Simulation Study of a Reactive Distillation Process for the Ethanol Production

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A simulation study of the effects of design and operating parameters under which optimal-stable steady states may occur in a reactive distillation process for synthesis of ethanol has been presented. The conceptual design of the reactive separation process is based on the element concept where the reactive driving force approach is employed. To validate the proposed design, steady state simulations using ASPEN PLUS® software package were accomplished, and a sensitivity analysis was done to establish the operating conditions of the process. The analysed parameters were as follows: i) the operating pressure and ii) the reflux ratio. The results showed that a new energy-efficient design with minimal energy requirements may be considered a viable technological alternative for ethanol synthesis. Also, this reaction-separation process allows to satisfy the design and operating constrains. This is, a novel reactive distillation process capable to increase the purity of the ethanol from a dilute solution, i.e., up to 30% ethanol in water under optimal operating conditions.

1. Introduction

Ethanol (EtOH) is one of the most versatile oxygen-containing organic chemicals because of its unique combination of properties as a solvent, a germicide, a beverage, an antifreeze, a fuel, a depressant, and especially as a chemical intermediate for other organic chemicals. The use of fermentation-derived ethanol as an automotive fuel additive to enhance octane and reduce emissions has seen explosive growth. Ethanol is a replacement for MTBE as an oxygenate for fuels. MTBE has been deemed an environmental risk because of its seepage into groundwater.

Nowadays, most of ethanol produce comes from fermentation processes; however, the growing interest in ethanol biofuels from biomass, as well as the increase in the demand for food due to the growth of the world population, has once again aroused interest in the synthetic routes for production of short-chain alcohols. Therefore, industrially, ethanol is produced synthetically from ethylene, as a by-product of certain operating conditions, or by other synthetic methods that have been investigated but have not become commercial. These include, e.g., the hydration of ethylene in the presence of dilute acids, the conversion of acetylene to acetaldehyde, followed by hydrogenation of the aldehyde to ethanol, and the Fischer-Tropsch hydrocarbon synthesis. If the synthetic pathway is considering (from petroleum feedstock), there are two main processes for the synthesis of ethanol from ethylene. The earliest to be developed (in 1930 by Union Carbide Corp.) was the indirect hydration process, variously called the strong sulfuric acid-ethylene process, the ethyl sulfate process, the esterification-hydrolysis process, or the sulfation-hydrolysis process. The other synthesis process, designed to eliminate the use of sulfuric acid and which, since the early 1970s, has completely supplanted the old sulfuric acid process is the direct hydration process.

The direct synthesis of ethylene to ethanol via a liquid-phase process catalysed by dilute sulfuric acid was first demonstrated more than a hundred years ago. In 1923, the passage of an ethylene-steam mixture over Al_2O_3 at 300 °C was found to give a small yield of acetaldehyde, and it was inferred that this was produced via ethanol. Since the late 1920s, several industrial concerns have expressed interest in producing ethanol

synthetically from ethylene over solid catalysts. However, not until 1947 was the first commercial plant for the manufacture of ethanol by catalytic hydration started in the United States by Shell; the same process was commercialized in the United Kingdom in 1951. There are two main process categories for the direct hydration of ethylene to ethanol. Vapor-phase processes contact a solid or liquid catalyst with gaseous reactants. Mixed-phase processes contact a solid or liquid catalyst with liquid and gaseous reactants. Generally, ethanol is produced by a vapor-phase process; mixed-phase processes are used for the analogous hydration of propylene to 2-propanol. Important exceptions to these two generalizations exist, but the discussion that follows emphasizes technology associated with the vapor-phase direct hydration of ethylene.

Synthetic fuels research has resulted in a whole new look at processes to produce lower molecular weight alcohols from synthesis gas. Therefore, Process Intensification (PI) can be applied to exploit new developments in reactive separations technology. PI is a tool for the targeted enhancement of involved phenomena at different scales to achieve a targeted benefit (Stankiewicz and Moulijn, 2000; Lutze et al., 2010a). In this sense, one aspect of PI is the combination of reaction and separation to shift the chemical reaction equilibrium to the side of the reaction product. For this reason, reactive distillation is one of the better-known examples of PI. Reactive distillation is considered as a highly promising process because it combines the requirements of *in-situ* separation with reaction. This integration brings several advantages, i.e., energy and capital savings, increased reactant conversion, enhanced product selectivity, and improved heat integration. Currently, more than 150 reactive distillation processes with annual capacities of 100−3000 ktonnes/y are in operation worldwide (Hiwale et al., 2004; Harmsen, 2007). A huge scholarly database dealing with the modelling, simulation, and industrial applications of reactive distillation can be found elsewhere (Taylor and Krishna, 2000; Lutze et al., 2010b). However, the design and operation issues of reactive distillation is more complex than those involved for either conventional chemical reactors or conventional (non-reactive) distillation columns due to the nonlinear behaviour that exists between vapor-liquid equilibrium, vapor-liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics, which may cause multiple steady states and complex dynamics (Yamaki and Matsuda, 2012; Xu et al., 2017). Thus, this paper presents an innovative reactive distillation process that allows the production of ethanol. During the conceptual design, a systematic study of the operating conditions is performed using built-in sensitivity analysis tool of in ASPEN PLUS®. The influence of these operating conditions over the main variable to control, i.e., the ethylene conversion is analysed.

