column, with a temperature of 154 °C and needs to be cooled to a temperature appropriate for storage; 2) the side-stream is withdrawn from the distillation column at 137 °C and 8.2 bar, and in order to be fed to the PV modules a cooling down to 70 °C is required; 3) the etherification reaction is reversible and exothermic and a certain amount of heat must be removed from the catalytic reactor in order to achieve high conversions. The base case corresponds to Fig. 2 with the entire energy requirement provided by utilities. Adopting a ΔT_{min} = 10 ºC, the energy target for the hot utilities (QH_{min}) is 2.50 MW, and that for cold utilities (QC_{min}) is 2.80 MW. After analyzing several scenarios, we have adopted the heat integration scheme that is detailed in Figure 12. First, the feed stream to the reactors resulting from the mixing of fresh reactant streams and recycled ethanol is at about 35 °C and requires to be heated to 73 °C. Part of the energy needed is provided by the ETBE product stream using an additional heat exchanger (E100). Second, the stream exiting the reactors is at 46 °C and requires to be heated to 72 °C to be fed to the distillation column. Part of the energy required is provided by the side stream withdrawn from the column using another additional heat exchanger (E101), and another part of the energy comes from the removal of the heat of reaction in the catalytic reactors (E102). According to these results, in this case it is possible to achieve savings of up to 18% in utilities consumption.

<Figure 12 near here>

Finally we have analyzed the energy integration options for the RD process. The ETBE product stream (bottoms stream of RD column) temperature is about 160 ºC (as saturated liquid at 10 bar), which means that some heat integration between the RD column outlet stream and the process streams that require heating before this column may be very convenient from the economic point of view. From the results of pinch analysis (Fig. 13), we have found that the bottom stream from the distillation column can be used to heat the stream coming out of the reactors to be fed to the RD column, using the same exchanger intended for use with utilities (E101), i.e. no additional heat exchanger is required in this case. In addition, heat integration from reactor heat to the initial feed stream with the purpose of achieving the target feed temperature also allows to reduce utilities consumption which requires incorporating an additional heat exchanger (E100).

<Figure 13 near here>

5. Discussion and conclusions

From the obtained results it is evident that the three processes evaluated allow to obtain ETBE with the required purity, but nevertheless they differ in the achieved productivity and the energetic consumption. For this reason the energy consumptions (Table 3) are expressed per ton of product.

In the case of the conventional process (after heat integration) the consumption of heating utilities is mainly related to the reboiler thermal duties of the three distillation columns, which consume 2.4 MW, 1.8 MW and 1.2 MW, respectively. Regarding the consumption of cooling utilities, this consumption is mainly due to the cooling needs in the condensers of the debutanizer column and the third column of the flowsheet (DC3), which consume 2.2 MW and 2.6 MW (with heat integration) respectively. Somewhat lower is the consumption of cooling utilities for cooling the catalytic reactor where the exothermic etherification reaction takes place (1.07 MW). This means that for the conventional process it is necessary to supply 884 kWh ton^{-1} by means of hot utilities and to remove 926 kWh ton^{-1} by means of cooling utilities. Therefore it seems evident that the possibilities to improve the energy efficiency of the process go through to modify the process of separation and purification of ETBE.

In the PV integrated hybrid process, an ETBE production of 6420 kg h^{-1} is achieved. The isobutene conversion is 94.3 %, as in the conventional process, because a molar stoichiometric excess of 10% ethanol is maintained in the reactor feed stream. In addition to energy saving, there is an improvement in productivity as the amount of unreacted ethanol recycled to the reaction zone is increased and also more than 99.9 % of the produced ETBE leaving the reactor is recovered from the bottom of the column. The consumption of heating utilities is basically due to the thermal duty of the debutanizer column reboiler (2.5 MW). The adiabatic-mode operation of the 7 PV modules makes necessary the re-heating of the retentate stream at the output of each PV module up to the specified temperature of 70 °C, which implies an additional consumption of 26 kW, which is evidently a minor contribution to the total energy consumption. Again, the consumption of cooling utilities is mainly due to the cooling needs in the condenser of the debutanizer column (2.2 MW) and partly in the cooling of the catalytic reactor (0.76 MW). Other minor contribution correspond the energy to be removed to achieve the condensation of the permeate stream (35 kW). Thus, as shown in Table 3, energy requirements in the PV integrated hybrid process were found to be considerably lower than the conventional process ones, with savings of 52% and 49% in heating and cooling utilities, respectively.

The results of the process that incorporates reactive distillation show an increase in production due mainly to the fact that this process leads to 98.9% isobutene conversion, much higher than the conversions reached in the other two alternative flowsheets. In contrast, the energy requirements are much higher than the previous cases due to the higher reflux ratio required to ensure high conversion and at the same time to achieve the target ETBE purity. Thus, the energy requirements for condensation (8.9 MW) and reboiler duty (9.2 MW) are appreciably greater than the consumption in the alternative cases. Taking into account the production capacity of ETBE using reactive distillation, it is found that the demand for utilities is 1291 kWh ton^{-1} (hot utilities) and 1205 kWh ton^{-1} (cooling utilities).

The good performance of RD to carry out the reaction/separation stages simultaneously contrasts with its high energy consumption. This suggests the opportunity to explore other options that allow energy savings in RD. In recent years many efforts to improve the thermal efficiency of distillation columns have been made attempting to implement the heat pump assisted distillation [47,48]. Heat integrated distillation column (HIDiC) is an advancement in this respect, which seeks to maximize the energy efficiency of a heat pump design by making use of internal heat-integration. The stripping section is typically separated from the rectifying section and the heat is transferred from the "hot" rectifying section, operating at a higher pressure than the "cold" stripping section, through the partition wall or using adequate means connecting equivalent stages [47]. Although few studies have addressed the integration of HIDiC with reactive distillation [49], the reported results are encouraging and suggest that its application to the ETBE case study should be studied.

In summary, the PV hybrid process appears as the best option to achieve energy savings compared to the conventional process, and it is also an attractive option to carry out a revamping of existing processes.

Acknowledgements

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References

[1] M.E. Bardin, A.M.T.A. El-Dein Hussin, P.A. Gushchin, V.A. Vinokurov, A.A. Burluka, Technical aspects of ethyl tert-butyl ether (ETBE) for large-scale use as gasoline improver, Energy Technol. 2 (2014) 194-204.

