Original Research

Simulation of the Hydrodealkylation of Toluene Using Conversion Reactor

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Abstract—*The hydrodealkylation of toluene is frequently used to produce the more valuable compound benzene. This process is widely employed in the petrochemical industry. Through hydrodealkylation, toluene undergoes a transformation, resulting in the production of valuable chemicals such as benzene and diphenyl. The objective of this study is to present the results obtained from simulating the process of toluene dealkylation using Aspen HYSYS. The feed to the reactor must contain toluene and hydrogen, while the recommended operating conditions are at 500 °C to 650 °C and 20 to 40 atm pressure to achieve 90% conversion. For this purpose, a conversion reactor has been selected as the preferred type. The simulation outcomes are particularly valuable during the initial stages of designing a production facility for benzene. The mass and energy balance calculations can be easily performed using Aspen HYSYS. Future research may focus on investigating different reactor types while considering the kinetics of the reaction.*

Keywords: aspen HYSYS, hydrodealkylation, simulation, toluene

Abstrak—*Hidrodealkilasi toluena sering digunakan untuk menghasilkan senyawa yang lebih bernilai yaitu benzene. Proses ini banyak digunakan dalam industri petrokimia. Melalui hidrodealkilasi, toluena mengalami transformasi, menghasilkan bahan kimia berharga seperti benzene dan diphenyl. Tujuan dari penelitian ini adalah untuk menyajikan hasil yang diperoleh dari mensimulasikan proses dealkilasi toluena menggunakan Aspen HYSYS. Umpan ke reaktor harus mengandung toluena dan hidrogen, sedangkan kondisi operasi yang direkomendasikan adalah pada suhu 500 °C hingga 650 °C dan tekanan 20 hingga 40 atm untuk mencapai konversi 90%. Untuk tujuan ini, reaktor konversi telah dipilih sebagai tipe yang disukai. Hasil simulasi sangat berharga selama tahap awal perancangan fasilitas produksi benzene. Perhitungan neraca massa dan energi dapat dengan mudah dilakukan menggunakan Aspen HYSYS. Penelitian masa depan dapat fokus pada penyelidikan berbagai jenis reaktor sambil mempertimbangkan kinetika reaksi.*

Kata kunci: aspen HYSYS, hidrodealkilasi, simulasi, toluene

INTRODUCTION

Benzene, toluene, ethyl benzene, and xylene (BTEX) originate from crude oil and can be found near natural gas and petroleum reserves (Bustillo-Lecompte et al., 2018).

Toluene is an organic compound that belongs to the group of aromatic hydrocarbons. It has a chemical formula of C_7H_8 and can be found in crude oil as well as some fossil fuel products. Toluene has good solvent properties and is widely used in the industry as a solvent, raw material in paint production, organic chemical, and also as a raw material in the production of explosives such as trinitrotoluene (TNT) (Atsdr, 2017; PubChem, n.d.).

Benzene is also an organic compound that belongs to the group of aromatic hydrocarbons with the chemical formula C_6H_6 (Trans Pacific Petrochemical Indotama, n.d.). This compound has a hexagonal ring structure consisting of carbon and hydrogen atoms. Benzene is a colorless compound that readily evaporates and has a distinct aroma. Benzene is used in various industries, including petrochemical, pharmaceutical, plastics, and solvents. However, benzene is also known to be a hazardous substance to humans. Long-term exposure to benzene can be associated with serious health risks, including the risk of developing blood cancer such as leukemia (Barton, 2023) (PubChem, n.d.). Benzene itself has been limited to less than 1% in gasoline due to its known carcinogenic properties in humans. Its non-industrial applications have also been restricted for the same reasons (Trans Pacific Petrochemical Indotama, n.d.).

Toluene hydrodealkylation into benzene is an important petrochemical process that represents the largest end use in the US and West Europe (Meidanshahi et al., 2011; Iranshahi et al., 2017) as well as in East Europe (Iranshahi et al., 2017). Because benzene is more valuable than toluene, the majority of the produced toluene is converted to benzene through

hydrodealkylation (Meidanshahi et al., 2011). This reaction is also known as toluene disproportionation.

Recent studies on the hydrodealkylation of toluene include the kinetic and thermodynamic analysis of this reaction under actual industrial operating conditions (Ali et al., 2022). Another study attempts to integrate stochastic programming and reliability in the optimal synthesis for this reaction (Chen et al., 2022). Furthermore, Liu (Liu et al., 2015) proposed a new double flash process and heat integration for improved energy utilization. Studies on various catalysts have also been conducted for the hydrodealkylation of toluene, resulting in different side products (varying composition of the resulting products) (Mesa et al., 2019) (Albahar et al., 2020).

