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Efficiency Comparison of Reactor Types for Benzene Pyrolysis: A Study of Equilibrium and Plug Flow Reactors

Ademola Bolanle **Raheem*,** Aliyu Abdulhameed **Bello**, Micheal Ayorinde **Dada**

Chemical Engineering Department, Faculty of Engineering, University of Port Harcourt, P.M.B. 5323, Choba, Port Harcourt, Rivers State, Nigeria.
Chemical Engineering Department, Faculty of Engineering and technology, University of Maiduguri, P.M.B. 1069 Bama Road Maiduguri, Borno State, Nigeria.
Sychar Water Technologies Houston, Texas, USA.

ABSTRACT: It is a study on benzene pyrolysis, a process crucial to the petrochemical industry and the production of various everyday materials. The focus is on understanding the chemistry behind the production of m-terphenyl, diphenyl, and hydrogen, which are important components in this industry. The study compares the efficiency of different reactor types (two plug-flow reactors, one plug-flow reactor, and an equilibrium reactor) under two different operating conditions. The operating conditions involve varying flow rates and temperatures while maintaining a constant pressure of 1 atm. The results indicate that the equilibrium reactor outperformed the other reactors in terms of product percentage under the specified operating conditions. The experimental results were used to validate the outcomes obtained from the other reactors. The results show the product compositions, percentage differential, and energy required by each and all the reactors. This research contributes to enhancing our understanding of benzene pyrolysis and optimizing production processes in the petrochemical industry.

KEY WORDS: Benzene, m-terphenyl. Diphenyl, hydrogen, pyrolysis, plug flow rector, and equilibrium reactor.

I. INTRODUCTION

The pyrolysis of benzene, a fundamental process in chemical engineering, holds significant importance in various industrial applications, including the production of valuable aromatic compounds such as m-terphenyl, diphenyl, and hydrogen (Aljaman, 2023). Understanding the most efficient reactor type for benzene pyrolysis is crucial for optimizing product yield and minimizing operational costs.

In this study, we investigate the effectiveness of different reactor types – including equilibrium reactors, plug flow reactors, and experimental setups – in converting liquid benzene into desired products under varying operating conditions. Specifically, we explore two key parameters: temperature and flow rate, which play pivotal roles in determining the reaction kinetics and product distribution.

The objective of this research is to provide insights into the comparative performance of different reactor types base on their compositions, percentage differential, and energy required, and to identify the most efficient configuration for benzene pyrolysis. By analysing the experimental data and reactor simulations, we aim to offer valuable recommendations for reactor selection and process optimization in industrial settings.

Through this study, we aim to contribute to the advancement of benzene pyrolysis technology, facilitating the development of more sustainable and economically viable processes in the chemical industry.

II. PYROLYSIS OF BENZENE TO DIPHENYL, m-TERPHENYL, AND HYDROGEN DESIGN, MODELING, AND SIMULATION (DMS) USING ASPEN PLUS.

Generally, liquid benzene as feed was either 0.0309 or 0.0095 Kg-mole/hr supplied at room temperature of 298 K and 101325 Pa. It was transported by pump-1 operating at 202650 Pa to heater-1 that heated liquid benzene to the required temperature of 1033.15 K, 958.15 K, and 202650 Pa, respectively. The heater vaporized the benzene before it entered the reactor. All the reactors operated at 101325 Pa, but at different temperatures of either 1033.15 K (for 0.0309 Kg-mole/hr) or 958.15 K (for 0.0095 Kg-mole/hr). 2 and 1 plug flow, as well as equilibrium reactors, were used

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for this study. The resulting gaseous product mixture was transported by compressor-1 to the separation and purification sections.

A Kinetics of Benzene Pyrolysis into Diphenyl, m-Terphenyl, and Hydrogen Process.

