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Journal of Chemical Engineering Research Progress, 1 (1) 2024, 42-53

Research Article

Benzene Purity Improvement and Feed Amount Reduction on Benzene Production

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Received: 28th December 2023; Revised: 11st January 2024; Accepted: 11st January 2024
Available online: 12nd January 2024; Published regularly: June 2024

Abstract

Global demand for benzene is expected to rise significantly. Previous research focused on extracting toluene from water, but a proposed shift towards preventive measures includes recycling toluene to avoid pollution and enhance benzene production. Emphasis on addressing separation ratios and material balance is crucial for successful simulations. Proposed innovations involve added splitters and shortcut columns for enhanced purity. Benzene production could be gained through the process of hydrodealkylation with some modifications. It shows the significant difference of the purity of benzene produced with the use of splitter and shortcut column compared to not using splitter and shortcut column. The recycling process effects the mass flow of the compound which picture the capability of a process to scale up. Through recycling the toluene, it also happens to cut or push the sum of the feed which leads the process to be more economical. Based on the modification of the benzene production it is resulted that the mass flow rate of the benzene production is significantly increased from 38.6 kg/h to 430.72 kg/h which gives possibility of the production to be higher in one go. Recycling toluene and hydrogen will also help the effectivity and efficiency of the process by its quality and specifically its quantity of the fresh feed. The modification also affects the purities of the benzene from 70.72% to 99.95%. Therefore, by doing the modification it will produce greater number of benzene with its high purities.

Keywords: Benzene; Conversion Reactor; Hydrodealkylation; Hydrogen; Toluene

How to Cite: D.N.A. Owena, B.W.S. Loeharja, H. Hardani, H. Cahyaningrum. (2024). Benzene Purity Improvement and Feed Amount Reduction on Benzene Production. *Journal of Chemical Engineering Research Progress*, 1 (1), 42-53 (doi: 10.9767/jcerp.20106)

Permalink/DOI: https://doi.org/10.9767/jcerp.20106

Supporting Information (SI): https://journal.bcrec.id/index.php/jcerp/article/downloadSuppFile/20106/5128

1. Introduction

The demand for base petrochemical feedstocks is predicted to grow, with expecting increases of 4.4%, 4.1%, 3% and 7.2% for ethylene, propylene, benzene and paraxylene respectively by 2022. This would put global benzene demand at 51 million tons per year. It is predicted by 2024 that the demand of benzene would go higher [1]. Besides fulfilling the needs of the chemical substances, the engineer designing a chemical process should include the aspects of economic and environmentally disciplines. Some substances that are released after the process has done can be detrimental to the environment. As engineers there are simulation application that can be used to calculate the consequences the factory could give to the environment and specifically about the economic aspect of the process would give before the factory is implementing the process that is done through the simulation application. Once a conceptual design is developed, one can focus on

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more details by performing simulation in which the simulation can provide a more rigorous and detailed analysis that increases confidence in a design [2].

In the previous research, the toluene was extracted from the water by porous materials to avoid damage for the environment [3]. The action of extracting toluene to keep the environment safe might be a good act, however the idea of preventing toluene contaminating the water itself or decreasing the amount of toluene that directly goes to the water after being used once should be done. The report analysis shows that the HDA process design on the gas recycle stream has better performance in both economic and environmental aspects compared to the other design process [4]. In the previous research, it has also implemented toluene recycling process with the purpose is gaining high purities of benzene. Other than improving the purities of the product, recycle could also help to alleviate kinetic limitation and improve the mass flow rate of substance production [5]. Recycling toluene and hydrogen for the benzene production then become a great solution for reducing the amount of feed itself to get bigger amount of production since we could reuse the toluene that has been recycled with some changes apply in the operation condition to maximize the result of the production.

In previous research, the specification of separation ratios has been identified as a factor leading to convergence, where, in practice, distillation columns specifications significantly influence purity. Similarly, the success of simulations for multiple units may be hindered by inconsistencies in material balance. For example, a distillation column simulation in this journal could fail if the product specifications are not consistently aligned with the feed. Specifications in relative mode, such as distillate/feed ratio or component recovery, are easier to implement, particularly when units are integrated into recycling loops [6]. The convergence may fail due to interrelated specifications, as exemplified by distillation columns. Recovery and purity specifications for components are not recommended due to their interdependence. Additionally, potential interdependent or conflicting specifications should be carefully examined when defining the control flowsheet. Normally, a splitter is specified in two ways, absolute product flow rates or relative fractions [7].

