Use of a Reactive Distillation in the Process of Producing Diethyl Ether Using Dewatering of Ethanol

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Abstract
Diethyl ether is considered as one of the simplest and lightest oxygenated fuels, which has higher octane and thermal energy than dimethyl ether. Diethyl ether can be considered as one of renewable fuels and is produced by applying a reactive distillation method. Reaction distillation is a complex process in the chemical industry in which the chemical separation and the chemical reaction are carried out simultaneously. In this paper, applying a high purity ethanol dewatering, the process of reactive distillation in the production of diethyl ether is simulated by using Aspen Hysys software. Different models of activity coefficients have been analyzed in this paper. The best model for molecular diethyl ether was found to be one of the most important cases in simulating a diethyl ether unit to obtain a strong thermodynamic model for highly unrealistic behavior of fluid-liquid-vapor balance in this system. Finally, results of simulation with the data are compared and a very good match has been observed.

Keywords: diethyl ether, dewatering of ethanol, sulfuric acid, static simulation, reactive distillation, ethyl alcohol

1. Introduction
In recent years, the decline in energy sources and pollution caused by fossil fuels has led researchers to develop clean and environmentally friendly fuels that not only prevent the loss of resources from fossil fuels, rather they use the resources to produce them that are replaceable and renewable (Jia et al., 2018). One of these renewable fuels is diethyl ether which is a renewable fuel for diesel engines and is a suitable solvent for fats, waxes, petroleum products, perfumes, resins, and paints (Ardebili et al., 2021). Being mixed with an ethanol, diethyl ether will become an excellent solvent which is also known as an anesthetic ether in surgeries (Ariyasingha et al., 2020). Having the chemical formula C4-H10-O, diethyl ether is the most important member of the ether family, which is a very volatile, colorless, steep and moderately soluble in water, and is a useful commercial source for ethylene in units that do not have access to unpurified gases (Nanthagopal et al., 2019). Diethyl ether can be prepared in a variety of ways, most notably:

1.1 First Method - Ethylene Watering Reaction
This method is used in petrochemical centers to produce both alcohol and ether by watering ethylene adjacent to sulfuric acid.

1.2 Second Method - Dewatering Reaction of Ethyl Alcohol With Sulfuric Acid
In this method, by dewatering of ethyl alcohol with concentrated sulfuric acid, diethyl ether will be produced.

1.3 Third Method - Dewatering of Ethyl Alcohol via Catalysts
In this method, the dewatering of ethyl alcohol is performed by solid catalysts. Considering that there is a possibility of producing ethyl alcohol by fermenting sugar in Iran factories, much of Iran alcohol supplies are produced in this way, and the availability of concentrated sulfuric acid (due to its production in the country), the second method will be investigated in this paper (Ai et al., 2019). But the problem with ethanol dewatering is that the process consumes a lot of energy. The most energy consumed in this process is the distillation tower reboiler. This amount of consumed energy causes an increase in operating costs (resulting in increase in overall annual costs) and environmental problems. To solve this problem, two solutions are suggested:

1) First, using the reactor and the distillation tower separately in the conventional process of diethyl ether production (the second method mentioned above).

2) Instead of using the conventional process (using the reactor and the distillation tower separately), applying a new process, which uses a distillation tower that reduces investment costs while the reaction heat is used as the required heat...
for the tower and as a result, the energy consumption in the distillation tower will be reduced. A reactive distillation process is a combination of a distillation process and a chemical reaction that occurs inside a tower. This compound is very effective for processes that respond to temperatures and pressures appropriate for separation. At the same time, the simultaneous separation of the product from the reaction removes the inadequate side products from the process. As a result, the efficiency of the operation increases and the problem of separating materials that have a close-together welding point or together with azotropic will be eliminated (Wang et al., 2015). The desired reactions can be catalytic homogeneous reactions and thermal reactions (non-catalytic) which have several advantages over the conventional processes. One of the advantages is that the reaction and the separation step are carried out sequentially while the product is separated from the reaction mixture simultaneously. Today, more than 100 catalytic distillation units are operating in a single unit, and most of these units have been built over the past 15 years (Bernal et al., 2018). This process is more effective by 20% in terms of initial investment, operating costs, and energy savings compared to conventional units that combine a reactor and a distillation system. Today, the use of reactive distillation has many advantages, including the integration of reactive stages and separation, reduction of initial and operational costs, overcoming the limitations of chemical balances, the use of a reaction heat in the distillation process, and an increase in the separation of azotropic mixtures (Segovia-Hernández et al., 2015). The process of reactive distillation due to the simultaneous separation and reaction in terms of simulation and control has some complexities. To investigate the complete behavior of the tower, the reaction and the isolation, researchers are undertaking wider studies on modeling and process simulation, column design, gas-liquid equilibrium behavior, and process control dynamics. The feasibility of a reactive distillation process is dependent on several important factors including parameter volatility, temperature, pressure of the tower, and the ratio of return flow (Li et al., 2019). The purpose of this study is to investigate the simultaneous production and separation of diethyl ether in a system, to study the simulation of reactive distillation tower, to overcome the constraints caused by chemical balances, to prevent the formation of azotropic, to increase the efficiency, and to determine the optimal values for different parameters.

