DESIGN OF ETHYLBENZENE PRODUCTION PROCESS

IBRAR UL SAMAD 1, KHAWLA HASIBA 1, ASEEL AWADALLA 1, SARA MAHMOUD 1

ABSTRACT

This paper presents rigorous design of a process used for the production of ethylbenzene. A number of processes with different design schemes were reviewed and evaluated. The most suitable processes was selected and simulated using Aspen HYSYS simulator. The capital cost of each equipment within the process was calculated using CAPCOST. Furthermore, the economics of the process was studied. It was found that the studied process had a discounted payback period of 4.2 years and generated an annual revenue of $121 million.

Keywords: Ethylbenzene, Aspen, HYSYS, CAPCOST, Process Design

1. INTRODUCTION

Ethylbenzene (C₆H₅CH₂CH₃) is an organic compound which is commonly known as phenylethane or alpha-methyltoluene [1]. The chemical nature of this compound make it miscible with most organic solvents however, it’s moderately soluble in water. This compound is considered as a volatile and highly flammable due to its flash point of 19-23 °C. Moreover, it’s a colorless liquid product which has a gasoline odor. In addition, it is considered as a monocyclic alkylaromatic compound in terms of its chemical structure which has a 106 g/mol molecular weight. The ethylbenzene production plays a significant role in the co-production of styrene where 99% of it is used to produce styrene and less than 1% of it is used as an intermediate for producing diethylbenzene, ethylanthraquinone and acetophenone [1]. To illustrate, it is used as a constituent of naphtha and asphalt as well as a minor usage in the coating industry for paints and varnishes [1].

Figure 1. Applications of Ethylbenzene [3]

Additionally, ethylbenzene can be found in various parts in the environment and it is on the hazardous list since it is a highly flammable compound and a fire hazard. Ethylbenzene has a lot of hazards where a contact between ethylbenzene and human in a short period of time will cause a lot of problems such as: irritation of the eyes, dryness of the skin, throat agitation, pain, redness in the eyes and dizziness. On the other hand, exposure to ethylbenzene in the long run can cause some bad effects on the blood, damage the liver, trouble

Different processes and technologies have been developed in order to produce ethylbenzene. During the 1960’s, several facilities were constructed in the United States, Japan and Europe to recover ethylbenzene through fractionation of mixed xylenes which mainly was formed in refinery catalytic reforming units. However, due to the high energy demand and investment costs, this practice has been discontinued [1]. The latest technologies mainly utilize a mixed liquid-vapor phase zeolite catalyst process, a Mobil-badger ethylbenzene process which is a vapor-phase zeolite catalyst process or a liquid phase Lummus-UOP process to produce ethylbenzene. Though, for each process there’s an economic, safety and environmental issues that should be taken into consideration before production. Based on that, an optimization for the mixed liquid-vapor phase process have been made since it has more advantages compared with other processes. According to some gas chromatography tests, the ethylbenzene produced has a purity greater than 99.5 % while the impurities are normally aromatic compounds in the range of C6-C10 and the non-aromatics are in the range of C7-C10 [1].
breathing, cancer and sometimes can lead to death. In addition, it has been found that ethylbenzene has some effects on the liver, kidneys and blood of the animals [4].

2. PROCESS DESIGN ALTERNATIVES

2.1. Literature Survey

S. Liu et al. [5] discussed the production of ethylbenzene using liquid-phase benzene and vapor-phase ethylene feed. This industrial process is highly selective in the production of ethylbenzene. The process involves an alkylation section (the reactor vessel) and a trans-alkylation section. Additionally, the ethylbenzene produced is used to heat the reactor vessel, saving in energy costs. This process combines the catalytic reaction and distillation into a single process, whereby the energy produced by the heat of reaction is used to drive the distillation of the produced products. The process was developed by the CDTECH. Lastly, the reactor operates at a temperature of 140-185 °C and a pressure of 1.6-2.1 MPa.

E. B. Pandhare [6] outlined the various different methods of the manufacture of ethylbenzene. Although it is a good reference, it will be primarily used for the study of the production of ethylbenzene using vapor-phase process that also involves the zeolite catalyst. This process was developed jointly by Mobil and Badger and is commonly referred to as the Mobil-Badger process. The Mobil-Badger process is also the most successful of all the vapor phase technologies used for the production of ethylbenzene. It involves the use of the reactants in vapor phase in the alkylation units. Additionally, the reaction is carried out at 400-450 °C and 2-3 MPa.

