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Research Article

Maximizing Chlorobenzene Product Yield by Modifying the Benzene Chlorination Process

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Abstract

Chlorobenzene is extensively used in the manufacture of phenol, aniline, and DDT; as a solvent for paints; and as a heat transfer medium. It is also occasionally used in the dry-cleaning industry. With the many uses of chlorobenzene, its production must have high efficiency both in terms of energy and mass in order to obtain maximum profits. In this paper, we will explain how to maximize chlorobenzene product yield by modifying the benzene chlorination process. The process modification was carried out by adding one distillation column unit and one mixer unit. Meanwhile, to carry out sensitivity analysis, case study tools on chemical engineering software were used. Based on process modifications, an increase in chlorobenzene yield was obtained from 83% to 98%. The results of the case study indicate that the higher the benzene pressure entering the reactor, the lower the yield of the liquid product exiting the reactor. Meanwhile, the higher the ratio of benzene mass flow to chlorine gas mass flow, the higher the yield of the liquid product exiting the reactor.

Keywords: Chlorobenzene; Chlorination; Benzene chlorination; Yield Maximizing

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1. Introduction

Monochlorobenzene or Chlorobenzene is a compound with the chemical formula C_6H_5Cl [1]. Chlorobenzene production has been declining since its peak in 1969, and is likely to continue declining due to the substitution of more environmentally friendly chemicals. Chlorobenzene is produced by chlorination of benzene in the presence of a catalyst, and is produced as an end product in the reductive chlorination of di- and trichlorobenzenes. Chlorobenzene is a semi-finished product commonly used as a raw material or supporting material in the chemical industry [2]. This compound is extensively used in the manufacture of phenol, aniline, and DDT; as a solvent for paints; and as a heat transfer medium. It is also occasionally used in the dry cleaning industry [3].

Zhang *et al.* [4], computing the benzene chlorination process with generalized disjunctive programming (GDP) models to find the optimal model for the reaction-separation-recycle using a rigorous model. The case study was carried out on a separation unit with variables in the form of the

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number of trays, the position of feed tray, and the reflux ratio in each column. The modification made was to use the number of trays in the first column as 20 with a reflux ratio of 1.05, while the number of trays in the second column was 14 with a reflux ratio of 0.3. The results of the modification succeeded in increasing conversion from 50% to 69%. Ma *et al.* [5], computing the benzene chlorination process with a mixed integer nonlinear programming (MINLP) formulation using the convex-hull method to find the optimal model for the reaction-separation-recycle using a rigorous model. The results obtained that the total annual cost (TAC) in the optimal design can reduce costs from 0.619 M€ yr-1 to 0.614 M€ yr-1 and can also reduce the reboiler duty from 0.5 MW to 0.49 MW. This can be achieved by using 18 stages in the first column and 11 stages in the second column.

No previous studies have examined the process modification by recycling the output from the top product of chlorination. Recycling the top products can occur by adding one distillation unit and one mixer unit. The distillation unit is added as an HCl remover, with the input consisting predominantly of HCl from the output of the chlorination reactor. Meanwhile, the mixer unit is added to combine the bottom stream from the distillation unit (HCl remover) and the top stream from the purification unit into the recycling loop. Subsequently, the recycled flow will carry the dominant benzene reactant (C_6H_6) from the mixer to the chlorination reactor. This process modification can enhance chlorobenzene production by minimizing the use of raw materials and energy.

The production process of monochlorobenzene through the gas-liquid phase chlorination of benzene operates at low temperatures and requires less energy, making it more economical compared to the gas-gas phase chlorination process. Therefore, the production of monochlorobenzene through the gas-liquid phase chlorination of benzene is chosen [6]. In the production of chlorobenzene, the modified process involves adding a recycle stream to continuously feed the benzene reactant (C_6H_6) from the mixer to the chlorination reactor. The purpose of this process modification is to maximizing chlorobenzene product yield by modifying the benzene chlorination process. In this modification, variations in pressure and mass flow variables are introduced. The aim of these variations is to observe their impact on the outcomes obtained in the chlorobenzene production system.

