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Production of hydrocarbon based solvent with low aromatic content using ASPEN Plus

D S Fardhyanti[1,]*, H Prasetiawan[1], A Hisyam[2], R D Kusumaningtyas[1], S T S Mulya[1], M A R Findriyani[1], N A Sasongko[3]

[1]Chemical Engineering Department, Faculty of Engineering, Universitas Negeri Semarang, Gd. E1 Kampus Sekaran, Gunungpati, Semarang, 50229, Indonesia
[2]Faculty of Chemical and Processing Technology, Universiti Malaysia Pahang, Pekan, Malaysia, 26300, Malaysia
[3]Centre for the Assesment of the Process and Energy Industry (PPIPE), Agency for the Assesment and Application of Technology (BPPT), Jakarta-Indonesia

dewiselvia@mail.unnes.ac.id

Abstract. The solvent is a liquid that can dissolve or extract specific materials. Solvents are needed for most chemical transformations to increase contact between reagents and catalysts. It also holds an important role in many studies, industrial chemical processes, coatings, and formulations of consumer products, however, most of the hydrocarbon-based solvents based still contain high aromatic content of benzene, toluene, and xylene which are carcinogenic chemicals. The separation of aromatic hydrocarbons from a mixture of C4-C10 aliphatic hydrocarbons is a complex process, due to its close boiling points and some combinations can form azeotropes. The general distillation process is not the right choice for the separation of aromatic hydrocarbons from a mixture of C4-C10 aliphatic hydrocarbons. Possible processes are liquid-liquid extraction, extractive distillation, and azeotropic distillation. In this study, extractive distillation using ASPEN Plus was performed to simulate the process. The crude feed composition used contains 77.13% aromatic compounds so that the separation technology used uses the extractive distillation process using sulfolane as a solvent. The variables used are the ratio of the crude feed to sulfolane (1:10, 1:15, 1:20), the number of stages (30, 40, 50), feed stage (15,20,25). Based on the simulation results, the best result was obtained by using the ratio of the crude feed to sulfolane of 1:10, with the number of stages 30, and the feed stage on the 25^{th} stage.

1. Introduction

The solvent is a liquid that has an ability to dissolve or extract other materials [1]. Solvent has changed modern life significantly and is an invaluable solution for a variety of industries that have several uses, namely for adhesives, coatings, electronics, inks, pesticides, pharmaceuticals, photography, and the textile industry [2]. Paints and coatings accounted for more than 60.0% of total volume in 2018. Even without solvents many products would not meet the current standards demand. Solvent is needed for most chemical transformations to increase contact between reagents and catalysts [3].

Solvent is the core of many research, industrial chemical processes, coatings and formulations of consumer products. However, solvents are widely recognized as a major environmental problem [4]. There are still many solvents which are made from hydrocarbons that have a high aromatic content.

Aromatic compounds in solvent such as Benzene, Toluene, and Xylene (BTX) are carcinogenic chemicals [5]. In case high aromatic levels can increase toxicity that will have an impact on the environment. For this reason, it is necessary to reduce the aromatic content of the resulting solvent.

Crude oil is the main source of raw material for solvents. Physical processes used in the petrochemical industry produce aliphatic and aromatic hydrocarbons. The reduction of aromatic content can be done by a separation process. The process of aromatic separation from a mixture of C4-C10 aliphatic hydrocarbons is a challenge because these hydrocarbons have boiling points in close proximity and some combinations can form azeotropes. The distillation process is generally not the right choice for the separation of aromatic hydrocarbons from a mixture of C4-C10 aliphatic hydrocarbons. The separation process is based on differences in interactions or affinity [6]. Possible processes are liquid-liquid extraction, extractive distillation, and azeotropic distillation.

Previous research by Meindersma [6] which separates aromatic compounds from naphtha using ionic liquid shows that ionic liquid is suitable for the separation of aromatic hydrocarbons from a mixture of aromatic and aliphatic hydrocarbons. The ionic fluid [bmim] BF4, [mebupy] BF4, [mebupy] CH3SO4, tested at 40° C, and also [emim] C7H7SO3, tested at 75° C, are most suitable for the toluene extraction from mixed toluene / heptane. The coefficient of toluene equilibrium distribution and toluene / heptane selectivity are higher with this ionic liquid compared to sulfolane. Ionic liquid [mebupy] BF4 shows the best combination of high toluene distribution coefficient and high toluene / heptane selectivity.