2. The reactive system

In the temperature range at which industrial catalysts operate, the vapor-phase hydration of ethylene to ethanol is a reversible reaction controlled by the equilibrium and it has been summarized (Nelson and Courter, 1954):

$$C_2H_4 + H_2O \leftrightarrow C_2H_6O \ (\Delta H = -43.4 \ kJ/mol) \tag{1}$$

A lower temperature favours higher ethylene conversion, but Reaction (1) is then accompanied by reversible formation of diethyl ether:

$$C_2H_4 + C_2H_6O \leftrightarrow C_4H_{10}O \tag{2}$$

Acetaldehyde, a deleterious by-product, is most likely formed from trace amounts of acetylene in the feed:

$$C_2H_2 \xrightarrow{H_2O} C_2H_4O \tag{3}$$
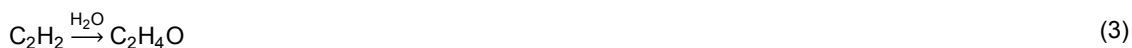
The acetaldehyde is particularly undesirable as it leads to the formation of crotonaldehyde, an impurity that adversely affects ethanol quality even at parts per million levels.

$$2C_2H_3O \rightarrow C_2H_4(OH)C_2H_3O \rightarrow C_4H_6O + H_2O \tag{4}$$

Both aldehydes can be hydrogenated to their saturated normal alcohols.

$$C_2H_4O + H_2 \rightarrow C_2H_6O \tag{5}$$

$$C_4H_6O + 2H_2 \rightarrow C_4H_{10}O \tag{6}$$
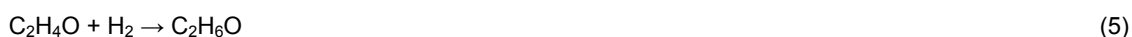
Higher hydrocarbons are formed by the polymerization of ethylene. Any higher unsaturated hydrocarbons present are converted to the corresponding alcohols by hydration. The silica gel-supported phosphoric acid catalyst (H_3PO_4/SiO_2) is used in this process at it has high selectivity in excess ethylene. The ethanol production rate increases remarkably with increasing phosphoric acid loadings. Under usual reactor conditions (approximately equimolar ethylene-water feed, 250-300 °C, 49- 79 atm), the conversion de ethylene is 7-22 %.

3. Reactive Distillation Process

Sánchez-Daza et al. (2003) developed a graphical method for the design of reactive distillation processes, where the driving force approach has been extended for reactive systems. This approach was adapted from binary component separations non-reactive driving force (Gani and Bek-Pedersen, 2000). The application of the reactive driving force method (Mansouri et al., 2016) permits the determination of important design variables in terms of two parameters, the location and the size of the maximum driving force, D_x and D_y, respectively. The feed stage location and the minimum reflux ratio, RR_{min}, (and/or the boilup ratio, RB_{min}) are determined from these two parameters for a given feed and product specification.