2. Methods

The simulation was carried out using Aspen HYSYS V11 by adding components such as C_6H_6, Cl_2, chlorobenzene, dichlorobenzene, and HCl. The fluid package employed was Peng-Robinson. To maximize the chlorobenzene yield, a process modification was carried out by adding a recycle from the top product chlorination reactor so that it returned to the chlorination reactor. Recycling the top products can occur by adding one distillation unit and one mixer unit. The distillation unit was added as an HCl remover, with the input consisting predominantly of HCl from the output of the chlorination reactor. Meanwhile, the mixer unit was added to combine the bottom stream from the distillation unit (HCl remover) and the top stream from the purification unit into the recycling loop. Subsequently, the recycled flow carries the dominant benzene reactant (C_6H_6) from the mixer to the chlorination reactor. This process modification can enhance chlorobenzene production by minimizing the use of raw materials and energy.

The results of the process modification show an improvement in the yield of chlorobenzene by recycling the output from the chlorination reactor back into the chlorination reactor. Chlorobenzene yield can be calculated using Equation (1):

$$\textit{Yield of Chlorobenzene}\ (\%) = (\textit{mol of chlorobenzene}) / (\textit{mol of benzene}) \times 100\% \quad (1)$$

From Equation (1), we have the result of yield of chlorobenzene. Table 1 shows comparison between processes with and without modification in terms of chlorobenzene yield.

3. Result and Discussion

3.1. Basic Process Flowsheet and Simulation

The most common method used in the production of monochlorobenzene is the chlorination process, which involves substituting an atom in a paraffinic or aromatic compound with chlorine [7]. The chlorobenzene production process is carried out through the chlorination of benzene with the assistance of a catalyst [8]. In most industries, this manufacturing process

Table 1. Comparison process without modification and with modification

Process	Chlorobenzene Yield (%)
Without modification	83
With modification	98

utilizes continuous liquid chlorination. The production of monochlorobenzene through gas-liquid phase benzene chlorination operates at low temperatures and requires less energy, making it more economical compared to benzene chlorination in gas-gas phase.

In the production of monochlorobenzene, liquid benzene is reacted with chlorine gas in a reactor, where the chlorine gas is bubbled at the bottom of the reactor through a perforated plate. The catalyst used is solid $FeCl_3$, which functions to accelerate the reaction rate and reduce side reactions [9]. The reaction takes place in a fixed bed multitube reactor, operating in a non-isothermal manner at temperatures of 20 – 40 °C to minimize the production of dichlorobenzene, which occurs at higher temperatures [10]. This temperature range is optimal for the large-scale production of monochlorobenzene. The reactor operates at a pressure of 2.3686 atm (2.4 bar). The feed, consisting of liquid benzene and chlorine gas, is at a temperature of 25 °C and atmospheric pressure. The liquid benzene feed flows through tubes containing the $FeCl_3$ catalyst, and similarly, chlorine gas is introduced into the reactor.

The production reaction of monochlorobenzene is an exothermic reaction [11]. An exothermic reaction is a reaction that releases a certain amount of heat from the system to the environment [12]. Therefore, to maintain the temperature within the reaction temperature range, a cooling process is employed. At excessively high chlorination reaction temperatures, there is a risk of a rapid combustion rate of benzene, leading to an uncontrolled and dangerous reaction as it releases a large amount of HCl gas into the atmosphere. Thus, adequate cooling is necessary to keep the temperature below 40 °C [13]. In the simulation of the chlorobenzene production process using the gas-liquid phase benzene chlorination method, it is designed for a production capacity of 24,500 tons per year.