Another experiment was carried out [7] to evaluate the efficiency of the difference in solvent selectivity used for the extraction of aromatic hydrocarbons from naphta (IBP 200°C) distilled from Saudi Arabian Light Crude Oil. The solvent used is 3-methoxypropionitrile, ethylene glycol, dimethylsulfoxide, sulfolane, phenol, and nitrobenzene with the ratio of solvent-crude oil is (range 1: 1-3-1). The results show that sulfolane has good extraction properties compared to other solvents. The advantage is that it has solvent properties with high density, low heat capacity, and proper boiling point. Sulfolane is also commercially viable as a solvent for aromatic extraction. The most widely used commercial extraction process is sulfolane as a solvent that has been licensed by UOP.

In this study, a preliminary study in the process of hydrocarbons based solvent production with low aromatic content using ASPEN Plus as simulation software.

2. Materials and Methods

Simulation of hydrocarbon based solvent with low aromatic content was carried out by using process simulation software ASPEN Plus licensed by Universiti Malaysia Pahang. The Hydrocarbon feed was obtained from Wang et al.[8]. The variable studied in this research were the ratio of crude feed to sulfolane (1:10; 1:15; 1:20), number of extractive distillation column stages (30; 40; 50), extractive distillation column feed stages (15; 20; 25). The process itself has three sub unit which are (1) Extractive distillation sub unit (2) Aromatic compound separation and (3) Final product separation.

2.1. Crude Feed Composition

Figure 1. shows the composition of the crude feed based on literature [8]. It consists of paraffin hydrocarbons, naphthenic hydrocarbons and aromatic compounds such as benzene, toluene, p-xylene, m-xylene, o-xylene. There is a hypothesis which states that paraffin content is n-paraffin, while naphthenic hydrocarbons are cyclohexane or n-alkyl-cyclohexanes [9].

Component ID	Type	Component name	Alias
BENZENE	Conventional	BENZENE	C6H6
TOLUENE	Conventional	TOLUENE	C7H8
P-XYLENE	Conventional	P-XYLENE	C8H10-3
M-XYLENE	Conventional	M-XYLENE	C8H10-2
O-XYLENE	Conventional	O-XYLENE	C8H10-1
N-BUT-01	Conventional	N-BUTANE	C4H10-1
N-PEN-01	Conventional	N-PENTANE	C5H12-1
N-HEX-01	Conventional	N-HEXANE	C6H14-1
N-HEP-01	Conventional	N-HEPTANE	C7H16-1
N-OCT-01	Conventional	N-OCTANE	C8H18-1
CYCLO-01	Conventional	CYCLOHEXANE	C6H12-1
CYCLO-02	Conventional	CYCLOHEPTANE	C7H14-1
CYCLO-03	Conventional	CYCLOOCTANE	C8H16-D6
SULFO-01	Conventional	SULFOLANE	C4H8O2S

Figure 1. Feed Composition in Simulation Using Aspen Plus Software.

2.2. *Determination of Simulation Design*
Extractive distillation equipment used in this simulation was extraction column in the form of RadFrac (ED). The feed stream consists of crude feed (CRUDEFED), sulfolane (SULFOLAN) and sulfolane recycle stream (RECSULFO). Extractive distillation column is a simultaneous extraction and separation process. The number of stages in extractive distillation column was varied to 30, 40 and 50 stages while the crude stage feed was varied into 15, 20 and 25th feed stage to get an optimum results. Figure 2 shows the simulation for extractive distillation sub unit.