Figure 1 shows the reactive driving force diagram for this reactive system. It can be seen clearly from the reactive diagram that ethylene could be separated in a reasonably pure format at the top of the process. Therefore, these slopes (reactive operating lines) are used in a reactive McCabe-Thiele method to find the theoretical reactive stages. The number of stages is found to be three reactive stages. Note that from a practical point of view, presence of reaction in reboiler and condenser has not been reported, therefore these two non-reactive stages (i.e., partial reboiler and partial condenser) are considered as stages. Thus, the number of stages including reboiler and condenser is five. However, in the bottom of the reactive zone there is a mixture of water, ethanol, and diethyl ether. To concentrate the water and minimize the diethyl ether, an additional stripping section is added below the reaction zone. In this sense, Sánchez-Daza et al. (2003) obtained a reactive distillation process that consists of nine total stages for the ethanol synthesis.
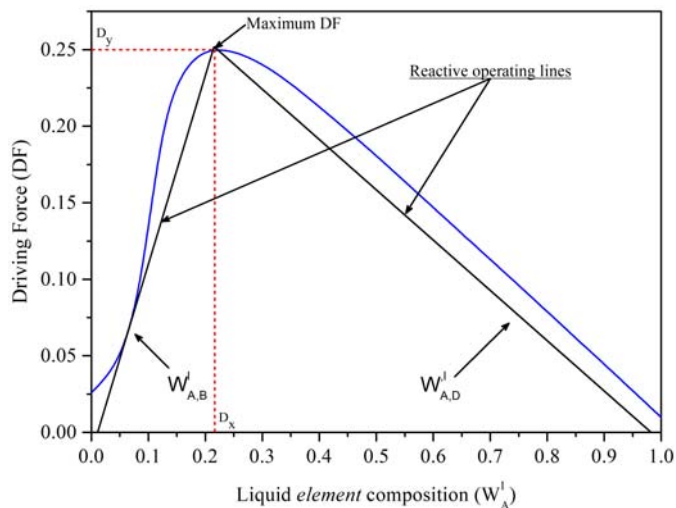

Figure 1: Reactive driving force diagram for ethanol synthesis proposed by Sánchez-Daza et al. (2003).
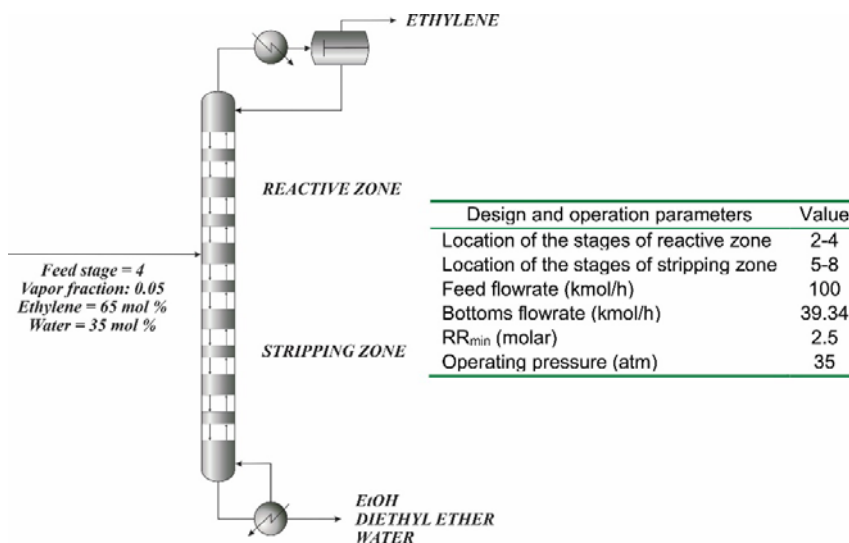

Design and operation parameters	Value
Location of the stages of reactive zone	2-4
Location of the stages of stripping zone	5-8
Feed flowrate (kmol/h)	100
Bottoms flowrate (kmol/h)	39.34
RR_{min} (molar)	2.5
Operating pressure (atm)	35

Figure 2: Design specifications of the reactive distillation process for ethanol production.

4. Steady state analysis

Figure 2 shows the process details used for the simulations. The feed is a mixture of ethylene and water, which enters at the reactive zone. Unreacted ethylene enters the top of the column and the ethanol-water mixture enters the bottom, together with a small amount of diethyl ether. Below the reactive zone there is a stripping zone to concentrate the ethanol and minimize the diethyl ether. In a process simulator, such as ASPEN PLUS®, it is possible to generate the previously configuration assuming chemical equilibrium on the reactive stages and using the equilibrium stage model. The nonidealities of the vapor and liquid phases were performed using the NRTL-RK model. Note that the selection of ideal gas for the vapor phase is based on an arbitrary assumption, as ethylene is a supercritical compound under the given operating conditions.

To analyse the steady-state solutions in the reactive distillation process using ASPEN PLUS®, two basic steps are required. First, the reactive distillation process was simulated using the RADFRAC module. For this task, ASPEN PLUS® required the specification of components, thermodynamic model, feed condition, operating pressure, column configuration (number of stages, feed stage location, reactive zone designation, type of condenser and reboiler), two operating specifications (in our case, reflux ratio and bottoms rate), and the reaction type. In the present study the reaction type was defined as an equilibrium limited system, where the chemical equilibrium constant is calculated from the Gibbs free energies. Afterwards, a sensitivity analysis was carried out to assess the influence of the design and operating parameters on the reactive distillation process performance. The sensitivity option in ASPEN PLUS® was selected so that current results were used as initial estimates for the next steady state solution. In this case, only one operating parameter and the initial estimates were variable. In this work, by sensitivity analysis, we mean the study of the effect of changes in input variables on process (model) outputs. Specifically, it means to perform in ASPEN PLUS® the following four steps: (i) specification of measured (sampled) variable(s); (ii) specification of manipulated (varied) variable(s); (iii) specification of the range(s) for manipulated (varied) variable(s); and (iv) specification of the quantities to calculate and tabulate. Also, sensitivity analysis is a tool helpful that can be observed as a very basic method to "optimise" the design and operating parameters in the reactive distillation process.