In the previous research, it was mentioned that toluene was extracted from water using porous materials to avoid damage to the environment. However, extracting toluene from water is not a preventive action. In the previous research, it was also mentioned that the specifications of the distillation column significantly affect the purity. However, the distillation column simulation in that research could fail if the product specifications are not consistent with the feed. Based on these problems, the purpose of this research is to make preventive innovations by recycling the residual toluene produced in the lower yield of distillation, so as to avoid water and environmental pollution, reduce raw material costs, and significantly increase the amount of benzene production. In addition, splitters and shortcut columns were added to improve the purity of benzene production [6].

2. Methods

2.1. Hydrodealkylation

Hydrodealkylation (HDA) is a chemical process used to create simpler aromatic hydrocarbons without their functional groups that involves the reaction of aromatic hydrocarbons (such as toluene) in the presence of hydrogen gas [8]. In this process, toluene is hydrodealkylated in a homogeneous, non-catalytic reactor where benzene and methane are produced as products. In another equilibrium reaction, benzene loses hydrogen and turns into diphenyl. Benzene is the main product while hydrogen and diphenyl are by-products [9]. The HDA process involves four main operations: the cleaning and mixing section at the inlet, the reaction system, the vapor recovery system (hydrogen recycling system), and the liquid separation [10]. The HDA process involves two reactions, the conversion of toluene to benzene as below [11]:

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \quad \Delta H^o_{298K} = -41.76 \text{ kJ/mol} \qquad (1)$$

Secondary reaction: formation of heavy by-products, modelled here as di-phenyl [12]:

$$2C_6H_6 \rightarrow C_{12}H_{10} + H_2 \quad \Delta H^o_{298K} = 16.6 \text{ kJ/mol} \qquad (2)$$

2.2. Methods to Increase Purity of Benzene

The production benzene from toluene is modified, where 3 recycles, splitter, tee and compressor are added. A splitter is used to separate a mixture of compounds into two or more fractions with different compositions. This can be beneficial in controlling the flow of compounds directed to subsequent units in the production process. It is used to adjust the composition ratio between two streams [11]. By controlling the flow distribution, you can achieve the desired composition in each fraction [7]. On S15-2 (benzene, toluene, hydrogen, and methane) which is the output from the heater and enters the splitter, a composition separation occurs. The top product (S16-2) contains hydrogen and methane, while the bottom product contains toluene and benzene (S17-2). The bottom product (S17-2) is then further processed in the shortcut column, and another separation occurs in the shortcut column (T-100-2). T-100-2 the top product benzene results in high purity.

2.3. Methods to Increase Mass Flow (Feed Amount Reduction) of Benzene

The production of benzene from toluene is modified, where a splitter, tee, compressor, and three of recycles are added. The first and second recycles (RYC-1 and RYC-2) are the products of the separator V-100-2 whose inputs are the top products of the gas-phase conversion reactor. The output compounds of this gas-phase reactor contain hydrogen, methane, benzene, and toluene. Separator V-100-2 works to separate most of the hydrogen and methane with benzene and toluene from the conversion reactor. Meanwhile, the third recycle (RYC-3) contains most of the toluene produced from the bottom of the shortcut column. To increase the mass flow of the product, a recycle method was tried, with RYC-1 going to the conversion reactor, RYC-2 going to MIX-100-2, and RYC-3 going to the tank (TNK-100-2). Advantages of incorporating a recycling is ensuring that hydrogen gas, being the most expensive raw material employed in the HDA process, is utilized without wastage.

3. Result and Discussion

3.1. Basic Process Flow Diagram of Benzene Production

Basic (unmodified) process flow diagram of benzene production is depicted in Figure 1, while the Aspen HYSYS simulation of the basic process is depicted in Figure 2. Meanwhile, results of mass balance and energy balance (using Apen HYSYS simulation) of the benzene production process through the basic process of hydrodealkylation is presented in Table S1 (Supporting Information).

3.2. Thermodynamics Review

Hydrodealkylation reaction can be expressed as:

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \; \Delta H^o_{298K}\text{=-41.76 kJ/mol} \quad (3)$$

For the determination of the nature of the reaction (exothermic / endothermic) and the direction of the reaction (reversible / irreversible), it is necessary to calculate the standard heat of reaction (ΔH^o_{298K}) at 1 bar and 298 K based on standard heat of formation of the reactants and products. The value of $\Delta H_f°$ and $\Delta G_f°$ can be seen in Table 1 [13].