R. E. Kirk et al. [7] provided a detailed outlook on many processes in the chemical industry including the ones that produce ethylbenzene. It also outlines a process called the Unocal-Lummus-UOP ethylbenzene process, where ethylbenzene using the reactants in the liquid phase on a zeolite catalyst. This process is quite similar to the Mobil-Badger process but the yield of ethylbenzene is low and is laced with impurities in the form of aromatics and non-aromatics. The reaction is carried out 270 °C and 3.79 MPa.

2.2. Mixed Liquid-Vapor Phase Zeolite Catalyst Process

2.2.1. Process Description

This process involves the use of a Y zeolite catalyst, capable of converting benzene and dilute ethylene to ethylbenzene [5],[8]. The catalyst itself has excellent resistances to sulfur and water and also has good regeneration qualities, all the while ensuring great ethylene conversion, good ethylbenzene selectivity and longer operational period [5]. The alkylation reactions take place in an alkylation reactor which primarily consists of two sections: the catalytic distillation section and the standard distillation section. The catalytic bed is found at the top of the column [8]. Benzene is fed as a liquid from the top of the column while the ethylene is fed as a vapor from the bottom of catalytic section. This counter-current action causes the ethylene to rapidly dissolve in the benzene liquid phase and react to form ethylbenzene on the catalyst sites. Since, the reaction is extremely exothermic, the energy is used to cause distillation of the products, namely, ethylbenzene & poly-ethylbenzene (PEB). The alkylation reaction is carried out at a temperature of 140-185 °C and a pressure of 1.6-2.1 MPa [5]. After separation of the PEB, the transalkylation reactions take place is another reactor.

2.2.2. Safety & Environmental Issues

There are no significant environmental and safety issues with this process as it operates at a relatively low temperature and pressure. However, it is important to note that this process still produces residual oil as one of its final by-products which can cause significant pollution and therefore, should be dealt properly by recycling or reusing it for other chemical processes. Additionally, the catalyst, albeit it has a long lifetime, still needs to be properly disposed off, as it can cause damage to the environment.

2.2.3. Economic Issues

1) The major cost in this process comes from the use of expensive catalysts that are crucial to the process.
2) Another important economic issue to consider would be the design and manufacture of the alkylation reactor. The alkylation would serve the dual purpose of housing the catalytic reaction and standard distillation. Combining both these processes together means that the reactor column has to be designed from scratch leading to increased capital costs.

2.3. Vapor-Phase Zeolite Catalyst Process

2.3.1. Process Description

The Mobil-Badger ethylbenzene process is considered to be the most successful vapor phase technology [6]. In this process, fresh benzene stream is vaporized and pre-heated to a certain temperature; after which it is fed to multistage of fixed-bed reactor containing the zeolite catalyst. Moreover, the ethylene stream is introduced to the reactor through multiple stages to enhance contact between the reactants. The alkylation occurs in the vapor phase at a temperature range from 400 °C to 450°C and the pressure for each plant is usually between 2-3 MPa [6]. The polyethylbenzene (PEB) recovered from the distillation column is mixed with benzene. After heating and vaporizing the mixture, it is fed into a transalkylator where the PEB reacts with the benzene to form additional ethylbenzene. The effluent from the reactor, consisting of unreacted benzene, PEBs, trace impurities and ethylbenzene, is fed into a “benzene column” for distillation. Benzene is removed from the top of the column, along with light hydrocarbons. These are stripped in an overhead stripper with the benzene being recycled to the reactor again, while the light hydrocarbons are vented to be used as a fuel [6]. The presence of light hydrocarbons can be attributed mostly to the ethane in the ethylene feed and non-aromatic components that decompose in the fresh benzene feed. The bottoms product from the benzene column is fed in the ethylbenzene column to recover ethylbenzene from the top, while the bottoms product consisting of PEB is fed into a PEB column for further distillation. This column generates PEB as an overhead product which is recycled to the transalkylator for the production of ethylbenzene. The bottoms product is known as “residue” and is usually found in very small quantities and is also used as a fuel [6].