For this purpose, the influence of two parameters such as operating pressure (P) and reflux ratio (RR) were analysed. These inputs (manipulated variables) were selected since they are key parameters to operate the process, while the conversion of ethylene is shown to be the output variable (measured quantity). Also, the effect of various feed locations (design parameter) on reboiler heat duty (QR) is determined.

4.1 Influence of operating pressure

The conversion of ethylene is the output variable determining the operability region. It can be noted in Figure 3(a) that this region is found between the P values of 22.8 and 35.3 atm; moreover, an ethylene conversion of 83.04 % is obtained for a P of 35 atm (reference steady state, RSS) with a molar ethylene to water feed ratio of 1.85. The vertical tie line in this figure represents the RSS. Here, to refine high values of the P, the simulation was reinitialized at each step with current solution as initial estimates, and then the step size was reduced by half until the step size was small enough and until divergence occurred (meaning that small changes in the P can lead to abrupt phase changes), i.e., convergence problems were found when P is increased above its nominal value of 35 atm. For this situation, only the decrement of this parameter was performed. Figure 3(a) shows that with a P of 26 atm or lower, a slightly high conversion of ethylene is achieved. Therefore, the simulation results reveal that the ethylene conversion decreases monotonically with the increase of operating pressure, demonstrating that a relatively low operating pressure is beneficial for the reactive distillation process (Wang et al., 2010). Nevertheless, the reduction of operating pressure helps to shift the equilibrium toward the production of ethanol (Le Chatelier's principle) and is favourable to reactant conversion and reaction heat load.

On the other hand, one procedure that can be effective for the reinforcement of internal heat integration in the design of the reactive separation process is the variation of feed stage allocation mainly in the reactive zone (Cheng and Yu, 2005; Huang et al., 2006). So, steady state simulations were carried out until the minimum energy consumption was reached. Figure 3(b) shows the influence of feed stage on heat duties of condenser and reboiler with the consideration of further internal heat integration. It is interesting to observe that minimum energy consumption obtained occurs when the feed stage rearrangement is located at stage 4, corresponding to the feed location predicted by reactive driving force approach (Sánchez-Daza et al., 2003). However, if the influence of feed stage on heat duties is performed with a P of 24 atm (84.55 % of ethylene conversion), it can be observed in Figure 4(a) that the amount of energy may be reduced and still a high conversion of ethylene is achieved. This configuration presents energy savings of 78.5 % over the scheme that operates with a pressure of 35 atm. But, when this operating parameter is selected, a convergence problem using the sensitivity analysis tool of ASPEN PLUS® was found, i.e., dried stages occurs for small values of P.
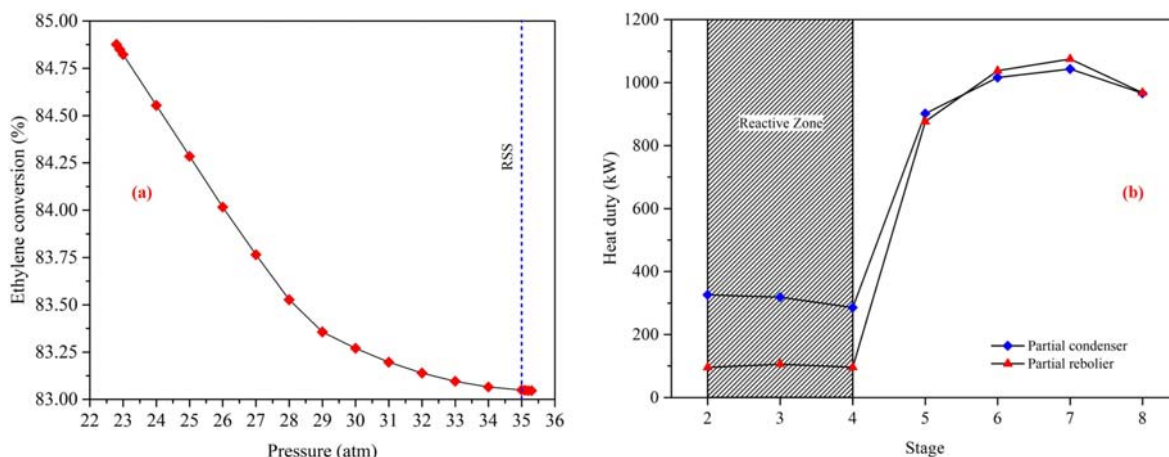
Figure 3: Operability diagrams for ethylene conversion and heat duties with the variation of (a) operating pressure and (b) feed stage (P = 35 atm; QR = 96.15 kW).