Table 3. The value of ΔH^o_f and ΔG^o_f of compounds

Compounds	Molecular Formula	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)
Hydrogen	H_2	0	0
Methane	CH_4	-74.520	-50.460
Benzene	C_6H_6	82.930	129.665
Toluene	$C_6H_5CH_3$	50.170	122.050

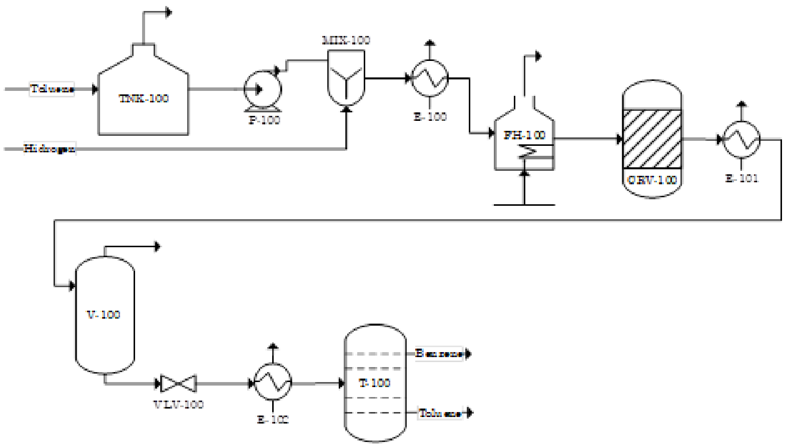

Figure 1. Fundamental process flow diagram of benzene production [8]

Standard heat of reaction at 298K (ΔH^o_{298K}):

ΔH^o_{298K} = ΣΔH_f° product - ΣΔH_f° reactant

= (ΔH_f° C_6H_6 + ΔH_f° CH_4) - (ΔH_f° $C_6H_5CH_3$ + ΔH_f° H_2)

= (82.930 + (-74.520)) – (50.170 + 0)

= -41.76 kJ/mol

Based on the calculations, we get the value ΔH^o_{298K}= -41.760 kJ/mol, which is a negative value so that the reaction is exothermic.

Gibbs energy (ΔG^o_{298K}):

ΔG^o_{298K} = ΣΔG_f° product - ΣΔG_f° reactant

= (ΔG_f° C_6H_6 + ΔG_f° CH_4) - (ΔG_f° $C_6H_5CH_3$ + ΔG_f° H_2)

= (129.6665 + (-50.460)) – (122.050 + 0)

= -42.845 kJ/mol

Equilibrium constant (K_2) in the standard state:

$$\Delta G^o_{298K} = -\mathrm{RT}\ln K$$

$$\ln K_2 = -\frac{\Delta G^o_{298K}}{\mathrm{RT}} = \frac{42.845\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol}\times 298\ \mathrm{K}} = 17.293$$

$$K_2 = 3.238 \times 10^7$$

Equilibrium constant (K_1) at reactor temperature T = 240 °C:

$$\ln\frac{K_1}{K_2} = \frac{-\Delta H_R°}{\mathrm{R}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

ΔH^o_{298K} = Standard heat of reaction at 25°C

$$\ln\frac{K_1}{3.238\times 10^7} = \frac{41.760\ \mathrm{J/mol}}{8.314\ \mathrm{J/mol.K}}\left(\frac{1}{513\ \mathrm{K}} - \frac{1}{298\ \mathrm{K}}\right)$$

$$\ln\frac{K_1}{3.238\times 10^7} = -7.064$$

$$8.553\times 10^{-4} = \frac{K_1}{3.238\times 10^7}$$

$$K_1 = 2.7695\times 10^4$$

Since the value of the equilibrium constant is relatively large, the reaction is irreversible, that is, to the right.

3.3. Process Modification: Increase purity of product (benzene)

Modified process and its Aspen HYSYS simulation are depicted in Figures 3 and 4, respectively. Meanwhile, results of mass balance and energy balance (using Apen HYSYS simulation) of the benzene production process through the modified process of