Lian (Lian et al., 2023) also conducted a study on benzene production from different routes, specifically the methane dehydroaromatization reaction.

The complete hydrodealkylation process of toluene encompasses 9 distinct unit operations, including a reactor, recycle compressor, furnace, 2 heat exchangers, vapor-liquid separator, and 3 distillation columns. The typical feedstocks for this process are hydrogen and toluene. The primary output of this process is benzene, accompanied by the secondary products of methane and biphenyl. (Iranshahi et al., 2017) (Douglas, 1988). This process can be conducted with or without the presence of catalysts. The catalytic process relies on the utilization of catalysts like nickel or clinoptilolite to facilitate the hydrogenation reaction.

In this process, toluene undergoes hydrodealkylation within a uniform and gaseous non-catalytic medium, resulting in the production of benzene and methane as primary products. Additionally, through an equilibrium reaction, benzene can lose hydrogen and transform into diphenyl. The main product obtained is benzene, while hydrogen and diphenyl (biphenyl) are generated as by-products. The reactions and their corresponding rate laws are provided below (Douglas, 1988; Luyben et al., 1999):

1. $C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \qquad \Delta H = -50 kJ/mole$
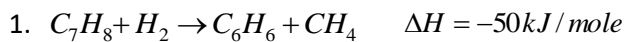
   ($Toluene + Hydrogen \rightarrow Benzene + Methane$)

   $$R_1 = 1.9580 \times 10^8 e^{(-25616/T)} p_T p_H^{1/2}$$

2. $2C_6H_6 \leftrightarrow C_{12}H_{10} + H_2 \quad \Delta H = 0 kJ/mole$
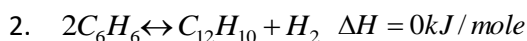
   ($2 Benzene \leftrightarrow BiPhenyl + Hydrogen$)

   $$R_2 = 1.2115 \times 10^6 e^{(-25616/T)} p_B^2 - 5.1662 \times 10^6 e^{(-25616/T)} p_D p_H$$

The aim of this paper is to conduct a steady state simulation for the toluene hydrodealkylation process using Aspen HYSIS. This is a preliminary study to enhance the utilization of HYSYS in order to conduct more advanced research.

Our paper focuses on the steady-state simulation of the toluene hydrodealkylation process using Aspen HYSYS. While there exist numerous studies and papers on simulation using HYSYS for various chemical reaction systems, our work delves into a specific reaction pathway that has significant industrial relevance due to the economic importance of benzene production from toluene.

The application of Aspen HYSYS for simulating the hydrodealkylation process holds immense significance in the petrochemical industry, where the conversion of toluene to benzene is a fundamental operation. By showcasing the utilization of HYSYS for this particular reaction, we contribute to the advancement of simulation techniques in a crucial industrial sector.

Our study incorporates key process parameters such as temperature, pressure, and reactor type, offering insights into optimizing the hydrodealkylation process for efficient benzene production. This integration of process parameters within the Aspen HYSYS framework adds value to our research by providing practical guidance for process engineers and researchers.

While our paper serves as a preliminary study, it lays the groundwork for more advanced research in the field of chemical process simulation. The utilization of Aspen HYSYS opens avenues for further investigations into reaction kinetics, catalyst selection, and process optimization, which are integral to enhancing the efficiency and sustainability of industrial processes.

METHOD

The Aspen HYSYS software would be used to simulate this process (toluene hydrodealkylation). All materials involved in the reaction are already available in the HYSYS component list. SRK were selected as the thermodynamic model (fluid package). The simulation procedure is as follows:

- Start
- Determining the involved components.
- Selecting SRK as the thermodynamic model.
- Creating a process flowsheet.
- Completing equipment specifications and operating conditions.
- Process simulation
- Evaluation
- End