[2] K.F. Yee, A.R. Mohamed, S.H. Tan, A review on the evolution of ethyl tert-butyl ether (ETBE) and its future prospects, Ren. Sust. Energ. Rev. 22 (2013) 604-620.

[3] X. Feng, R.Y.M. Huang, Liquid separation by membrane pervaporation: A review, Ind. Eng. Chem. Res. 36 (1997) 1048-1066.

[4] B. Smitha, D. Suhanya, S. Sridhar, M. Ramakrishna, Separation of organic-organic mixtures by pervaporation - A review, J. Membr. Sci. 241 (2004) 1-21.

[5] S. Zereshki, A. Figoli, S.S. Madaeni, F. Galiano, E. Drioli, Pervaporation separation of ethanol/ETBE mixture using poly(lactic acid)/poly(vinyl pyrrolidone) blend membranes, J. Membr. Sci. 373 (2011) 29-35.

[6] F.H.H. Abdellatif, J. Babin, C. Arnal-Herault, C. Nouvel, J. Six, A. Jonquieres, Bio-based membranes for ethyl tert-butyl ether (ETBE) bio-fuel purification by pervaporation, J.Membr.Sci. 524 (2017) 449-459.

[7] P. Lutze, A. Gorak, Reactive and membrane-assisted distillation: Recent developments and perspective, Chem.Eng.Res.Design 91 (2013) 1978-1997.

[8] K.K. Sirkar, A.G. Fane, R. Wang, S.R. Wickramasinghe, Process intensification with selected membrane processes, Chem. Eng. Process. 87 (2015) 16-25.

[9] F. Lipnizki, R.W. Field, P.K. Ten, Pervaporation-based hybrid process: A review of process design, applications and economics, J. Membr. Sci. 153 (1999) 183-210.

[10] J. Holtbrügge, Membrane-assisted (reactive) distillation, in P. Lutze and A. Górak (Ed.), Reactive and membrane-assisted separations, De Gruyter, Berlin, 2016, pp. 237-310.

[11] T. Keller, Reactive distillation, in A. Górak and Ž. Olujić (Ed.), Distillation: Equipment and processes, Academic Press, Boston, 2014, pp. 261-294.

[12] J.G. Segovia-Hernández, S. Hernández, A. Bonilla Petriciolet, Reactive distillation: A review of optimal design using deterministic and stochastic techniques, Chem. Eng. Process. 97 (2015) 134-143.

[13] D. Stupp, M. Gass, H. Leiteritz, C. Pijls, S. Thornton, J. Smith, et al, Gasoline ether oxygenate occurrence in Europe, and review of their fate and transport characteristics in environment, CONCAWE, report no. 4/12 2012.

[14] Ethyl Tertiary Butyl Ether (ETBE): 2014 World market outlook and forecast up to 2018, Merchant Research & Consulting ltd., Birmingham, UK 2014.

[15] G.S. Luo, M. Niang, P. Schaetzel, Separation of ethyl tert-butyl ether-ethanol by combined pervaporation and distillation, Chem. Eng. J. 68 (1997) 139-143.

[16] B. González, I. Ortiz, Modelling and simulation of a hybrid process (pervaporation-distillation) for the separation of azeotropic mixtures of alcohol-ether, J. Chem. Technol. Biotechnol. 77 (2002) 29-42.

[17] A. Arpornwichanop, U. Sahapatsombud, Y. Patcharavorachot, S. Assabumrungrat, Hybrid process of reactive distillation and pervaporation for the production of tert-amyl ethyl ether, Chin. J. Chem. Eng. 16 (2008) 100-103.

[18] A. Arpornwichanop, K. Koomsup, S. Assabumrungrat, Hybrid reactive distillation systems for n-butyl acetate production from dilute acetic acid, Journal of Industrial and Engineering Chemistry 14 (2008) 796-803.

[19] K.L. Jensen, R. Datta, Ethers from ethanol. 1. Equilibrium thermodynamic analysis of the liquid-phase ethyl tert-butyl ether reaction, Ind. Eng. Chem. Res. 34 (1995) 392-399.

[20] M.G. Sneesby, M.O. Tadé, R. Datta, T.N. Smith, ETBE synthesis via reactive distillation. 1. Steady-state simulation and design aspects, Ind. Eng. Chem. Res. 36 (1997) 1855-1869.

[21] M. Vila, F. Cunill, J. Izquierdo, J. Tejero, M. Iborra, Equilibrium constants for ethyl tert-butyl ether liquid phase synthesis, Chem. Eng. Commun. 124 (1993) 223-232.

[22] J.F. Izquierdo, F. Cunill, M. Vila, M. Iborra, J. Tejero, Equilibrium constants for methyl tert-butyl ether and ethyl tert-butyl ether liquid-phase syntheses using C4 olefinic cut, Ind. Eng. Chem. Res. 33 (1994) 2830-2835.

[23] A. Rehfinger, U. Hoffmann, Formation of Di-isobutene, main by-product of methyl tertiary butyl ethyl ether synthesis catalyzed by ion exchange resin, Chem. Eng. Technol. 13 (1990) 150-156.

[24] A.A. Abufares, P.L. Douglas, Mathematical modelling and simulation of an MTBE catalytic distillation process using SpeedUp and AspenPlus, Trans. IChem. Part A 73 (1995) 3-12.

[25] J. Gmehling, J. Menke, J. Krafczyk, K. Fischer, A data bank for azeotropic data - status and applications, Fluid Phase Equilib. 103 (1995) 51-76.

[26] J.-H. Oh, S.-J. Park, Isothermal vapor-liquid equilibria at 333.15 K and excess molar volumes at 298.15 K of ethyl tert-butyl ether (ETBE) + alcoh-1-ol (C1-C4) mixtures, J.Chem.Eng.Data 43 (1998) 1009-1013.

[27] K. Kammerer, S. Schnabel, D. Silkenbäumer, R.N. Lichtenthaler, Vapor-liquid equilibria of binary mixtures containing an alcohol and a branched ether. Experimental results and modeling, Fluid Phase Equilib. 162 (1999) 289-301.