2. Ethanol

Ethanol can not only be produced biochemically (fermentation) from carbohydrate sources namely corn, sugar cane, sugar beet, potatoes, and cereal grains but lignocellulosic feedstocks hydrolysates (the so-called second generation) can be fermented to produce ethanol. Production of bioethanol used for fuel has grewed substantially in China, Brazil, US, and EU lately with the total annual production of fifty-two million MT in 2020 (Tse et al., 2021). Vehicles can run on a mixture of gasoline with up to ten percent dry ethanol. The raw ethanol obtained from the fermentation broth is purified from the distillation purification. The removal of water from the ethanol is a process which demands heat, which sparks an interest in the application of hydrous ethanol (Santasnachok et al., 2019).

2.1 Ethanol to a Variety of Products

HZSM-5 which is the most widely used catalyst, can catalyse the conversion of ethanol into a variety of products which differs with the addition of promoters as well as the temperature. Van der Borght et al. (2016) proposed a simplified reaction scheme (Figure 1) for the formation of diethyl ether, ethylene and C3+ hydrocarbons on zeolites.

![Figure 1. Reaction Scheme for Ethanol Conversions on Zeolites](http://ijc.ccsenet.org)

Adámková et al. (2021) illustrated how the selectivity towards various products of ethanol conversion on ZSM-5 varies with temperature from 100-700°C. The first product diethyl ether, common to all zeolites, drops off from 200°C, whilst propylene and ethylene increase. The aromatics, depending on the SiO2/Al2O3 ratio, also start appearing at low selectivities above 200°C as compared to the olefins (>60%) but with the highest aromatics selectivity of xylenes and C9+ (2-4%). Benzene starts off at higher temperatures. The highest SiO2/Al2O3 ratio with the lower acidity of the zeolite is reflected in the lower selectivity towards the aromatics formation. The modification of HZSM-5 with Mo2C will diminish ethylene selectivity from 65% above 400°C and increases the benzene selectivity amongst aromatics, generally increasing the aromatics selectivity. In order to summarize, the preferred temperature regions for the conversion of ethanol into various products on HZSM-5 is illustrated as Figure 2:
3. Ethanol to Diethyl Ether

Diethyl ether can be used as diesel fuels. Diethyl ether has excellent cold-start properties and can reduce formations of NO in exhaust gases from diesel engines. In experimental studies on a sole cylinder, four stroke, water-cooled DI diesel engine diethyl ether was co-fed with LPG as an ignition improver. Findings showed that as compared to diesel at full loads, Diethyl ether lowers cylinder gas temperatures and reduces the NO in the exhaust gas by about 65% (Phung et al., 2015-a). In a very early study (Phung et al., 2015-b), IR spectra showed how both Brønsted and Lewis acid sites catalyse the conversion of ethanol to diethyl ether. Low calcined zeolites having both types of sites show the highest activity and the lowest optimum temperature for diethyl ether. From TPD for diethyl ether adsorption over HZSM-5 (calcined at 540°C) it was found that diethyl ether was not desorbed at temperatures over 200°C in accordance with its low presence above that temperature under catalytic testing. The phosphoric acid treated ZSM-5 showed no coke formation. A reaction mechanism of the reaction between an adsorbed ethyl species with a gas phase ethanol molecule was postulated. In the more recent study (Garbarino et al., 2018) the coupling between two adsorbed ethanol yielding diethyl ether is suggested. Two zeolites with a SiO2/Al2O3 of 80 and 280 respectively were compared. The lower number of Brønsted sites on the 280 version was reflected in a lower activity at low temperature, however in both cases the formation of diethyl ether diminished from 200°C and ceased at 300°C. Belhadj et al. (2021) showed that the formation of diethyl ether only requires weak acid sites. Diethyl ether has recently been proposed as an ignition enhancer in internal combustion engines, where the diethyl ether is formed by dehydration of an ethanol containing fuel over a zeolite in a preconversion step before injection (De Oliveira et al., 2018).