The process diagram is shown in Fig.1, meanwhile, the feed composition to the process is indicated in Table 1.
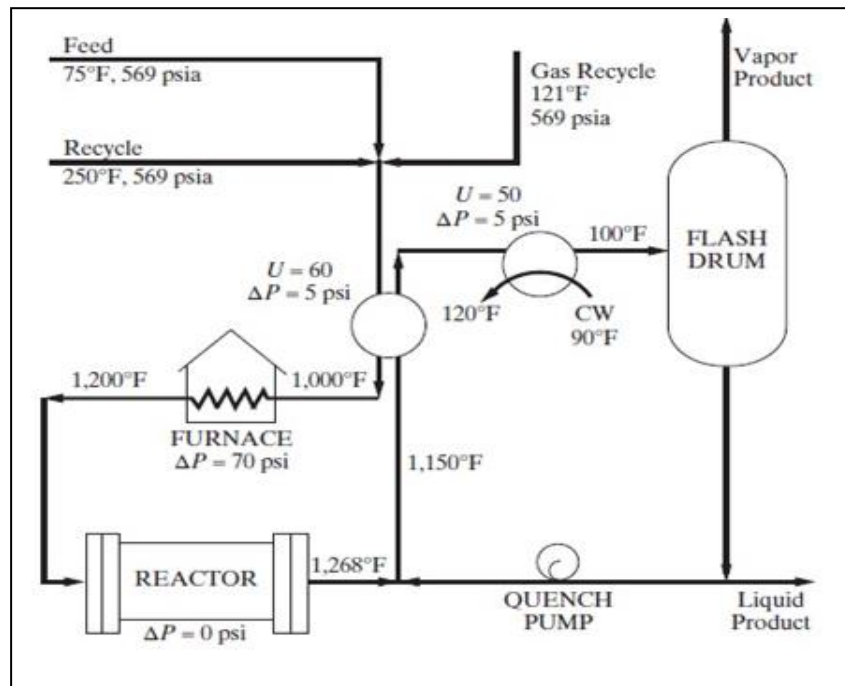

Fig. 1. Toluene hydrodealkylation process

Table 1
Feed Composition

Component	Feed (lbmole/h)	Recycle (lbmole/hr)	Gas Recycle (lbmole/hr)
H_2	0	0	2045.9
CH_4	0	0	3020.8
C_6H_6	0	3.4	42.8
C_7H_8	274.2	82.5	5.3
$C_{12}H_{10}$	0	1.0	0

The SRK (Soave-Redlich-Kwong) equation of state is a widely accepted thermodynamic model for hydrocarbon systems, chosen for its accuracy in predicting phase behavior and properties such as vapor-liquid equilibrium. In our study, the SRK model was specifically selected from within the Aspen HYSYS software's available thermodynamic models due to its established reliability and applicability to the toluene hydrodealkylation process.

Variations in this experiment might include:

1. Temperature Variation:

   The first experiment involves varying the temperature at the reactor inlet within the range of 1100 to 1400°F. This variation aims to understand the impact of initial temperature on the reactor outlet temperature and overall energy consumption.

2. Operating Pressure Variation:

   The second experiment includes varying the operating pressure of the reactor within the range of 20 to 60 atm. The goal is to evaluate how operating pressure affects the conversion of toluene into benzene and other by-products.

3. Feed Composition Variation:

   The third variation involves changes in feed composition, particularly the concentrations of toluene and hydrogen. This experiment helps understand the reactor's response to changes in feed composition. This paper will show the results based on Table 1 Feed Composition.

4. Use of Different Reactor Types:

   The last experiment involves using different types of reactors, such as conversion reactors, catalyst reactors, or reactors with modified designs. This variation can be done to compare the performance and efficiency of different reactors in the hydrodealkylation process. However, this paper focused on the use of conversion reactor only.

RESULTS AND DISCUSSION

Figure 2 shows the process flowsheet in Aspen HYSYS with temperature and pressure specified for each stream. It appears that the temperature exiting the reactor is 1263 oF (not 1268 oF as in Figure 1). To simplify the calculations, a panel heater (E-101) was used here as a replacement for the furnace. Then, the type of reactor used is a conversion reactor because it is known that the conversion of toluene in the reactor is 75%, and 2 mol percent of benzene remaining after the first reaction is converted into biphenyl (also known as diphenyl).