[28] J. Rarey, S. Horstmann, J. Gmehling, Vapor-liquid equilibria and vapor pressure data for the systems ethyl tert-butyl ether + ethanol and ethyl tert-butyl ether + water, J.Chem.Eng.Data 44 (1999) 532-538.

[29] K. Fischer, S. Park, J. Gmehling, Vapor-liquid equilibria for binary systems containing methanol or ethanol, tert-butyl methyl ether or tert-amyl methyl ether, and butane or 2-methylpropene at 363 K, ELDATA Int.Electron.J.Phys.-Chem.Data 2 (1996) 135-148.

[30] M. García-Echevarría, La producción de biocarburantes por Petronor contribuye al uso de energías renovables, DYNA 78 (2003) 26-30.

[31] I. Miracca, L. Tagliabue, R. Trotta, Multitubular reactors for etherifications, Chem. Eng. Sci. 51 (1996) 2349-2358.

[32] L. Domingues, C.I.C. Pinheiro, N.M.C. Oliveira, J. Fernandes, A. Vilelas, Model development and validation of ethyl tert -butyl ether production reactors using industrial plant data, Ind. Eng. Chem. Res. 51 (2012) 15018-15031.

[33] P. Alonso-Dávila, Diseño de un proceso óptimo para la producción de éter etil tert-butílico, Doctoral thesis, Universidad de Cantabria (2003).

[34] A. Quitain, H. Itoh, S. Goto, Reactive distillation for synthesizing ethyl tert-butyl ether from bioethanol, J. Chem. Eng. Jpn. 32 (1999) 280-287.

[35] C. Streicher, L. Asselineau, A. Forestière, Separation of alcohol/ether/hydrocarbon mixtures in industrial etherification processes for gasoline production, Pure Appl. Chem. 67 (1995) 985-992.

[36] A. Pucci, P. Mikitenko, and M. Zuliani, Process for the separation of tert. butyl ethyl ether from mixtures, US Patent 5,158,652, 1992.

[37] A. Norkobilov, D. Gorri, I. Ortiz, Process flowsheet analysis of pervaporation-based hybrid processes in the production of ethyl tert-butyl ether, J. Chem. Technol. Biotechnol. 92 (2017) 1167-1177.

[38] I. Ortiz, P. Alonso, A. Urtiaga, Pervaporation of azeotropic mixtures ethanol/ethyl tert-butyl ether: Influence of membrane conditioning and operation variables on pervaporation flux, Desalination 149 (2002) 67-72.

[39] W.L. Luyben, Control of a column/pervaporation process for separating the ethanol/water azeotrope, Ind. Eng. Chem. Res. 48 (2009) 3484-3495.

[40] R.W. Baker, Membrane technology and applications, 3rd ed., John Wiley & Sons, Chichester, 2012.

[41] M.A. Al-Arfaj, W.L. Luyben, Control study of ethyl tert-butyl ether reactive distillation, Ind. Eng. Chem. Res. 41 (2002) 3784-3796.

[42] M. Sharifzadeh, Implementation of a steady-state inversely controlled process model for integrated design and control of an ETBE reactive distillation, Chem. Eng. Sci. 92 (2013) 21-39.

[43] Ethers, Hydrocarbon processing’s 2008 Refining processes handbook (2008), pages 141-147.

[44] R. Khaledi, B.R. Young, Modeling and model predictive control of composition and conversion in an ETBE reactive distillation column, Ind. Eng. Chem. Res. 44 (2005) 3134-3145.

[45] G. Daniel, M. Jobson, Conceptual design of equilibrium reactor-reactive distillation flowsheets, Ind. Eng. Chem. Res. 46 (2007) 559-570.

[46] M. Carrera-Rodríguez, J.G. Segovia-Hernández, A. Bonilla-Petriciolet, Short-cut method for the design of reactive distillation columns, Ind. Eng. Chem. Res. 50 (2011) 10730-10743.

[47] A.A. Kiss, Ž. Olujić, A review on process intensification in internally heat-integrated distillation columns, Chem. Eng. Process. 86 (2014) 125-144.

[48] K. Huang, Q. Lin, H. Shao, C. Wang, S. Wang, A fundamental principle and systematic procedures for process intensification in reactive distillation columns, Chem. Eng. Process. 49 (2010) 294-311.

[49] A. Vanaki, R. Eslamloueyan, Steady-state simulation of a reactive internally heat integrated distillation column (R-HIDiC) for synthesis of tertiary-amyl methyl ether (TAME), Chem. Eng. Process. 52 (2012) 21-27.

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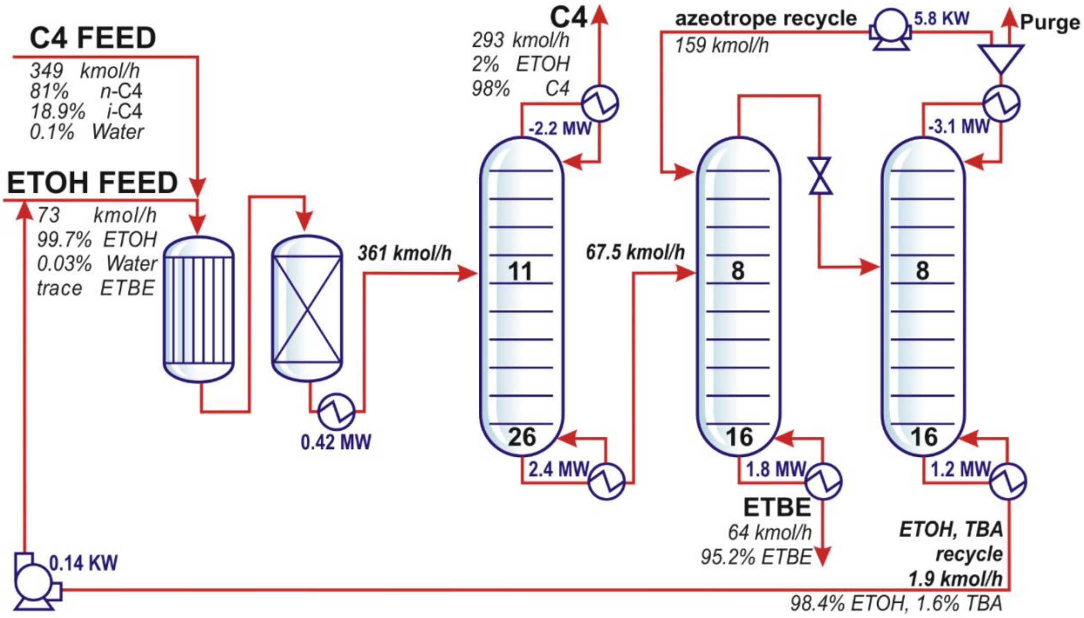

Fig. 1. The conventional process for the production of ETBE with pressure swing distillation for product purification.