4. Different Techniques of Preparing Anhydrous Bio-Ethanol from the Water–Ethanol Azeotropic Mix

Either first, second, or third generations of feedstock are applied, fermentation will only produce an alcohol-lean broth (12–15 vol% when using first generations, and <=6 vol% for generation two and three). Fractional distillation will concentrate ethanol to 95.6 vol% (89.5 mol%), the azeotrope with a boiling point of 78.2°C (Gabriel et al., 2019). It is impossible to enrich further ethanol by common distillation, while various alternatives are possible which include:

1) Adding entraining agents, such as cyclohexane, benzene, and heptane, in order to form a new ternary azeotrope comprising water, ethanol, and entraining agents.

2) The application of vacuum distillation: the composition of the ethanol–water azeotrope changes to ethanol-rich mixtures at various pressures below atmospheric pressures, while azeotropes disappear at pressures below 9333 kPa, which makes it possible to distil absolute ethanol from an ethanol–water mixture. This high vacuum operation is obviously not economical.

3) The use of pressure-swing distillations.

4) The application of molecular sieves, namely synthetic zeolite in pellet form to adsorb water from the 95.6 vol% ethanol solutions. The zeolite could be regenerated by drying in an unlimited number of times.

5) The application of membranes to separate water and ethanol: as membrane separation is not based on vapor-liquid equilibriums, and as a result not subject to the limitations of the water–ethanol azeotrope, the selective permeation of one of the components is possible by applying either hydrophilic membranes (water permeates) or hydrophobic membranes (ethanol permeates).

6) The use of other techniques, i.e. the extraction of ethanol from the fermenter broth by supercritical CO2, a liquid–liquid extraction of ethanol from an aqueous solution, (Zhang et al., 2018 and Bermejo et al., 2016) or the use of Pressure Swing Adsorption (Singh et al., 2019).

These options are only at the very early phases of experimental investigation. Among these techniques, membrane techniques and molecular sieves are the ones that need more focus.

5. The Traditional Molecular Sieve Process to Prepare Fuel-Grade Bio-Ethanol

In the bio-ethanol distillation train, the water–ethanol azeotrope is condensed as top product of the final distillation column. Its temperature is around 95°C at 189 kPa. The further water removal to near-anhydrous ethanol takes place in the molecular sieving process, where the azeotropic feed is superheated to >110–120°C, and sent to one of the sieve columns, while the other column is being regenerated (release of adsorbed water). The column regeneration is performed using superheated dry ethanol, condensed and returned to the final distillation column of the bio-ethanol.
process as “light ethanol”. Both columns adsorb and regenerate alternately, and ensure the uninterrupted continuous production. The recovered heat in the condensers can be used in the low temperature reboilers (distillation) or for preheating. The mass and energy balances of the molecular sieve process for a typical 200,000 tpa bio-ethanol plant, i.e. 26,000 kg/h of pure ethanol, (Kang et al., 2015 and Srivastava et al., 2020) are given in Table 1.

### Table 1. Mass and Energy Balance of the Molecular Sieve Process

<table>
<thead>
<tr>
<th>Mass balance</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed water concentration (wt%)</td>
<td>5.6</td>
</tr>
<tr>
<td>Product water concentration (wt%)</td>
<td>0.8</td>
</tr>
<tr>
<td>Total feed flow rate (kg/h)</td>
<td>27,542</td>
</tr>
<tr>
<td>Feed ethanol (100%) flow rate (kg/h)</td>
<td>26,000</td>
</tr>
<tr>
<td>Product mass flow rate (kg/h)</td>
<td>25,209</td>
</tr>
<tr>
<td>Water absorption (kg/h)</td>
<td>1,333</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy balance</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporator heat</td>
<td></td>
</tr>
<tr>
<td>Product heat (kJ/kg)</td>
<td>844</td>
</tr>
<tr>
<td>Heat content of steam (kJ/kg)</td>
<td>2,061</td>
</tr>
<tr>
<td>Absorption column</td>
<td></td>
</tr>
<tr>
<td>Steam consumption (kJ/h)</td>
<td>23,267,784</td>
</tr>
<tr>
<td>Absorption column</td>
<td></td>
</tr>
<tr>
<td>Steam consumption (kg/h)</td>
<td>11,291</td>
</tr>
<tr>
<td>Regeneration column</td>
<td></td>
</tr>
<tr>
<td>Steam consumption (kJ/h)</td>
<td>1,719,600</td>
</tr>
<tr>
<td>Regeneration column</td>
<td></td>
</tr>
<tr>
<td>Steam consumption (kg/h)</td>
<td>835</td>
</tr>
<tr>
<td>Total steam (kg/h)</td>
<td>12,126</td>
</tr>
<tr>
<td>(kg steam/kg ethanol)</td>
<td>0.47</td>
</tr>
</tbody>
</table>