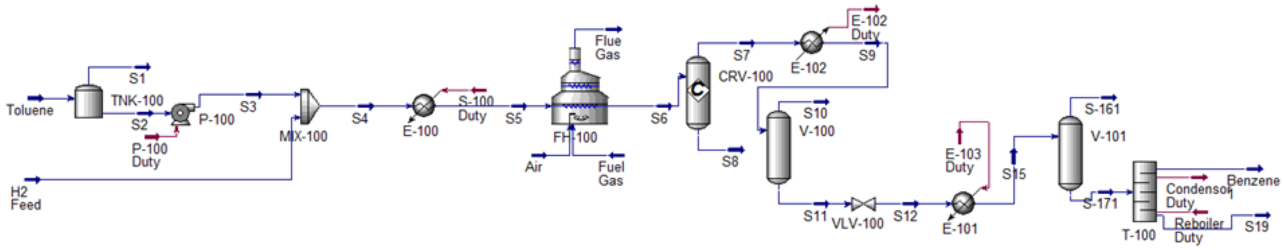

Figure 2. Aspen HYSYS simulation of the basic (unmodified) process

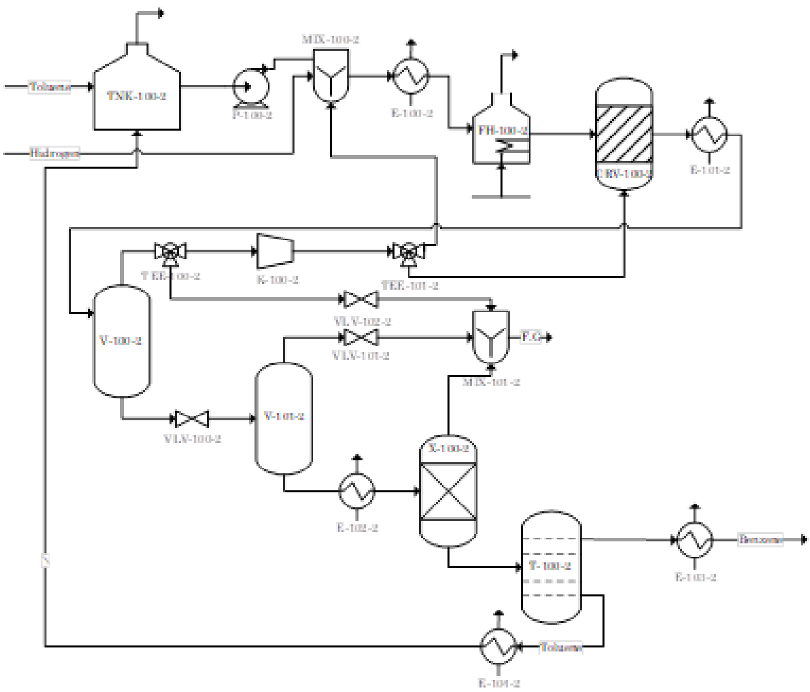

Figure 3. Modified process flow diagram of benzene production

hydrodealkylation is presented in Table S2 (Supporting Information). Increasing purity usually occurs through tools, such as separators, splitters, and shortcut columns, to achieve high purity. First, the S9-2 stream enters V-100-2 (Separator), where a separation occurs into top product and bottom product. In the top product, the composition of hydrogen, methane, benzene, and toluene is respectively 0.9340; 0.0658; 0.0001; and 0.0031, while in the bottom product, the composition is hydrogen, methane, benzene, and toluene respectively at 0.0064; 0.0040; 0.0104; and 0.9793. This bottom product will be used to increase benzene production. To further increase purity, a splitter is also used. The specification of the splitter, as the ratio of output flow to input flow, can eliminate uncertainties due to the variation of the input flow during successive iterations [7]. The splitter, or X-100-2, is used to separate the composition. The top product in the S16-2 stream contains 0.7665 methane and 0.2335 hydrogen, while the bottom product in the S17-2 stream contains 0.0105 benzene and 0.9896 toluene. Subsequently, the bottom product (S17-2) will enter the distillation process. In the distillation process, attention must be paid to material balance modes such as determining products and reflux rates, as well as checking temperature profiles and compositions [7]. The shortcut column (T-100-2) separates the composition from the S17-2 stream into a top product with 0.9995 benzene and 0.0005 toluene, and a bottom product with 0.0030 benzene and 0.9970 toluene.

The production benzene from toluene is modified, where 3 recycles, splitter, tee and compressor are added. In this case, the splitter helps to improve the purity of benzene, resulting in an attainment of 99.95% (Table 4). The specification of the splitter, as the ratio of output flow to input flow, can eliminate uncertainties due to the variation of the input flow during successive iterations [7].