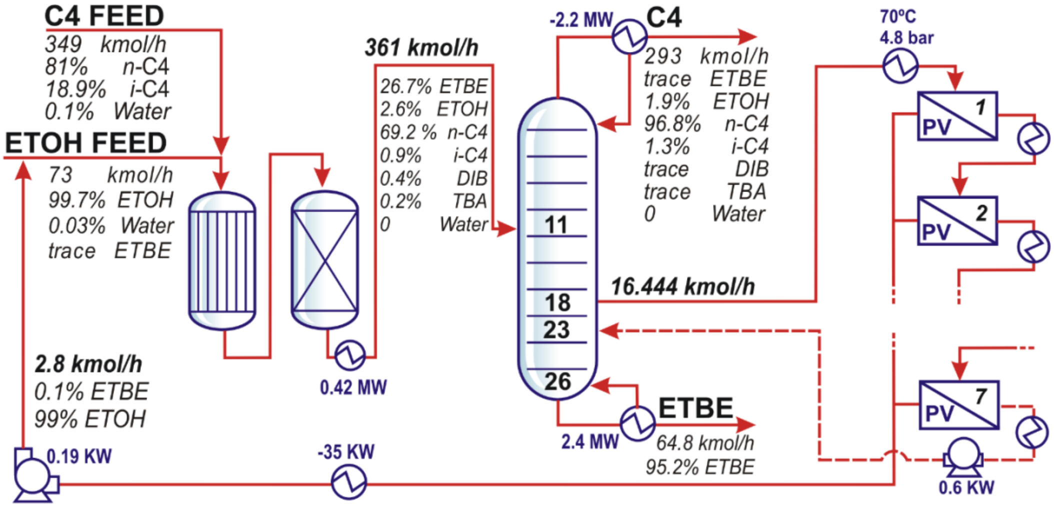

Fig. 2. Schematic diagram of the pervaporation integrated hybrid process

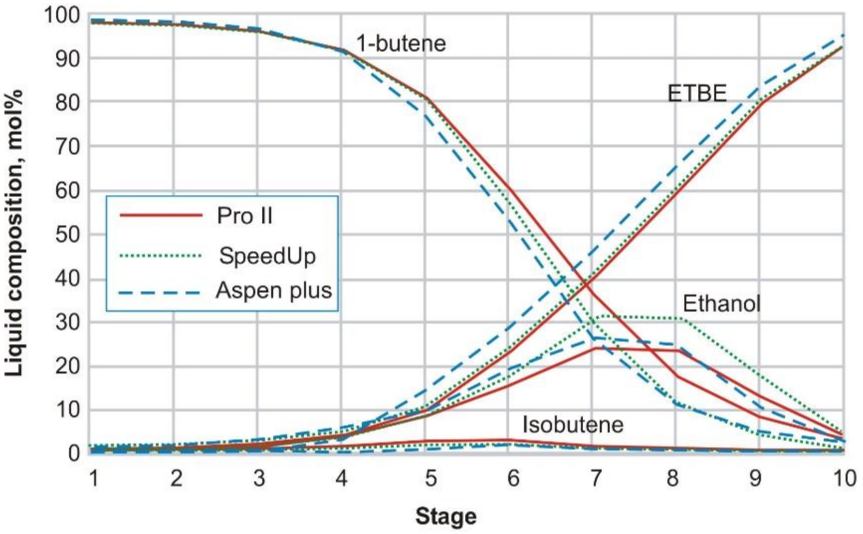

Fig. 3. Comparison of simulation results for the case reported by Sneesby et al. [20]

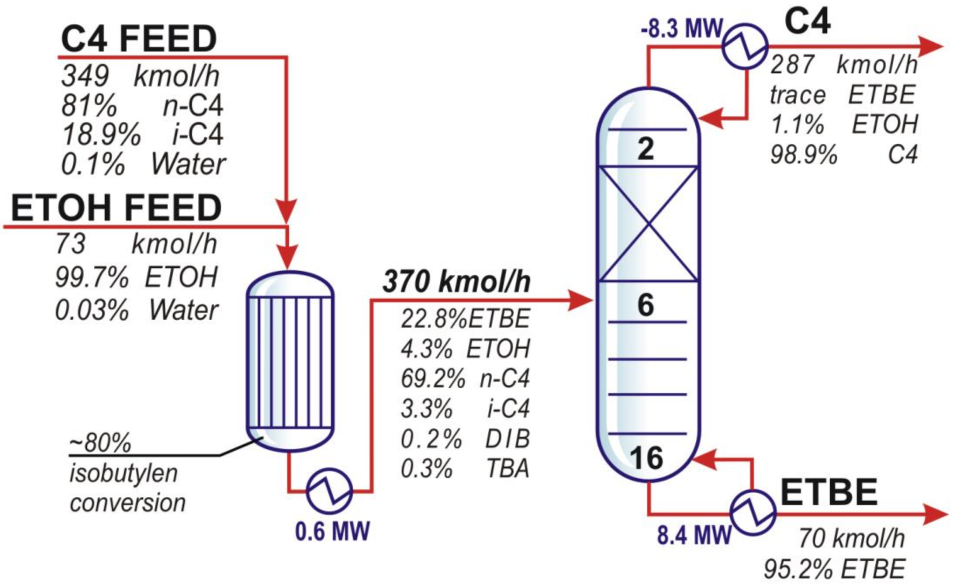

Fig. 4. Schematic diagram of the reactive distillation process for ETBE production