Diphenyl ($C_{12}H_{10}$) is an important industrial intermediate (Robiati, 2021). One production scheme involves the pyrolytic dehydrogenation of benzene (C_6H_6) (Fogler and Gurmen, 2022). During the process, m-triphenyl ($C_{18}H_{14}$) is also formed by a secondary reaction, and hydrogen (H_2) is produced. The reactions are as follows:

$$2\ mole\ of\ \underset{Benzene}{C_6H_6} \underset{\leftarrow}{\rightarrow} 1\ mole\ of\ \underset{Diphenyl}{C_{12}H_{10}} + 1\ mole\ of\ \underset{Hydrogen}{H_2} \quad (1)$$

$$1\ mole\ of\ \underset{Benzene}{C_6H_6} + 1\ mole\ of\ \underset{Diphenyl}{C_{12}H_{10}} \underset{\leftarrow}{\rightarrow} 1\ mole\ of\ \underset{m-Triphenyl}{C_{18}H_{14}} + 1\ mole\ of\ \underset{Hydrogen}{H_2} \quad (2)$$

Murhpy, Lamb, and Watson presented some laboratory data regarding these reactions originally carried out by Kassell (Fogler and Gurmen, 2002). In these experiments, liquid benzene was vaporized, heated to the reaction temperature, and fed into a plug-flow reactor (PFR) that might be one or two sets up. The same procedure was used for the equilibrium reactor. The product stream is condensed and analysed for various components, and the energy demanded by each and all the reactors is compared.

Equation 1 above shows that 2 moles of benzene are pyrolyzed into 1 mole of diphenyl and 1 mole of hydrogen. It was a reversible reaction, and the forward reaction led to the production of diphenyl and hydrogen. The reverse reaction led to Equation 2, which reacted 1 mole of benzene with 1 mole of diphenyl produced in Equation 1. It also gave a reversible reaction; the forward reaction promoted the production of 1 mole of m-triphenyl and 1 mole of hydrogen. Its reverse reaction produced diphenyl and benzene. This is a reason that benzene cannot be totally consumed as a reactant in the process. It becomes pertinent to study the compositions of the products under different operating conditions and the energy required by the reactor to perform its functions. The design, modelling, and simulations (DMS) were done based on the kinetics.

With the representation of the symbol as A = C_6H_6; B = $C_{12}H_{10}$; C = $C_{18}H_{14}$; and D = H_2, respectively. The rate of consumption of benzene in Equation 1 above and that of diphenyl in Equation 2 were based on their partial pressures, as shown in Equations 3 and 4 below.

$$-r_{1A} = k_{1A}\left(p_A^2 - \frac{p_B p_D}{k_{1A}}\right) \quad 3$$

$$-r_{2B} = k_{2B}\left(P_A P_B - \frac{p_C p_D}{k_{2B}}\right) \quad 4$$

Where $-r_{1A}$ and $-r_{2B}$ are the rates of consuming benzene and diphenyl. k_{1A} and k_{2B} are the specific rate constants of benzene and diphenyl consumptions. P_A, P_B, P_C, and P_D are partial pressures of benzene, diphenyl, m-terphenyl, and hydrogen respectively. The specific rate constants (Fogler and Gurmen, 2022) for Equations 3 and 4 are given in Equations 5 and 6 below.

$$k_{1A} = A_1 exp\left(-\frac{E_1}{RT}\right) \quad 5$$

$$k_{2B} = A_2 exp\left(-\frac{E_2}{RT}\right) \quad 6$$

Where A_1 and A_2 are the Arrhenius constants (the frequency factor or pre-exponential factor); E_1 and E_2 are the activation energy (in the same units as R*T); R is universal gas constant; and T is absolute temperature (in Kelvin). The equilibrium constants (Fogler and Gurmen, 20220) are given in Equations 7 and 8 below.

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$$In\ k_{1A} = A' + \frac{B'}{T} + C'ln(T) + D'T + E'T^2 \quad 7$$

$$In\ k_{2B} = A'' + \frac{B''}{T} + C''ln(T) + D''T + E''T^2 \quad 8$$

The parameters for design, modeling, and simulation are E_1 = 126314.96 J/mol; E_2 = 126314.96 J/mol; A_1 = 1.1672E-2; A_2 = 1.3545E-2; A' = -19.76; B' = -1692; C' = 3.13; D' = -1.63E-3; E' = 1.96E-7; A'' = -28.74; B'' = 742; C'' = 4.32; D'' = -3.15E-3; and E'' = 5.08E-7. The Table 1 below is showing the reactor sizing for simulation.