The steam duty of the complete distillation plant is ~1.3 kg steam/kg ethanol (Baeyens et al., 2015). The molecular sieve unit hence represents about 27% of the total steam duty. Since current distillation units bio-ethanol already integrate an extensive heat recovery from high pressure condensers to low pressure reboilers, no excess heat is available. The heat duty of the molecular sieve operation needs to be entirely supplied from the plant steam boiler.

### 6. Experimental Section

First, two flows of ethyl alcohol enter the first reactor that 95% of its weight is ethanol, 5% of its weight is water with 98% sulfuric acid flow, at a temperature of 25°C, a pressure of 1200kPa, and without any heat exchanges. The first reactor is a complete mixing reactor. The main reaction of diethyl ether is produced as the Equation (1) below:

$$2C_2H_5OH \rightarrow C_2H_5OCH_2 + H_2O$$

Equation (1)

In this reactor, ethanol is converted to 98.94% purity and the output liquid product of the reactor which is produced due to the heat generated by the reaction to a temperature of 140°C, reaches the second reactor to achieve a higher conversion rate as a feed. At this stage and before entering the second reactor, the alkaline flow of soda is combined with this flow. The second reactor is a type of conversion reactor; the Equation (2) here is the same as the reaction to neutralize sulfuric acid:

$$H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$$

Equation (2)

The main flow and diethyl ether produced at a temperature of 53.91°C and a pressure of 900kPa will go through the separation stage. At this stage, in order to separate a solid, first physical separation is applied and a solid-free part enters a distillation tower. This tower will be launched to produce high purity diethyl ether. As shown in Figure 3, this tower is of a tray type and includes 32 trays such as a full condenser, a reboiler, and two entrances (Su et al., 2016).
While the water goes out from the bottom of the tower, the liquid diethyl ether in the tower will have a purity of approximately 99%. An appropriate temperature for production of diethyl ether with the use of alcohol in the presence of sulfuric acid as a catalyst is 130°C to 140°C, while in Equation (3) ethyl sulfuric acid is produced at lower temperatures, and ethylene is produced at higher temperatures.

\[
2C_2H_5OH \xrightarrow{H_2SO_4} (C_2H_5)_2O + H_2O
\]

Equation (3)

The input flow enters into the 16th tray of distillation tower. In this reactive distillation tower, the reaction occurs in a liquid phase, with a catalyst, and within the trays 2nd to 30th. The speed equation of the heterogeneous catalytic reaction which occurs in the tower is illustrated as Equation (4).

\[
r = \frac{60.6e^{(-22599[J/mole]/RT)C_{EtOH}^2}}{1+(1.19e^{(-40500[J/mole]/RT)C_{EtOH}+4.8e^{(-3200[J/mole]/RT)C_{DEE}+3.87e^{(-2500[J/mole]/RT)C_{H_2O}}}) \times 10^{-6}}
\]

Equation (4)

In the case of using sulfuric acid as a catalyst, it requires an extra step in the process which is usually using (NaOH) to neutralize the acid and remove it from the process. The process is illustrated as Equation (5):

\[
H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O
\]

Equation (5)

7. Simulation

To simulate the distillation tower reactive and define the reaction packet in the software, two distinct equations are defined:

1) The first reactive packet involves the production of diethyl ether with the use of alcohol in the presence of sulfuric acid as a catalyst:

\[
2C_2H_5OH \xrightarrow{H_2SO_4} (C_2H_5)_2O + H_2O
\]

Equation (6)

2) The second packet is the sulfuric acid neutralization reaction:

\[
H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O
\]

Equation (7)
Aspen Hysys software has been used to simulate the diethyl ether production process. In the conventional process, first, a complete mixing reactor and a distillation tower will be applied separately. The second reactor in this process is the type of conversion reactor and also the reaction in the second reactor is the same as the reaction to neutralize the sulfuric acid. The product of the liquid outlet from the first reactor to achieve more conversion enters in the second reactor as a feed. To separate the diethyl ether from this process, tray distillation tower will be used. This tower contains two products on the top and the bottom that the product on the top has a purity of 95% for diethyl ether. An overview of the simulated process of the conventional process of diethyl ether production in Aspen Hysys software is illustrated as Figure 4.