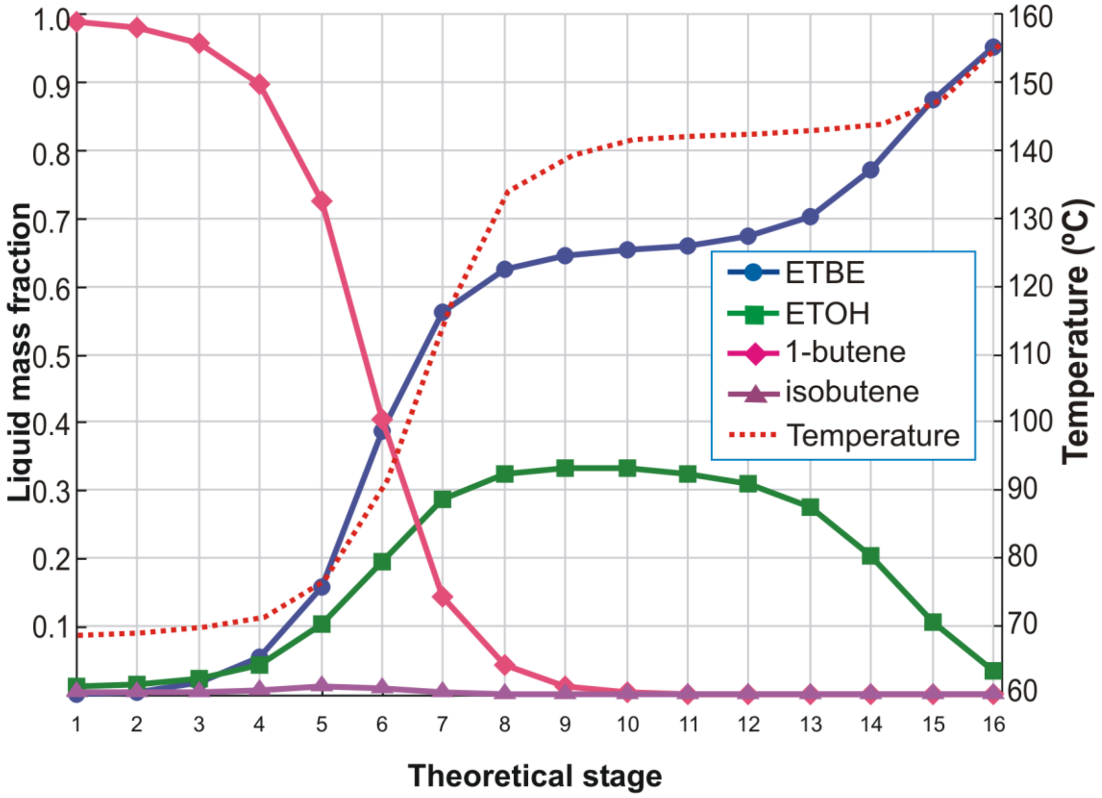

Fig. 5. Concentration of main components and temperature profile in the RD column

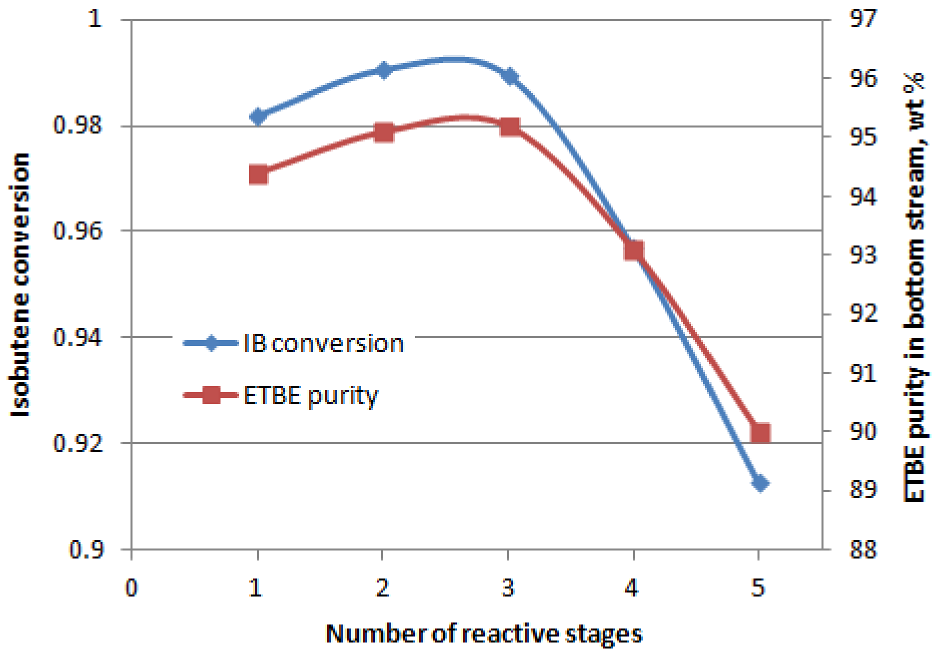

Fig. 6. Effects of reactive stages on isobutene conversion and ETBE purity

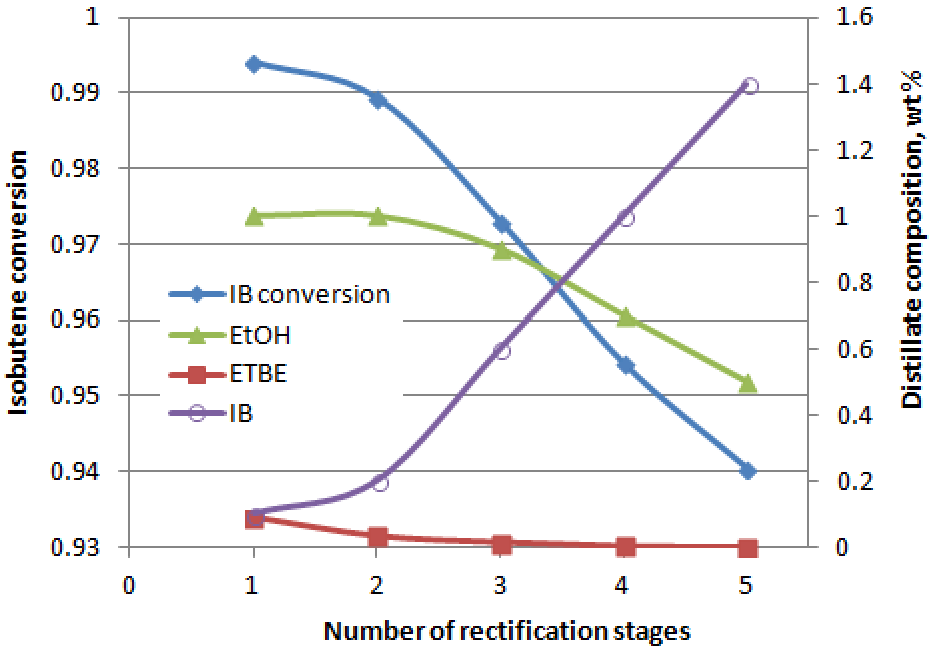

Fig. 7. Effects of the number of rectification stages on isobutene conversion and distillate composition