Table 1. Reactors Sizing at Different Flow rates, Temperatures and 101325 Pa

Type of reactor	Reactor 1				Reactor 2			
	Length (m)	Diameter (m)	Flow rate (Kg-mol/hr)	Temperature (K)	Length (m)	Diameter (m)	Flow rate Kg-mol/hr)	Temperature (K)
1 PFR	0.9525	0.0127	0.0095	958.15	NR	NR	NR	NR
1 PFR	0.9525	0.0127	0.0309	1033.15	NR	NR	NR	NR
2PFR	0.9525	0.0127	0.0095	958.15	0.9525	0.0127	0.0095	958.15
2 PFR	0.9525	0.0127	0.0309	1033.15	0.9525	0.0127	0.0309	1033.15
Equil.	NR	NR	0.0095	958.15	NR	NR	NR	NR
Equil.	NR	NR	0.0309	1033.15	NR	NR	NR	NR

*PFR is Plug flow reactor. *Equil. is the Equilibrium reactor. *NR is not required.

B DMS of Pyrolysis of Benzene to Diphenyl, m-Terphenyl, and Hydrogen Process

The simulation was done based on the computational flow diagram (CFD) and shown in Figures 1 (a - f) below:

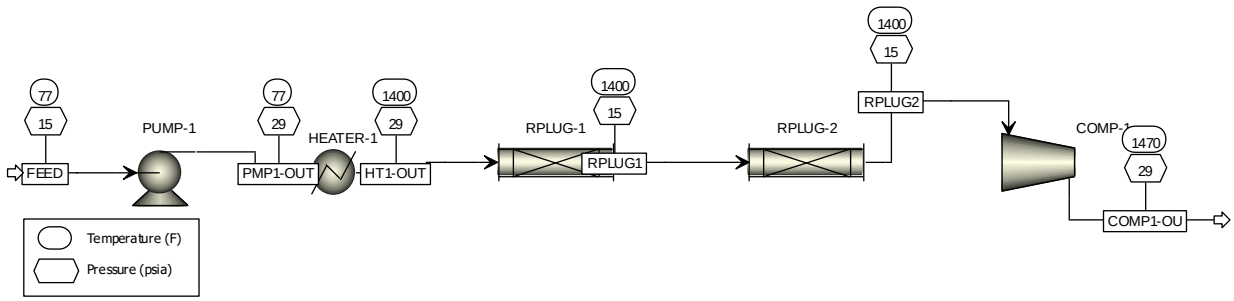

Figure 1a: Process flow diagram of Benzene Pyrolysis using 2 Plug flow reactor Operating at 0.0309 Kg-mol/hr, 1033.15 K and 101325 Pa.

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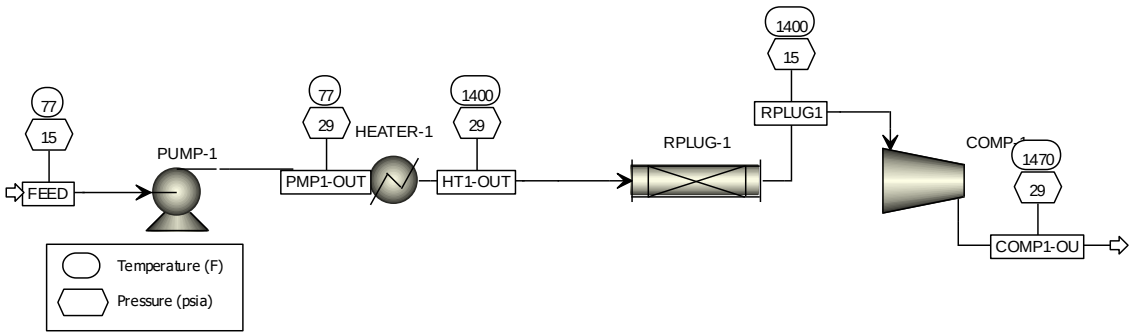

Figure 1b: Process flow diagram of Benzene Pyrolysis using 1 Plug flow reactor Operating at 0.0309 Kg-mol/hr, 1033.15 K and 101325 Pa.