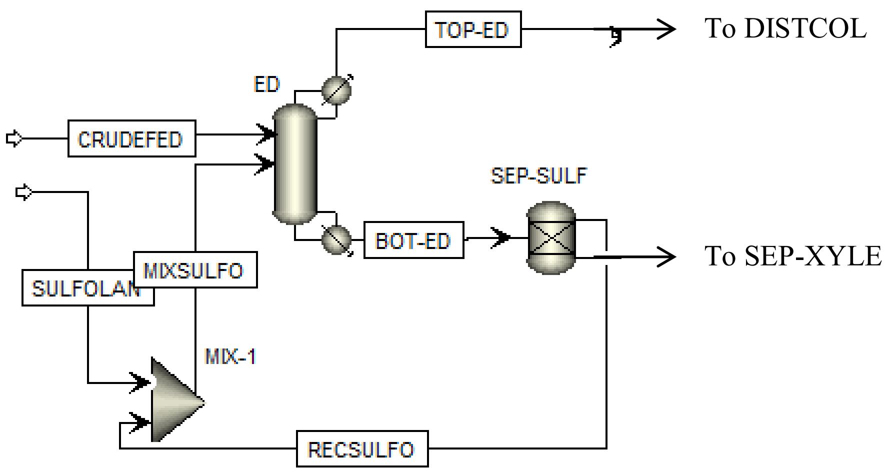

Figure 2. Extractive Distillation Sub Unit

In the aromatic compound separation unit as shown in Figure 3, the equipment used were the distillation column (DISTCOL) and benzene separator (SEP-BENZ) with a split fraction of 0.99. The top results from DISTCOL will then go to benzene separator (SEP-BENZ) to separate the benzene from paraffin compounds. While, the bottom results of DISTCOL will be processed further in the toluene separator (SEP-TOLU) to separate the toluene from the rest of the paraffin compound.

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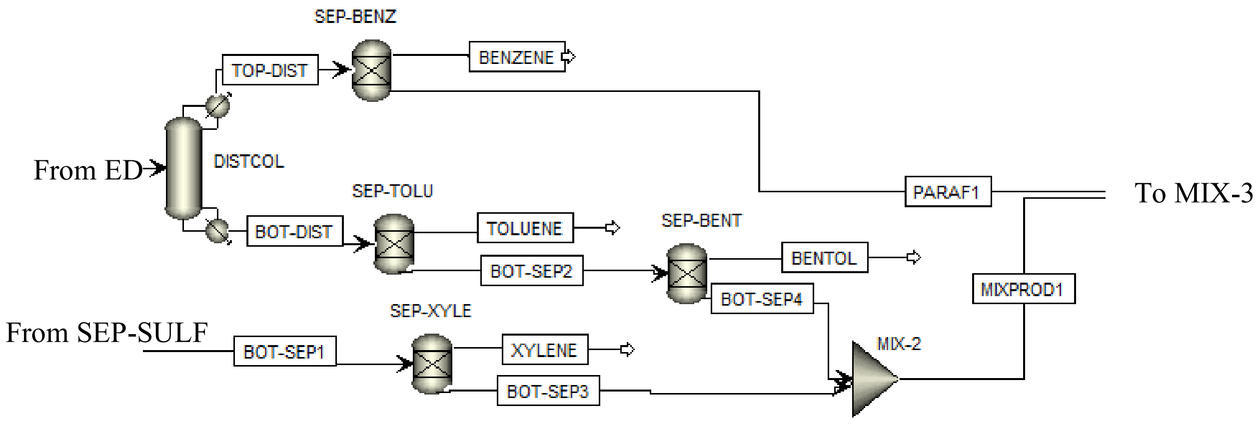

Figure 3. Aromatic Compound Separation Sub Unit

In Figure 4, stream PARAF1 which still contains a lot of paraffin compounds and a little aromatic compound was mixed into a mixer (MIX-3) at a pressure of 1 bar. In the last process, the stream was then separated again using a separator (SEP-PROD). In the separator, the final separation process occurs between the aromatic compound and the product.

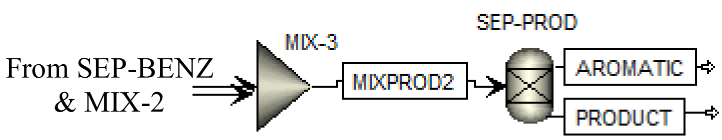

Figure 4. Product Separation Sub Unit

3. Results and Discussion

This research discusses to get a preliminary study in the process of producing hydrocarbon solvents with low aromatic content. This research was conducted by using Aspen Plus software simulations. Simulations were conducted to minimize the risk of costs and technical errors compared to direct experiment conducted in a laboratory. Based on the literature, the determination of aromatic compound separation technology is influenced by the composition of the feed or material used.

3.1. Crude Feed Composition

Table 1. shows the mass fraction of each crude feed component with total aromatic content of 77.13%.