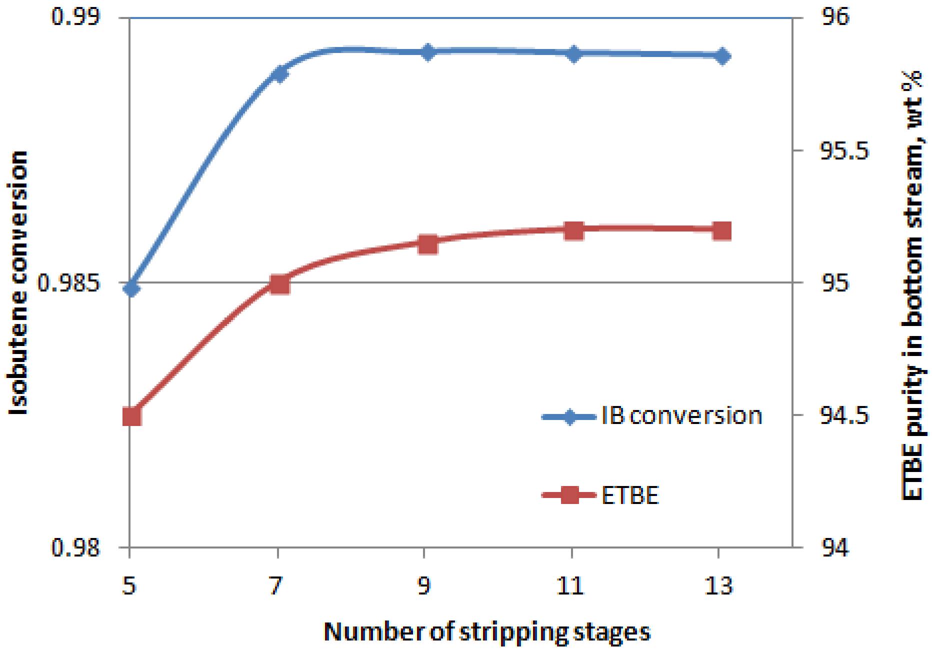

Fig. 8. Effects of the number of stripping stages on isobutene conversion and ETBE purity

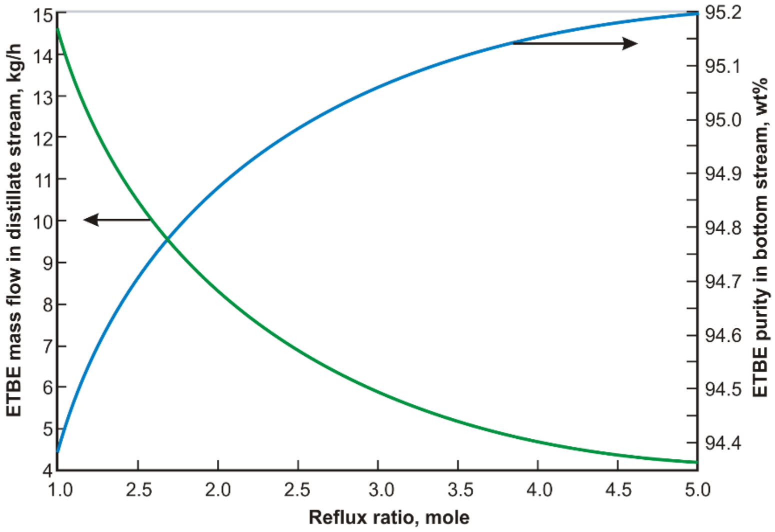

Figure 9. Effect of reflux ratio on ETBE purity in bottom stream and ETBE losses with distillate stream.

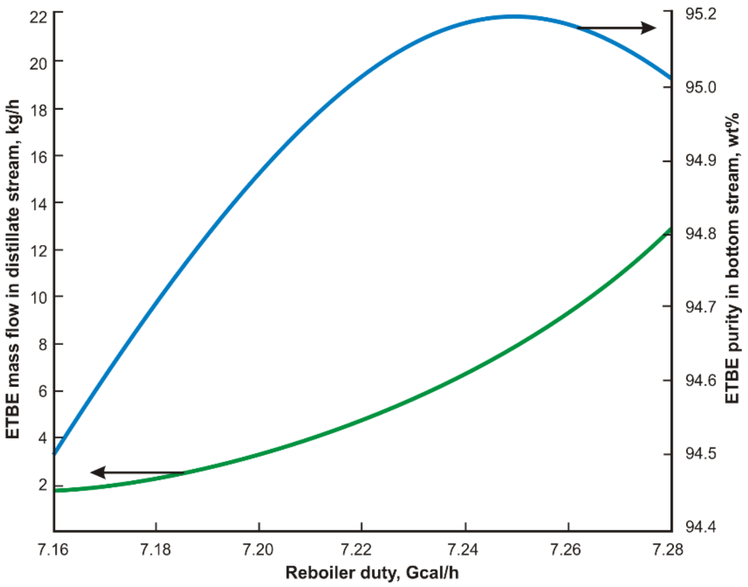

Fig 10. Effect of reboiler duty on ETBE purity in bottom stream and ETBE losses with distillate stream.