The catalyst in this process is zeolite based and “is less sensitive to water, sulfur and other poisons than the Lewis acid catalysts” [6]. Due to coke formation overtime as a result of high temperature, the catalyst becomes deactivated. Hence, it is important to regenerate the catalyst from time to time. This regeneration takes up-to 36 hours and is important after every 6-8 weeks of operation [6]. Therefore, it is important that the process has two parallel reactors, where one reactor is used when the other is taken out of production because catalyst regeneration.

2.3.2. Safety & Environmental Issues

1) The alkylation reaction takes place at high temperature (400-450 °C) and high pressure (2-3 MPa). This means that the column would need to be constructed out of special materials of construction in order to safely accommodate such high pressures and temperatures.
2) Formation of coke on the catalyst means that it needs to be regenerated from time to time. This regeneration is done by burning the catalyst to form CO₂. CO₂ is a greenhouse gas and causes significant environmental damage by destroying the ozone layer.

3) High temperatures also result in side-reactions of byproducts, such as aromatics, to be known as carcinogenic and also mutagenic.

2.3.3. Economic Issues

1) In order to regenerate the catalyst, specific regeneration equipment would be required which increases the capital cost of the plant [6].

2) Since the reactors are taken off for catalyst regeneration, a substitute reactor needs to be present to continue production. This also causes the capital cost to be increased.

3) High temperatures and pressures mean that the equipment needs to be made out of special materials of constructions which can be expensive, leading to increased costs.

4) Lastly, high temperatures and pressures also cause an increase in energy costs which lead to an increase in operating costs.

2.4. Liquid-Phase Zeolite Catalyst Process

2.4.1. Process Description

This process is similar to the Mobil-Badger vapor phase ethylbenzene process. However, some differences arise in the catalysts, reactor sizes, yields, reaction conditions and product specifications. In order to maximize the productivity of the catalyst in the Lummus process, the reactors have to operate nearly to the critical temperature of the reaction mixture which is around 270 °C, and an appropriate pressure is required in order to keep the reaction mixture in the liquid phase which is approximately 3.79 MPa [7]. In addition, a compressor is needed unless the ethylene’s supply pressure is enough to deliver it to the reactor [7]. Furthermore, large amount of catalyst is required in two multistage transalkylator and alkylators and water is added to moderate the activity of the catalyst. On the other hand, the benzene feed is pretreated in a clay treaters; while the remaining C6 nonaromatics are removed by purging a portion of the recycled benzene which is called “drag benzene”. The overall yield of the ethylbenzene produced from this process is around 98.98%, with the residue of the PEB column being the reason for a low yield of ethylbenzene. This process isn’t recommended for low concentration ethylene feeds and in order to have enough liquid to dissolve the diluents (mainly, C1, C2 and hydrogen), the benzene recycle would have been raised up to an uneconomical level. Additionally, the ethylbenzene produced from this process also contains significant amount of impurities in the form of aromatics. These aromatics include xylene, cumene and ethyltoluene. Moreover, there are aromatic compounds present in the product [7].

2.4.2. Safety & Environmental Issues

1) The reactor operates at 3.79 MPa which is a very high pressure. Hence, the reactor needs to have a greater thickness in order to accommodate such high pressure.

2) The production of residue and drag benzene could cause environmental pollution if not disposed properly.

2.4.3. Economic Issues

1) More alkylation reactors are needed leading to increase in capital costs.

2) The feed needs to be pure ethylene and benzene; hence, specific equipment needs to be installed for pre-treatment. This leads to increase in capital costs.

3) To accommodate the high pressure in the reactor, more material is required for safe use. This also leads to an increased expenditure in capital costs.

3. PROCESS SELECTION

Based on the literature review, it was decided to opt for the mixed liquid-vapor phase process for the production of ethylbenzene. This process has many more advantages over the other processes. One of the key advantages is that it does not need a pure ethylene and benzene feed and can therefore, produce ethylbenzene feed from dilute feeds. Furthermore, this process would not require a pre-treatment phase, reducing any operating and capital costs. Additionally, the mixed liquid-vapor phase has a high yield and selectivity of ethylbenzene [5] when compared to other processes. Lastly, the process operates at reasonable temperatures and pressures that are not too high. Not only would this reduce operating and capital costs, but would also provide a safe working environment as there is less danger for an explosion or fire to take place. Considering all these factors and comparing them to the other two processes it seems reasonable to select the mixed liquid-vapor phase process developed by CDTECH.