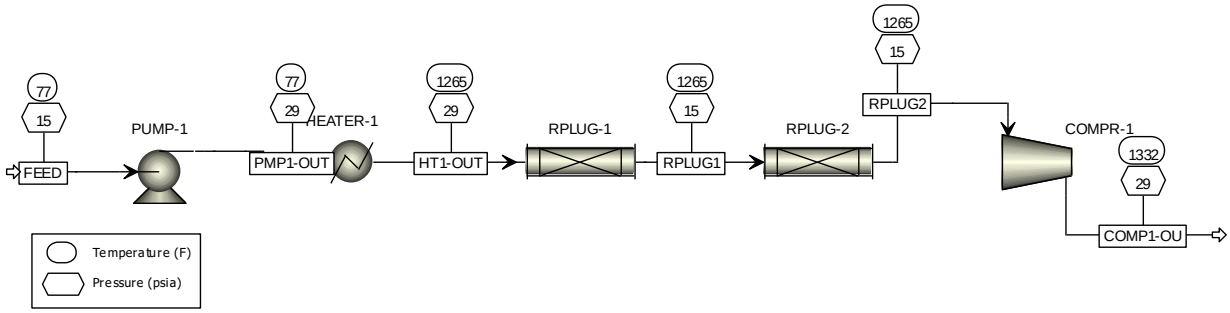

Figure 1c: Process flow diagram of Benzene Pyrolysis using 2 Plug flow reactor Operating at 0.0095 Kg-mol/hr, 958.15 K and 101325 Pa.

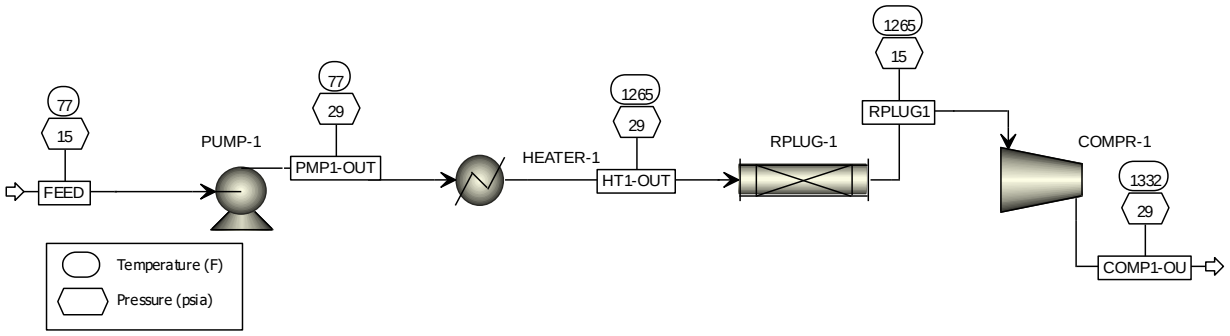

Figure 1d: Process flow diagram of Benzene Pyrolysis using 1 Plug flow reactor Operating at 0.0095 Kg-mol/hr, 958.15 K and 101325 Pa.

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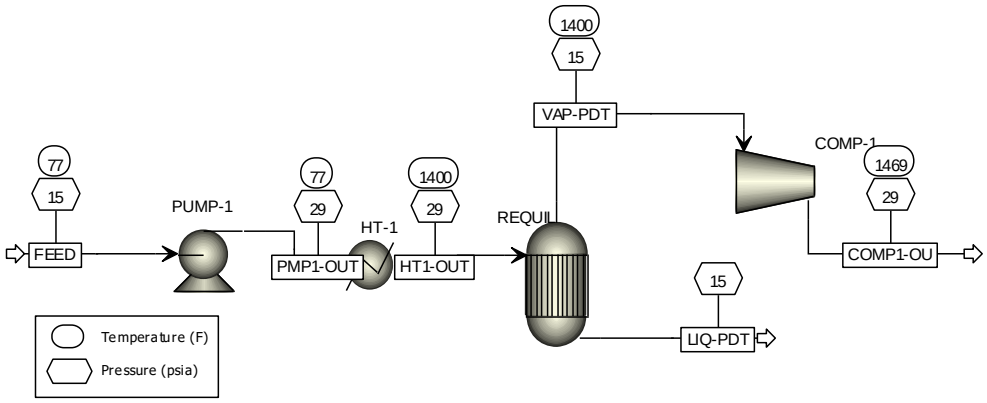

Figure 1e: Process flow diagram of Benzene Pyrolysis using Equilibrium reactor Operating at 0.0309 Kg-mol/hr, 1033.15 K and 101325 Pa.