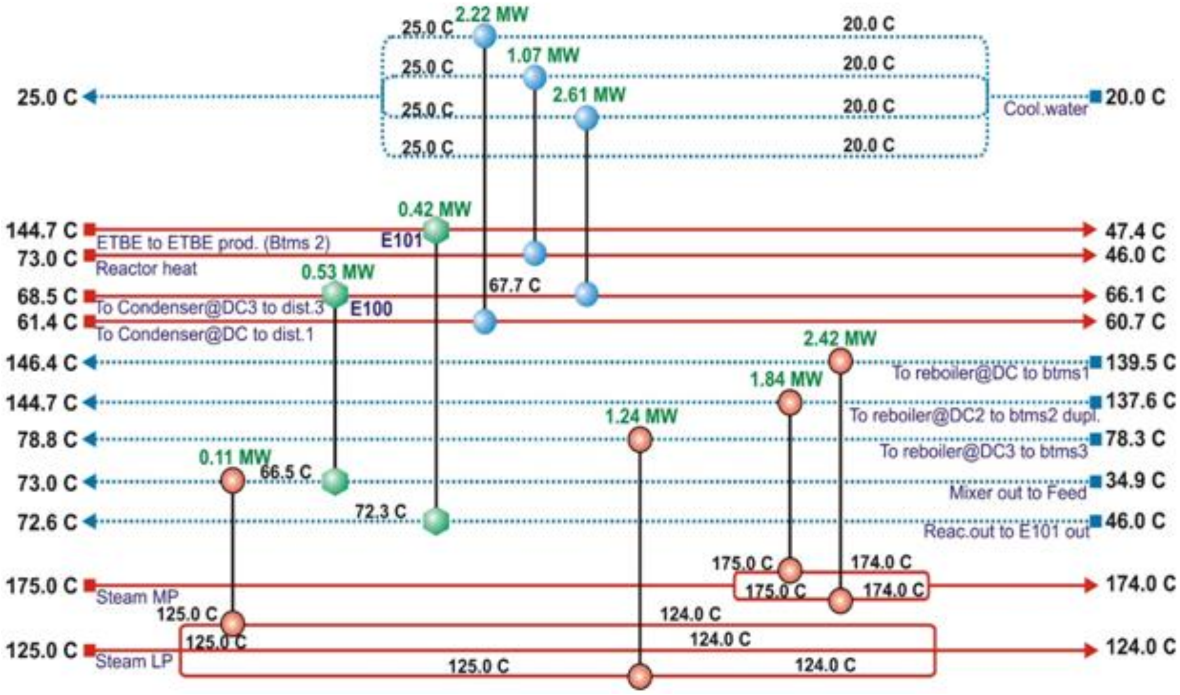

Fig 11. Heat exchanger network design for the PSD process

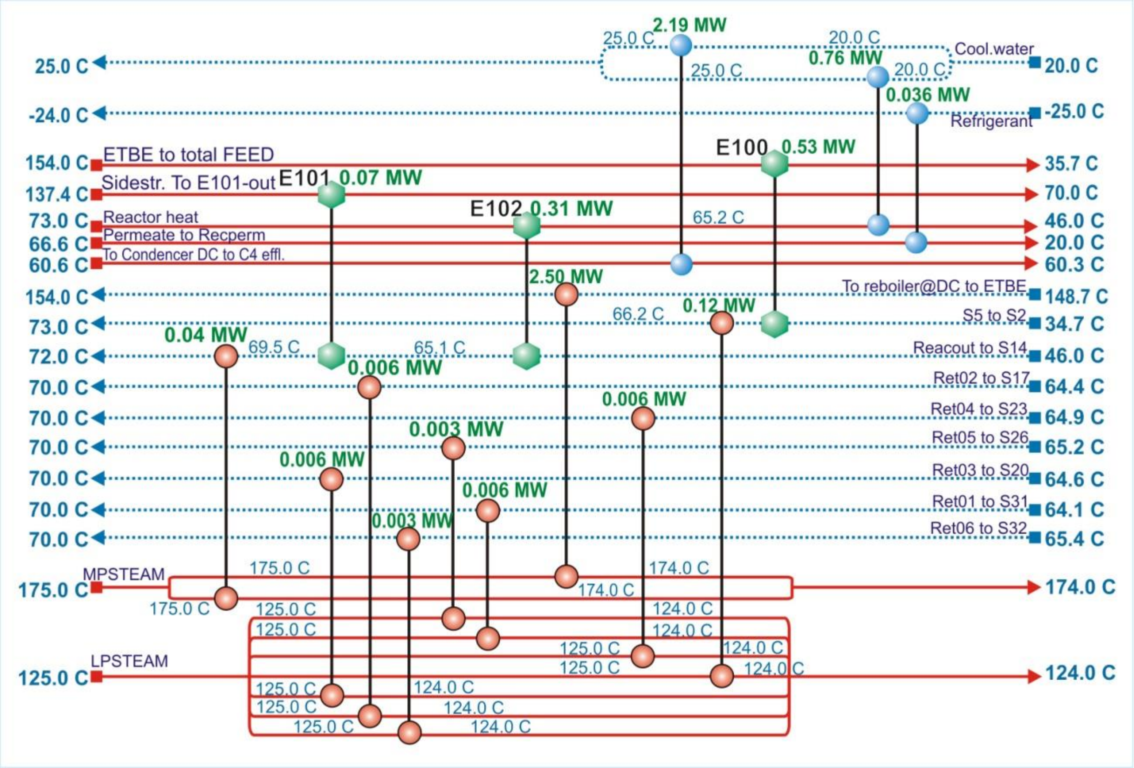

Fig 12. Heat exchanger network design for the PV-integrated hybrid process

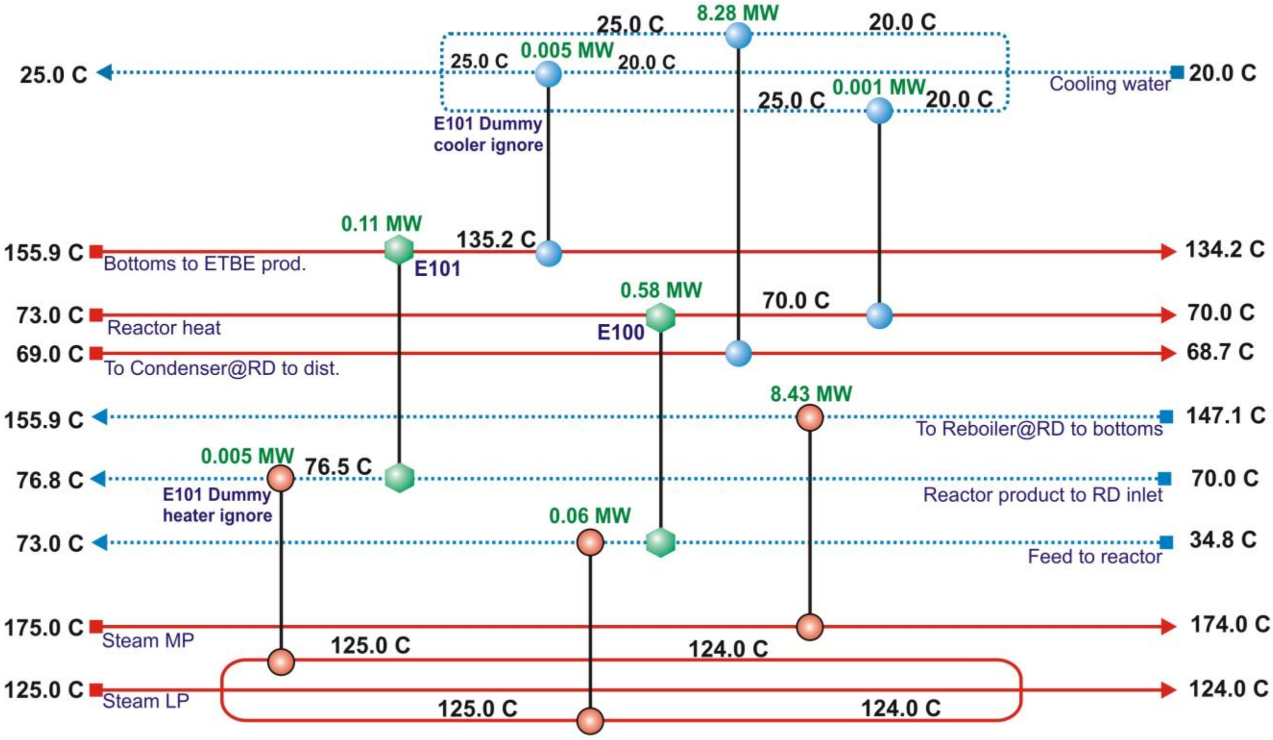

Fig 13. Heat exchanger network design for the reactive distillation process

Table 1. Parameters of the pervaporation model for EtOH/ETBE mixtures permeating through PERVAP 2256 membrane (65 ºC)

	EtOH	ETBE	
		$X_{ETBE} > 0.78$	$X_{ETBE} < 0.78$
A_i	$4.79\text{x}10^{-3}$	$8.61\text{x}10^{-3}$	$7.57\text{x}10^{-4}$
B_i	0.186	$- 4.04\text{x}10^{-4}$	$- 3.03\text{x}10^{-4}$
C_i	8.208	$- 1.43\text{x}10^{-4}$	$- 7.08\text{x}10^{-4}$
$E_{act,\,i}$ (kJ mol^{-1})	- 3.35	- 3.91	

Table 2. Summary of material balances for each process configuration.

Conventional process

	Total feed (kmol h^{-1})	Reactor outlet (kmol h^{-1})	Btm.1 (kmol h^{-1})	Dist.1 C4 stream (kmol h^{-1})	Btm.2 ETBE product (kmol h^{-1})	Dist.2 (kmol h^{-1})	Btm.3, Recycle tc reactor (kmol h^{-1})	Dist.3, Recycle to DC2 (kmol h^{-1})
ETBE	trace	59.80	59.80	< 0.001	59.10	69.64	trace	69.64
ETOH	72.66	12.87	6.04	6.82	3.27	91.15	1.88	89.27
1-butene	282.68	282.68	0.001	282.68	trace	0.08	trace	0.08
Isobutene	66.06	3.76	trace	3.76	trace	< 0.001	trace	trace
TBA	0.02	0.79	0.79	0.001	0.77	0.23	0.02	0.21
Water	0.773							
DIB	trace	0.86	0.86	trace	0.86	0.09	trace	0.09
Total	422.2	360.76	67.5	293.26	64	160.8	1.9	158.9
T (^{o}C)	73	46	151	60	145	131	78	66
P (bar)	14	10	8.4	7.8	7.5	7.5	1.013	1.013

PV integrated hybrid process