3.4. Process Modification: Increase Mass Flow (Feed Amount Reduction) of Benzene

Increasing mass flow (feed amount reduction) can be done by recycling the main raw materials of benzene production by hydrodealkylation process, namely toluene and hydrogen (Table 5). Recycle hydrogen is obtained from the upper product of V-100-2 and recycle

Table 4. Benzene purity before and after modification ratio

Treatment	Benzene Purity (%)	
	Top Product	Bottom Product
Before Modification	70.72	0.3
After Modification	99.95	0.3

Table 5. Mass flow benzene before and after modification ratio

Treatment	Feed Amount (kg/h)		Mass Flow of Benzene (kg/h)
	Hidrogen	Toluene	
Before Modification	812.8	9951	38.6
After Modification	1,153.85	82,989.43	469.36

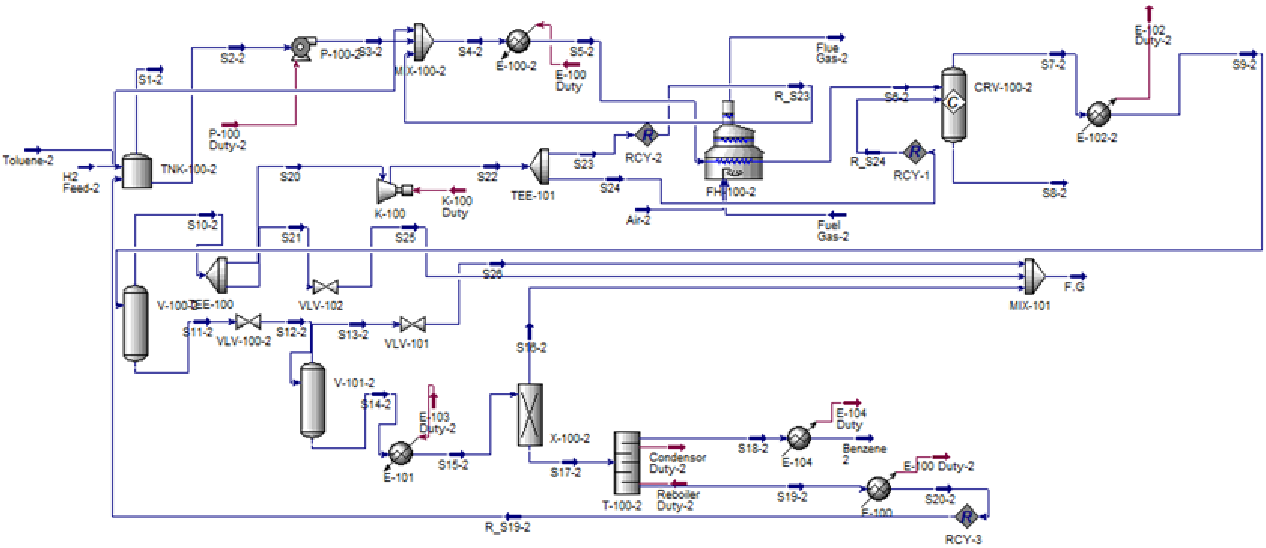

Figure 4. Aspen HYSYS simulation of modified process for benzene production

toluene is obtained from the lower product of T-100-2 shortcut column. Based on the table, there is a significant increase in the mass flow of benzene produced, which is 430.72 kg/h with the same feed. This means that if desired to produce 160,000 tons/year (18,264.84 kg/h) with the recycle system created, it can save feed by 12x than before modification.

Recycling process in this process would allow change to happen in the feed characteristic that leads to the need of the feed itself. Through involving the recycling process to the whole process could suppress the need of another new batch of feed to be entered in this case the demand of hydrogen and toluene for starting another cycle of hydrodealkylation reaction and the whole process of benzene production process [14]. In addition, the benefit of hydrogen gas recycle in benzene production is that hydrogen is not wasted so that it can reduce production costs because it is the most expensive raw material used in the HDA process [15].

4. Conclusion

The modification of the benzene production should be done to prevent the substance that is involved in the process to be specific toluene will contaminate the environment. Recycling toluene and hydrogen is taken not only to save the environment but also to increase the mass flow rate production of benzene from 38.6 kg/h to 469.36 kg/h and to also reduce the amount of fresh feed since the toluene and hydrogen will be able to be recycled and be used for another batch of production processes. The process modification could also affect the purities of benzene from 70.72% to 99.95% by involving splitter to maximize the work of the distillation column and other tools that are initially existed. The suggestion that should be executed is that how the engineers should find the alternatives to lowering the use of the energy for benzene production without significantly decrease the quality of the improved process result.

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