4.2 Influence of reflux ratio

The influence of the RR, as operating parameter, was analysed in the interval 8≤RR≤100. Again, the conversion of ethylene is the output variable determining the operability region. As shown in Figure 4(a), the vertical tie line corresponds to RSS (RR = 11). To achieve a complete elimination of ethylene, the RR should be large than 30 causing an increase of the energy consumption to condensate partially the vapor distillate flowrate, especially when the highly volatile C_2H_4 is present. Also, an excessive reflux leads to an incomplete conversion and operating problems, i.e., the percent flood is exceeded and therefore can cause flooding in the stages along the process [Figure(b)].
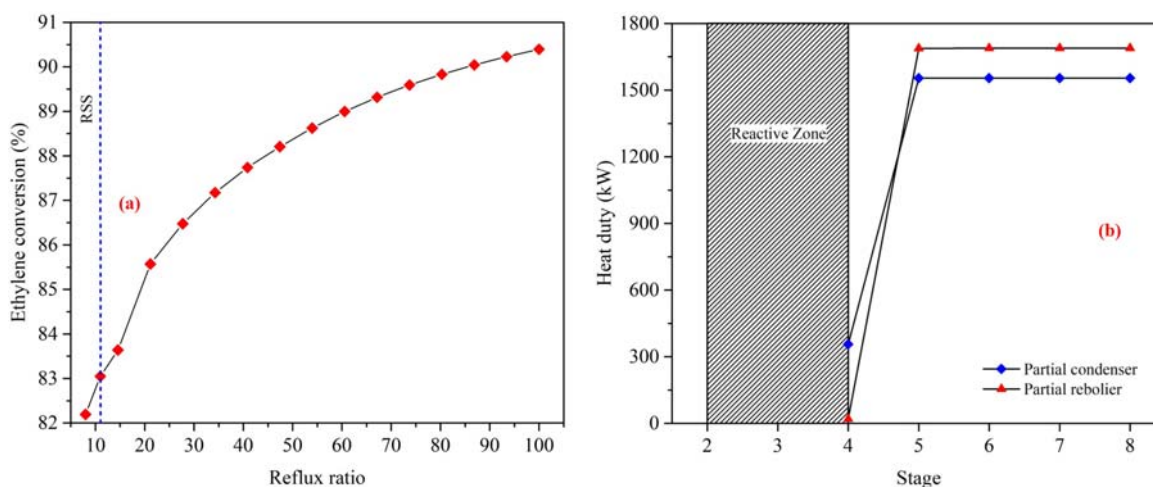

Figure 4: Operability diagrams for heat duties and ethylene conversion with the variation of (a) feed stage and (b) reflux ratio (P = 24 atm; QR = 20.66 kW).

5. Conclusions

A simulation study of the effects of design and operating parameters under which optimal-stable steady states may occur in a reactive distillation process for synthesis of ethanol has been presented. The conceptual design of the reaction-separation process was performed through the reactive driving force approach in term of elements. Two parameters such as operating pressure and reflux ratio of the reactive separation process were analysed. The simulation results reveal that an increase of operating pressure causes a corresponding increase in ethanol production rate. Higher pressures also increase polymer formation. On the other hand, reaction velocity is low at low temperatures. Hence it is necessary to use catalysts and relatively high temperatures to approach equilibrium within a reasonably short time. Therefore, operating pressure must be selected carefully to maximize reactant conversion and reaction heat load, reinforcing reactive system

between the reaction operation and the separation operation involved. Reflux ratio impact both reaction and separation performance in the reactive distillation. For equilibrium limited systems, a high reflux rate increases the separation of products from reactants, thereby increasing the reaction driving force. Therefore, it is desirable to operate the process at lower values of reflux ratio. After investigating the influence of P and RR, a new energy-efficient design of the reactive distillation process will be used for a control study (e.g., complex nonlinear dynamics). As an overall conclusion, our findings suggest that, under optimal design and operating conditions, reactive distillation could be considered as a viable technological alternative for ethanol production.

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