	Total feed to reactor (kmol h^{-1})	Reactor outlet (kmol h^{-1})	Btm.1 ETBE product (kmol h^{-1})	Dist.1 C4 stream (kmol h^{-1})	Side stream (kmol h^{-1})	Total retentate stream (kmol h^{-1})	Total permeate stream (kmol h^{-1})
ETBE	0.017	59.81	59.797	< 0.001	8.80	8.78	0.017
ETOH	72.66	12.87	3.377	6.76	7.37	4.64	2.733
1-butene	282.68	282.68	0.001	282.68	0.073	0.073	
Isobutene	66.06	3.767	< 0.001	3.767	0.001	0.001	
TBA		0.763	0.76	0.004	0.143	0.143	
Water	0.763						
DIB		0.865	0.865	trace	0.063	0.063	
Total	422.2	360.75	64.8	293.21	16.444	13.695	2.75
T (^{o}C)	73	46	154	60.3	137.4	65.6	66.6
P (bar)	10	10	8.4	7.8	8.2	4.8	0.026

Reactive distillation process

	Total feed to pre-reactor (kmol h^{-1})	Reactor outlet (kmol h^{-1})	Btm.1 ETBE product (kmol h^{-1})	Dist.1 C4 stream (kmol h^{-1})
ETBE		51.23	63.91	0.054
ETOH	72.66	21.43	5.19	3.51
1-butene	282.68	282.68	< 0.001	282.68
Isobutene	66.06	13.32	trace	0.703
TBA		0.773	0.769	0.004
Water	0.773			
DIB		0.363	0.309	trace
Total	422.2	369.8	70.18	286.95
T (^{o}C)	73	70	155.9	68.7
P (bar)	10	10	10	9.5

Table 3. Energy use details for each process configuration (kWh per ton of product)

	Conventional process		**PV integrated hybrid process**		**Reactive distillation**	
	without integration	after integration	without integration	after integration	without integration	after integration
Low pressure steam	363	213	105	23	111	9
Middle pressure steam	671	671	454	395	1228	1228
Total hot utilities	**1034**	**884**	**559**	**418**	**1339**	**1237**
Cooling water	1008	926	520	460	1291	1205
Refrigerant	-	-	5	5	-	-
Total cold utilities	**1008**	**926**	**525**	**465**	**1291**	**1205**