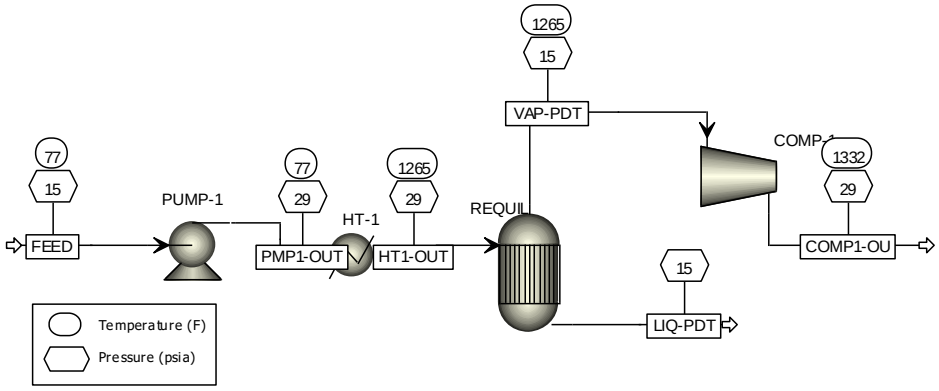

Figure 1f: Process flow diagram of Benzene Pyrolysis using Equilibrium reactor Operating at 0.0095 Kg-mol/hr, 958.15 K and 101325 Pa.

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III. Results and Discussion for the Benzene Pyrolysis to Diphenyl, m-Terphenyl, and Hydrogen Results

Table 2: Mole Fractions of Benzene, Diphenyl, m-Triphenyl, and Hydrogen for Reactors at Operating Conditions

	Experi-mental result – Plug flow	2 Plug flow reactors	1 Plug flow reactors	Equilib-rium reactor	Experi-mental results – Plug flow	2 Plug flow reactors	1 Plug flow reactors	Equilib-rium reactor
Phase	Vapour	Vapour	Vapour	Vapour	Vapour	Vapour	Vapour	Vapour
Temperature (K)	1033.15	1033.15	1033.15	1033.15	958.15	958.15	958.15	958.15
Pressure (Pa)	101325	101325	101325	101325	101325	101325	101325	101325
Mole flow (Kg-mol/hr)	0.0309	0.0309	0.0309	0.0309	0.0095	0.0095	0.0095	0.0095
BENZE-01		0.0257	0.0259	0.0154		0.0079	0.0079	0.0050
DIPHE-01		0.0205	0.0022	0.0043		0.0006	0.0007	0.0013
M-TER-01		0.0004	0.0002	0.0023		0.0001	0.0001	0.0006
H_2		0.0029	0.0026	0.0089		0.0009	0.0009	0.0026
Mole fraction								
BENZE-01	0.8410	0.8287	0.8350	0.4957	0.8280	0.8247	0.8313	0.5301
DIPHE-01	0.0695	0.0661	0.0711	0.1399	0.0737	0.0673	0.0725	0.1350
M-TER-01	0.00680	0.0130	0.0076	0.0748	0.00812	0.0136	0.0079	0.0666
H_2	0.0830	0.0922	0.0863	0.2895	0.0900	0.0944	0.0883	0.2683

Discussion of results.

It was observed that the results of both one- and two-plug flow reactor systems were closely related to the experimental results (Fogler and Gurmen, 2022; Fogler and Gurmen, 2002) that were used to validate them. These were the cases for the two operating conditions of temperatures of 1033.15 K and 958.15 K at 101325 Pa pressure. The results for equilibrium reactors for the two operating conditions were quite different. It has shown much improvement in the production of diphenyl, m-terphenyl, and hydrogen in both operating conditions. Although the results at 1033.15 K were better than those at 958.15 K, The results at 1033.15 K are shown to be a bit better than those at 958.15 K for both single and double plug flow reactors.

All these were glaring from the tables below, which show the percentage of their differences from the experimental values. The best one has much m-terphenyl production, followed by diphenyl, and then hydrogen.

2 plug-flow reactors produced the highest mole fraction for m-terpheny than 1 plug-flow reactor and experimental cases, respectively. 1 plug-flow reactor showed better results for diphenyl production than 2 plug-flow reactors at both 1033.15 K and 958.15 K operating conditions.