Table 2 displays the material streams, whereas Table 3 presents the composition of each flow. Table 4 provides the energy demands for the heat exchanger (E-100) and furnace (E-101). From Table 2, it is evident that the reactor output has a molar flow rate of 5476 lbmole/hr.
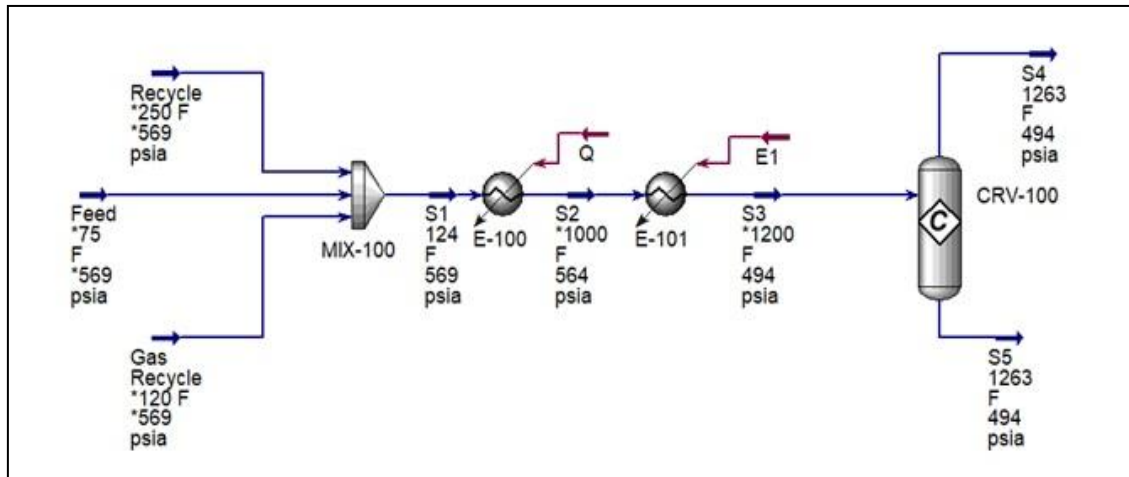
Figure 2. Process flowsheet.

Table 2
Material Streams

		Feed	Recycle	Gas Recycle	S1	S2	S3	S4	S5
Vapour Fraction		0	0	1	0.9265	1	1	1	0
Temp.	F	75	250	120	124	1000	1200	1263	1263
Press.	Psia	569	569	569	569	564	494	494	494
Molar Flow	lbmole /hr	274.2	86.9	5115	5474	5476	5476	5476	0
Mass Flow	lb/hr	2.53e+4	8021	5.64e+4	8.97e+4	8.97e+4	8.97e+4	8.97e+4	0
Liquid Volume Flow	Barrel /day	1988	629.1	1.54e+4	1.80e+4	1.80e+4	1.804e+4	1.82e+4	0
Heat Flow	Btu/hr	1.45e+6	1.17e+6	-9.43e+7	-9.17e+7	-2.57e+7	-8.453e+6	-8.45e+6	0

Table 3
Compositions (Component Mole Fractions)

Compositions								
	Feed	**Recycle**	**Gas Recycle**	**S1**	**S2**	**S3**	**S4**	**S5**
Toluene	1	0.9494	0.0010	0.0661	0.0661	0.0661	0.0615	0.0615
Benzene	0	0.0391	0.0084	0.0084	0.0084	0.0084	0.0569	0.0569
BiPhenyl	0	0.0115	0	0.0002	0.0002	0.0002	0.0008	0.0008
Methane	0	0	0.5906	0.5517	0.5517	0.5517	0.6012	0.6012
Hydrogen	0	0	0.4000	0.3736	0.3736	0.3736	0.3246	0.3246

Table 4
Energy Streams

		Q	**E1**
Energy Streams			
Heat Flow	Btu/hr	6.597e+007	1.729e+007

The inlet temperature of the reactor is 1200°F (649 °C), and the outlet temperature (or temperature within the reactor) is 1263 °F (684 °C) due to the exothermic nature of the reaction. Meanwhile, the pressure in the reactor is 494 psia (33.6 atm). The recommended operating temperature and pressure for this reaction are at 500°C – 650°C and 20 to 60 atm pressure (Liquisearch, n.d.; Wikipedia, n.d.).

The exothermic nature of the hydrodealkylation reaction plays a crucial role in the overall process dynamics. As toluene undergoes conversion to benzene and other by-products, a significant amount of heat is liberated. This heat release is attributed to the breaking of chemical bonds and the formation of new compounds with lower energy states. The exothermicity of the reaction necessitates careful consideration of temperature control within the reactor system. Efficient heat management becomes paramount to prevent overheating, maintain optimal reaction rates, and ensure the stability and longevity of catalysts if used. Strategies such as heat exchangers, cooling systems, and precise control of feed rates are employed to manage the exothermic heat generation effectively. Additionally, understanding the exothermic nature of the reaction aids in designing safer and more efficient industrial-scale processes, contributing to overall sustainability and process optimization in the petrochemical industry.