One of the most important cases in the simulation of a unit of diethyl ether is to obtain a strong thermodynamic model for the highly unrealistic behavior of liquid-liquid-vapor balance in this system. In this simulation, the calculation of all non-ideal liquid phase activity coefficients and the Glycole Package activity coefficient equation are used as the basis for the steam-liquid equilibrium. It should be noted that Spare Continuation Solver will be used to solve this distillation tower reactive in the software which is the most powerful method of solving distillation towers reactive. An overview of the simulated process of the reactive distillation of diethyl ether production in Aspen Hysys software is shown as Figure 5.
8. Results and Discussion

Figure 6 shows the variations in the composition of the molar percentage of components in the conventional process tower as it approaches the top of the tower, the composition of the percentage of diethyl ether (red curve) as the main product which is more at the top of the tower, and the composition of the water percentage (blue curve) which is reduced as a heavy component. As illustrated, the purity of diethyl ether at the top of the tower reaches 95%.

Figure 6. The Variation in Compositions of the Molar Percentages in the Distillation Tower of the Unit of Diethyl Ether Production in the Conventional Process

The final composition of the product at the top of the tower is illustrated as Table 2.

Table 2. Combining the Final Percentage of the Main Product Flow of the Diethyl Ether Unit in the Conventional Process

<table>
<thead>
<tr>
<th>Compositions</th>
<th>More Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>DiE-Ether</td>
<td>0.9532</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0361</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.0000</td>
</tr>
<tr>
<td>H2SO4</td>
<td>0.0000</td>
</tr>
<tr>
<td>H2O</td>
<td>0.0107</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Figure 7 shows the variations in the composition of the molar percentage of components in a distillation tower reactive. It can be observed that whatever approaches the top of the tower, the percentage of diethyl ether (red curve) as the main product which is more at the top of the reactor distillation tower increases and the water percentage (blue curve) is reduced as a heavy component. As noted, the purity of diethyl ether at the top of the tower is about 99%.
Figure 7. Changes in the Composition of the Molar Percentage of Components in the Tower

The final composition of the product at the top of the tower is highlighted as Table 3.

Table 3. Combining the Final Percentage of the Main Product of Diethyl Ether in the Reactor Distillation Tower Reactive

<table>
<thead>
<tr>
<th>Compositions</th>
<th>More Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>DiE-Ether</td>
<td>0.9885</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0006</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.0000</td>
</tr>
<tr>
<td>H2SO4</td>
<td>0.0000</td>
</tr>
<tr>
<td>H2O</td>
<td>0.0109</td>
</tr>
</tbody>
</table>

9. Conclusions

In this research, the distillation tower reactive has been successfully simulated for the production of diethyl ether by Aspen Hysys software. Different parameters influence the tower performance and diethyl ether approximate purity of 99%. Results show that the Glycole Package activity coefficient model has the highest purity of diethyl ether at the top of the tower. Also, the optimum amount for the flow rate in the top of the tower is equal to a mole per hour, while the location of the feeding place and the location of the reaction are optimized. It is also concluded that both the sulfuric acid and the ethanol enter the 16th tray of the distillation tower reactive and the location of the reaction is in the range of trays 2nd to 30th. Using a distillation tower reduces investment costs while the reaction heat is used as the required heat for the tower and as a result, the energy consumption in the distillation tower will be reduced. Comparing to the conventional process, the reactive distillation process of diethyl ether has two important characteristics:

1) By removing one of the reactors, the costs of the process will be reduced significantly.

2) By increasing the purity of diethyl ether in the final product of distillation tower reactive from 95% to 99%, the purity of diethyl ether in the process of reactive distillation will be about 4.21% higher than the conventional process. Clearly, this growth in the purity increases the sales price of the product and thereby increases the profitability of the process.

Acknowledgments

I would like to thank my parents for their encouragement and support, especially within my last months of my studies, without whom I would never have enjoyed so many accomplishments. Love you both.

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