The importance of the results was based on the economic importance of the products, which shows that m-terphenyl > diphenyl > hydrogen > benzene, respectively. Products percentage (%) difference from experimental molar fraction results at 1033.15 K, 101325 Pa, and 0.0309 Kg-mol/hr as shown in Table 4.

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Table 3: Energy Demand by Reactors for the Processes

Reactor Type	Energy Demand (KJ/hr)	Flow rate (Kg-mol/hr)	Temperature (K)
1 PFR	22.1951	0.0095	958.15
1 PFR	72.5814	0.0309	1033.15
2 PFR	23.6209	0.0095	958.15
2 PFR	77.1170	0.0309	1033.15
Equilibrium	66.5228	0.0095	958.15
	239.3150	0.0309	1033.15

Table 4: Percentage Difference of Molar Fractions of the Products for the Reactors Performance at 1033.15 K, 101325 Pa, and 0.0309 Kg-mol/hr in Comparison with Experimental Results.

Mole fraction	Experi-mental result of Plug flow reactor	2 Plug flow reactors	% difference of 2 RPlug	1 Plug flow reactors	% difference of 1 RPlug	Equilib-rium reactor	% difference of Equilib-rium reactor
BENZE-01	0.8410	0.8287	-0.0146	0.8350	-0.0071	0.4957	-0.4106
DIPHE-01	0.0695	0.0661	-0.0489	0.0711	0.0230	0.1399	1.0129
M-TER-01	0.0068	0.0130	0.9118	0.0076	0.1176	0.0748	10.0000
H_2	0.0830	0.0922	0.1108	0.0863	0.0398	0.2895	2.4880

2 plug-flow reactors showed 91.18 % m-terphenyl and 11.08 % H_2 increments over experimental results. 1 plug flow reactor shown 2.30 % diphenyl, 11.76 % m-terphenyl, and 3.98 % H_2 increments, respectively, over experimental results. Equilibrium reactor shown 101.29 % diphenyl, 1000.00 % m-terphenyl, and 248.80 % H_2, respectively, over experimental results. 2 and 1 plug flow as well as equilibrium reactors show a % decrease of -1.46 %, -0.71 %, and -41.06 % benzene in the product stream, respectively, in comparison to the experimental results. The product percentage (%) difference from the experimental molar fraction results at 958.15 K, 101325 Pa, and 0.0095 Kg-mol/hr as shown in Table 5 below.

At 958.15 K, 101325 Pa, and 0.0095 Kg-mole/hr operating conditions, 2 plug flow reactors showed 67.90 % m-terphenyl and 04.89 % H_2 increments over experimental results. 1 plug flow reactor showed 0.40 % more benzene in the product stream than experimental results. Equilibrium reactor shown 83.18 % diphenyl, 722.22 % m-terphenyl, and 198.11 % H_2, respectively, over experimental results. It followed the same trend of the best being an equilibrium reactor, followed by a 2-plug flow reactor, and the least being a 1-plug flow reactor.

Table 5: Percentage Difference of Molar Fractions of the Products for the Reactors Performance at 958.15 K, 101325 Pa, and 0.0095 Kg-mol/hr in Comparison with Experimental Results.

Mole fraction	Experi-mental result of Plug flow reactor	2 Plug flow reactors	% difference of 2 RPlug	1 Plug flow reactors	% difference of 1 RPlug	Equilib-rium reactor	% difference of Equilib-rium reactor
BENZE-01	0.8280	0.8247	-0.0040	0.8313	0.0040	0.5301	-0.3598
DIPHE-01	0.0737	0.0673	-0.0868	0.0725	-0.0163	0.1350	0.8318

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M-TER-01	0.0081	0.0136	0.6790	0.0079	-0.0247	0.0666	7.2222
H_2	0.0900	0.0944	0.0489	0.0883	-0.0189	0.2683	1.9811

The energy demand results show that the higher the temperature, the higher the energy demanded by the reactor. At 958.15 K, the energy demanded by 1 PFR is the least, followed by 2 PFR, and the equilibrium reactor has the most. It followed the same trend for temperature at 1033.15 K. The two cases show a very significant increase in energy demand for equilibrium reactors, of about triple in quantity compared to the PFR reactors, as shown in Table 3.