Table 1. Mass Fraction on Each Crude Feed Component

Composition	Mass Fraction
Benzene	0.378
Toluene	0.387
p-xylene	0.002
m-xylene	0.004
o-xylene	0.00084
n-butane	0.00016
n-pentane	0.016
n-hexane	0.108
n-heptane	0.055
n-octane	0.014
Cyclohexane	0.019
Cycloheptane	0.012
Cyclooctane	0.004

3.2. Extractive Distillation Process Technology

The selection of process technology is the first step in determining the optimum operating conditions including the selection of aromatic compound separation methods, and the right solvent for the separation process. The separation of aromatic hydrocarbons from a mixture of C4-C10 aliphatic hydrocarbons is a complex process, since these hydrocarbons have close boiling points and some components combinations can form azeotropes point. Several possible processes for this case are liquid-liquid extraction, extractive distillation, and azeotropic distillation.

The process of separation from aromatic and aliphatic hydrocarbons such as liquid-liquid extraction is appropriate if the aromatic content of the feed is 20-65%, the extractive distillation process is suitable in the range of aromatic content of 65-90%, and azeotropic distillation with a high feed of aromatic content is> 90% [6]. In Table 1 it can be seen that the composition of crude feed contains 77.13% aromatic compounds so that the separation technology used uses the extractive distillation process. In addition, the selection of the right solvent is very important in the extractive distillation process. The solvent used is recommended to have high selectivity and high solubility. Diethylene glycol (DEG), triethylene glycol (TEG), dimethyl sulfoxide (DMSO), N-methyl pyrrolidone (NMP), sulfolane, N-formyl morpholine (NMF) are solvents that can be used to separate aromatic compounds using extractive distillation (Kiss. et al, 2013). However, the most popular solvent is sulfolane due to its high selectivity, high dissolving capacity, boiling point and higher thermal stability. Therefore sulfolane was chosen as a solvent in the separation process using extractive distillation.

3.3. Analysis of Simulation Results

Process simulation variations are useful to show the effect of process conditions on the production of hydrocarbon based solvent with low aromatic content. The variation with the highest aromatic content in the 17th variation, while the variation with the lowest aromatic content in the 7th variation. The effect of process conditions included the ratio of sulfolane: crude feed, number of stages, stage of crude feed.

Table 2. Results of the process simulation.

Variation	Sulfolane Ratio: Crude Feed	Number of Extractive Distillation Column Stages	Feed Stage on Crude Feed	Aromatic Content (w/w)
1	1:10	30	15	0.687633435
2	1:10	30	20	0.687517542
3	1:10	30	25	0.687513371
4	1:10	40	15	0.687222198
5	1:10	40	20	0.687100377
6	1:10	40	25	0.687094957
7	1:10	50	15	0.686882591
8	1:10	50	20	0.686970357
9	1:10	50	25	0.686963727
10	1:15	30	15	0.68899762
11	1:15	30	20	0.688832517
12	1:15	30	25	0.688823481
13	1:15	40	15	0.688488175
14	1:15	40	20	0.68812416
15	1:15	40	25	0.688121427
16	1:15	50	15	0.688106647
17	1:15	50	20	0.689729854
18	1:15	50	25	0.689523647
19	1:20	30	15	0.689510009
20	1:20	30	20	0.6895166588
21	1:20	30	25	0.688930204
22	1:20	40	15	0.688912638
23	1:20	40	20	0.688788504
24	1:20	40	25	0.688713654
25	1:20	50	15	0.688788504
26	1:20	50	20	0.688713654
27	1:20	50	25	0.688690883

3.3.1. Effect of Number of Stages on Aromatic Content

Figure 2 shows the effect of the number of stages on the aromatic content. The feed stage as a fixed variable so that the feed stage has no effect. It represent that the more the number of stages, the more ideal for the separation process. It can be seen that with the increase of number of stages, the lower the aromatic content. This is consistent with experimental data [10] explained by the more number of stages (stages), the product will be more easily purified so that the content of aromatic compounds in the product decreases.