4. RESULTS & DISCUSSION

4.1. HYSYS Simulation

Figure 2. HYSYS Simulation

Table 1. Material stream results

<table>
<thead>
<tr>
<th>Material Flowrate</th>
<th>Light Fraction</th>
<th>Medium Fraction</th>
<th>Heavy Fraction</th>
<th>Coke</th>
<th>Total Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate (kmol/hr)</td>
<td>1.000</td>
<td>0.600</td>
<td>0.400</td>
<td>0.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 2. Stream Compositions

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Ethylene</th>
<th>Propylene</th>
<th>Butenes</th>
<th>Pentanes</th>
<th>Hexanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate (kmol/hr)</td>
<td>0.8800</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Table 3. Energy streams

<table>
<thead>
<tr>
<th>Energy Streams</th>
<th>Heat Flow (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Flow (kW)</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
4.1.1. Simulation Assumptions

- No material lost due to leaks
- Pure product formed (i.e. no formation of heavy flux oil)
- Pure ethylene and benzene available
- All reflux ratios are 1.5 times the minimum reflux ratio
- For reactive distillation, the column is divided into a conversion reactor and shortcut distillation column to aid in simulation design
- Only diethylbenzene is produced in the side reaction
- Conversion of ethylene and benzene to ethylbenzene is kept at 85% in CR-100. While for formation of diethylbenzene, conversion is 10%
- Conversion of diethylbenzene in the second reactor, CRV-101, is at 90%
- Column for purification of product from flux oil not required, as it is assumed no flux oil is produced

4.2. List of Equipment, Sizing & Cost

Table 4. Equipment, Sizing and Cost

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Number Required</th>
<th>MOC</th>
<th>Power (HP)</th>
<th>Area (m²)</th>
<th>Volume (m³)</th>
<th>Bare Module Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor</td>
<td>1</td>
<td>Carbon Steel</td>
<td>699.1</td>
<td>N/A</td>
<td>N/A</td>
<td>46,000</td>
</tr>
<tr>
<td>Pump</td>
<td>2</td>
<td>Stainless Steel</td>
<td>N/A</td>
<td>25</td>
<td>149,000</td>
<td></td>
</tr>
<tr>
<td>Distillation Tower</td>
<td>3</td>
<td>Stainless Steel</td>
<td>N/A</td>
<td>26</td>
<td>71,600</td>
<td></td>
</tr>
<tr>
<td>Heaters</td>
<td>1</td>
<td>Stainless Steel/ Stainless Steel</td>
<td>N/A</td>
<td>68</td>
<td>130,000</td>
<td></td>
</tr>
<tr>
<td>Coolers</td>
<td>1</td>
<td>Stainless Steel/ Stainless Steel</td>
<td>N/A</td>
<td>30</td>
<td>164,000</td>
<td></td>
</tr>
<tr>
<td>Total Vessel</td>
<td>1</td>
<td>Carbon Steel</td>
<td>N/A</td>
<td>0.51</td>
<td>13,000</td>
<td></td>
</tr>
</tbody>
</table>

Total Bare Module Cost: $4,664,800

4.2.1. Assumptions for Sizing & Cost Analysis

- Length between each plate in the towers is 1.5 m
- For flash vessel, HYSYS is used for sizing
- CAPCOST is used for costing

4.3. Cost Analysis using CAPCOST

Payback Period (Discounted): 4.2 years
Payback Period (Non-Discounted): 3.0 years
Annual Revenue: $121,035,000

Since, the final NPV value is positive ($9.72 million) in year 12, it can be concluded that this project is profitable. Additionally, as per our findings using CAPCOST, the discounted payback period is 4.2 years. This indicates that the project starts to have a profit after 4.2 years, hence it is feasible. In order to calculate these values, the annual cost of product and raw materials needed to be found. Using [9], the price of benzene and ethylene was found to $0.74/Kg and $0.978/Kg, respectively. However, to have a more conservative estimate due to fluctuations in prices, both the prices of benzene and ethylene are taken to be $1/Kg.
This paper presented a rigorous design of a process used for the production of ethylbenzene. It was found that the most suitable process had a discounted payback period of 4.2 years and generated an annual revenue of $121 million.

**CONFLICT OF INTERESTS**

The authors declare that there is no conflict of interest related to the publication of this article.