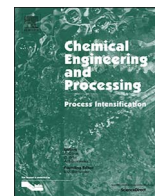




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Comparative study of conventional, reactive-distillation and pervaporation integrated hybrid process for ethyl tert-butyl ether production

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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.

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 resin 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

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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:



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:

$$K = 7.40 \times 10^{-5} \exp [4262.21/T] \quad (4)$$

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:

$$\ln K = 95.2633 + 5819.8644/T - 17.2 \ln T - 0.0356T \quad (5)$$

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 °C [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.

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