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IV. Analysis and Interpretation of Results

The results indicate that the equilibrium reactor outperformed the other reactor types in the pyrolysis of benzene under the specified operating conditions. This suggests that the equilibrium reactor provided the most favourable conditions for achieving the desired product distribution, likely due to its ability to maintain thermodynamic equilibrium within the system.

The two plug-flow reactors followed the equilibrium reactor in effectiveness. While not as efficient as the equilibrium reactor, the two plug-flow reactors still demonstrated notable performance, indicating that they could effectively facilitate the conversion of benzene into the desired products.

The 1-plug-flow reactor ranked third in effectiveness. This suggests that its design or operating conditions may not have been as conducive to achieving optimal product distribution compared to the other reactor types under the given circumstances. It's important to note that the experimental method served as a validation source, indicating that the results obtained from the reactor simulations align with real-world observations. This strengthens the reliability of the findings.

Overall, the preference for the equilibrium reactor followed by the two plug-flow reactors underscores the significance of considering thermodynamic equilibrium and efficient flow patterns in reactor design for the pyrolysis of benzene. Further analysis could explore the specific product distributions and reaction kinetics within each reactor type to gain deeper insights into their performance differences. Additionally, investigating the cost-effectiveness and scalability of each reactor type could provide valuable information for industrial applications.

V. CONCLUSION AND FUTURE WORK

In terms of efficiency, the best scenario is an equilibrium reactor at 1033.15 K and 101325 Pa. The second-best is the equilibrium reactor at 958.15 K and 101325 Pa. The third best is two plug-flow reactors at 1033.15 K and 101325 Pa. The fourth best is two plug-flow reactors at 958.15 K and 1013225 Pa. The fifth-best is the 1-plug flow reactor at 1033.15 K and 101325 Pa. The worst scenario is the 1-plug flow reactor at 958.15 K and 101325 Pa. An equilibrium reactor at 1033.15 K and 101325 Pa at any flow rate is recommended for the conversion of liquid benzene to m-terphenyl, diphenyl, and hydrogen, respectively. The energy demand by equilibrium reactor was the highest for the two cases of 239.3150 KJ/mol at 1033.15 K and 66.5228 KJ/mol at 958.15 K, followed by 2 PFR of 77.1170 KJ/mol at 1033.15 K and 23.6209 KJ/mol at 958.15 K, and least by 1 PFR of 72.5814 KJ/mol at 1033.15 K and 22.1951 KJ/mol at 958.15 K. It is recommended that the full industrial simulation that will handle separation, purification, costing, and cost-benefit analysis be done for the final choice of the process route.

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AUTHOR'S BIOGRAPHY

Engr. Dr. Ademola Bolanle **Raheem** B.Eng. (Chemical Engr), PGD (Petroleum Engr), M.Eng (Chemical Engr), PhD. (Chemical Engr), R. Eng, MNSE, MNSChE, SPE.
Office: Department of Chemical Engineering, Faculty of Engineering, University Park, Choba, East-West Road, Port Harcourt, Rivers State, Nigeria
Email: ademola.raheem@uniport.edu.ng; rahbol_debven@yahoo.com
Phone number: +2348038273654
Birthday: 27th September

Dr. Ademola is an academic staff member in the Chemical Engineering Department at the University of Port Harcourt. He has been in the service of the university for more than a decade. He has a Ph.D. (chemical engineering) in University Technology Malaysia (UTM, Malaysia). He is a scholar of the Tertiary Education Trust Fund (TETFund) 2015. His research area is the design, modelling, simulation, and optimization of industrial processes. He is accredited with many awards, including the Petroleum Technology Development Fund (PTDF) and Nigerian National Petroleum Corporation (NNPC) engineering design training, among others. He has had experience in process and engineering design as well as petroleum refining (Engineering and Technical Services Department) at Warri Refining and Petrochemical Company Ltd. (a subsidiary of NNPC) since 2013. He is also into engineering data analysis and management, sustainable and green technology, environmental impact assessment, and enhanced polymer materials. Ademola has supervised many degree projects. He has presented his research outcomes at international conferences. He has published in many reputable journals, including Q1 journals. He can be reached at ademola.raheem@uniport.edu.ng, rahbol_debven@yahoo.com, or +2348038273654, and his birthday is September 27th.