According to Figure 3, altering the initial temperature of the reactor inlet within the range of 1100 to 1400 F will impact the reactor outlet temperature. This temperature alteration also affects the utility energy at E1, as shown in Figure 4. However, it is important to note that this temperature change will not have any effect on the pressure inside the reactor or the molar flow of vapor (S4). This is because the mass balance calculations adhere to the given conditions (i.e., the conversion of toluene in the reactor is 75%, and 2 mol percent of benzene remaining after the first reaction is converted into biphenyl).
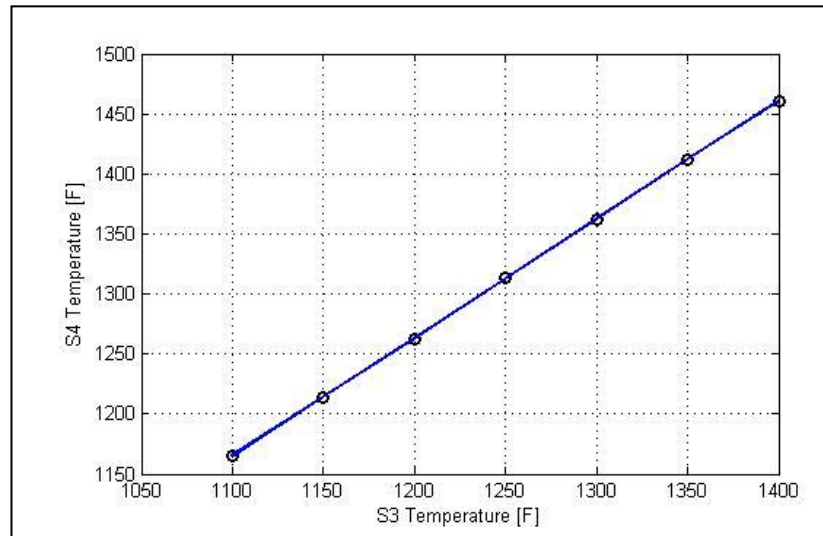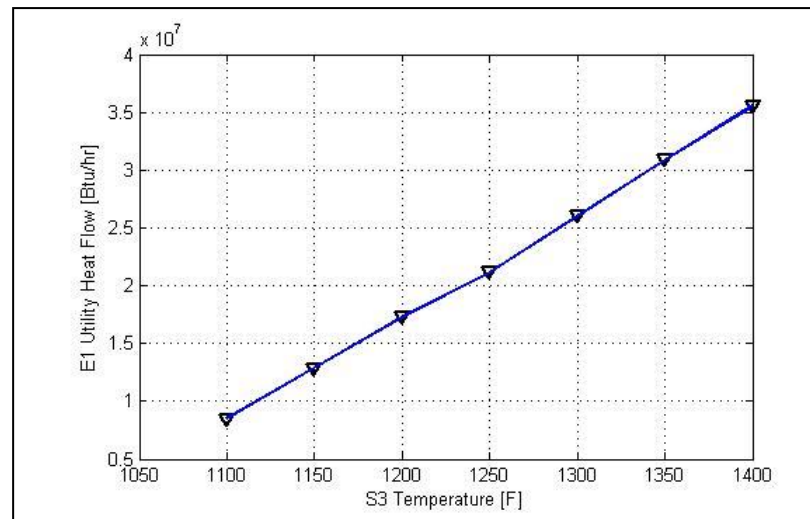
Figure. 3. Plot the Temperature of S4 vs S3.

Figure 4. Plot of E1 vs S3.

CONCLUSIONS

The simulation of the conversion reactor for toluene hydrodealkylation has demonstrated the efficiency of conducting mass balance and heat balance calculations using Aspen HYSYS. These results are instrumental in the initial design phase of a benzene plant employing the hydrodealkylation process of toluene. The ability to accurately model the process parameters and assess the energy requirements lays a solid foundation for further engineering and optimization efforts. Moving forward, future research endeavors will delve into exploring different reactor types while delving deeper into the kinetics of the hydrodealkylation reaction. This comprehensive approach will contribute to refining process efficiencies and advancing the understanding of key reaction mechanisms, ultimately enhancing the overall viability and sustainability of benzene production processes.

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