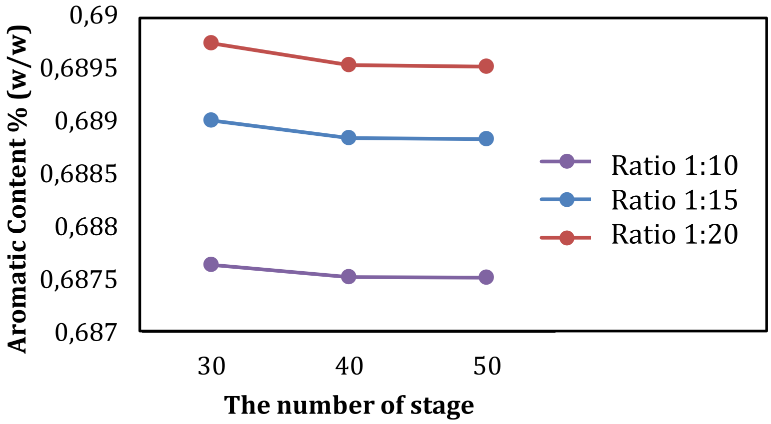

Figure 5. Effect of number of stages to the aromatic content.

3.3.2. Effect of Feed Ratio on Aromatic Content

Figure 6 shows the effect of the ratio of feed to aromatic content with the number of stages as a fixed variable so that the number of stages has no effect. It can be seen that the greater the ratio of aromatic content the smaller the aromatic compounds produced. In accordance with experimental data conducted by [11] the results show that sulfolane has good extraction properties compared to other solvents. The advantage is that it has solvent properties with high density, low heat capacity, and proper boiling point. Sulfolana is also commercially viable as a solvent for aromatic extraction.

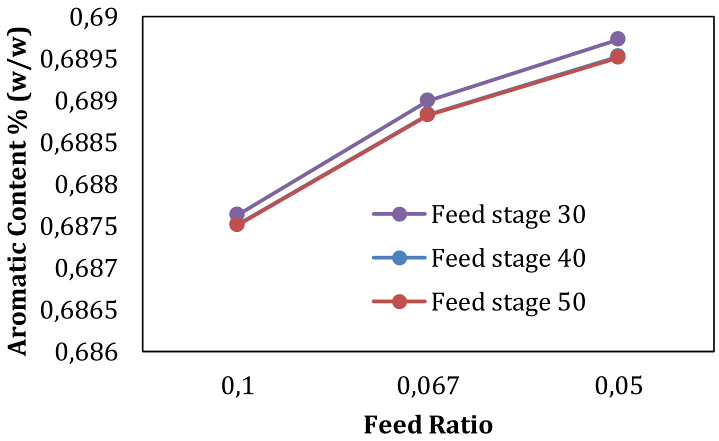

Figure 6. Effect of Feed Ratio Against Aromatic Content.

3.3.3. Effects of Feed Stage on Aromatic Content

Figure 7 represent the effect of the feed stage on aromatic content. The feed ratio was set as fixed variable. The lower of the feed stage, the higher the aromatic content due to the difficulty of separating extractant (sulfolane) from the product so that it requires a higher load of reboiler and condenser to achieve certain purity [10]. Figure 4.4 shows the relation between the feed stage and aromatic content. According to the reference, the lower the feed stage, the higher the aromatic content.

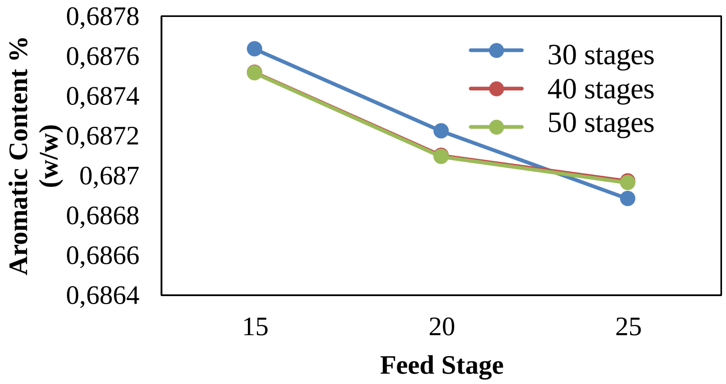

Figure 7. Effect of Feed Stage Against Aromatic Content.

4. Conclusion

Based on research that has been done, it can be concluded that process technology selection in the simulation of crude feed as a solvent based hydrocarbon processing technology containing 77.13% aromatic compounds so the separation technology used uses the extractive distillation process and sulfolane solvent. The effect of the ratio of crude feed to sulfolane on the aromatic content is that the greater the ratio of aromatic content, the smaller the aromatic compound produced. Effect of the number of stages on the aromatic content is the more number of stages shows the more ideal for the separation process so that the lower aromatic compounds in the product. The impact of the feed stage on the aromatic content is the lower the feed stage, the higher the aromatic content.

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