Chemical reactions [14]:

$C_6H_{6\,(l)} + Cl_{2\,(g)} \rightarrow C_6H_5Cl_{\,(l)} + HCl_{\,(g)}$

$\Delta H_{\text{reaction 1}} = -123.39$ kJ/mol (1)

$C_6H_5Cl_{\,(l)} + Cl_{2\,(g)} \rightarrow C_6H_4Cl_{2\,(l)} + HCl_{\,(g)}$

$\Delta H_{\text{reaction 2}} = -122.13$ kJ/mol (2)

$$\Delta H_{\text{total reaction}} = \Delta H_{\text{f reaction 1}} + \Delta H_{\text{f reaction 2}} = -244520\ \text{J/mol} \quad (3)$$

Based on the calculation of the total reaction enthalpy (ΔH) at a temperature of 298 K, the result shows a negative ΔH value. Therefore, it can be concluded that the ongoing reaction is an exothermic reaction that releases heat. The ΔG_f data for each component at a temperature of 298 K can be seen in the Table 2 [14].

Calculation of ΔG_f Reaction (1) as a main reaction:

$$\Delta G_{\text{f reaction 1}} = \Delta G_{\text{f (product)}} - \Delta G_{\text{f (reactant)}} = (G_f\,HCl + G_f\,C_6H_5Cl) - (G_fCl_2 + G_f\,C_6H_6) = -125800\ \text{J/mol}$$

$$\Delta G_{f\,298} = -R\,T\ln K_{298} \quad (4)$$

$$\ln K_{298} = \frac{\Delta G_{f\,298}}{-R\,T}$$

$$\ln K_{298} = \frac{-125800\,\frac{\text{J}}{\text{mol}}}{-\left(8.314\,\frac{\text{J}}{\text{mol. K}}\right)(298\ \text{K})}$$

$$\ln K_{298} = 50.776$$

$$K_{298} = 1.126 \times 10^{22}$$

At operating temperature of 40 °C (313 K):

$$\ln\frac{K_T}{K_{298}} = -\frac{\Delta H_{f\,298}}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right) \quad (5)$$

$$\ln\frac{K_{313}}{1.126 \times 10^{22}} = -\frac{-123390\,\frac{\text{J}}{\text{mol}}}{8.314\,\frac{\text{J}}{\text{mol. K}}}\left(\frac{1}{313\ \text{K}} - \frac{1}{298\ \text{K}}\right)$$

$$\ln\frac{K_{313}}{1.126 \times 10^{22}} = -2.387$$

$$K_{313} = 1.035 \times 10^{21}$$

Because the value of $K_{313} > 1$, thus, the first reaction (main reaction) is irreversible.

Calculation of ΔG_f Reaction (2) as a side reaction:

$$\Delta G_{\text{f reaction 2}} = \Delta H_{\text{f (product)}} - \Delta H_{\text{f (reactant)}} = (G_f\,HCl + G_f\,C_6H_4Cl_2) - (G_fCl_2 + G_f\,C_6H_5Cl) = -117310\ \text{J/mol}$$

$$\Delta G_{f\,298} = -R\,T\ln K_{298}$$

$$\ln K_{298} = \frac{\Delta G_{f\,298}}{-R\,T}$$

$$\ln K_{298} = \frac{-117310\ \frac{\text{J}}{\text{mol}}}{-\left(8.314\ \frac{\text{J}}{\text{mol. K}}\right)(298\ \text{K})}$$

$$\ln K_{298} = 47.349$$

$$K_{298} = 3.659 \times 10^{20}$$

At operating temperature 40 °C (313 K):

$$\ln\frac{K_T}{K_{298}} = -\frac{\Delta H_{f\,298}}{R}\left(\frac{1}{T} - \frac{1}{T_{298}}\right)$$

$$\ln\frac{K_{313}}{3.659 \times 10^{20}} = -\frac{-121130\,\frac{\text{J}}{\text{mol}}}{8.314\,\frac{\text{J}}{\text{mol. K}}}\left(\frac{1}{313\ \text{K}} - \frac{1}{298\ \text{K}}\right)$$

Table 2. Data of ΔG_f for each component at temperature 298 K

Compound Name	Molecular Formula	$G_{f,\,298\ K}$ (kJ/mol)
Benzene	C_6H_6	129.66
Chlorine	Cl_2	0
Chlorobenzene	C_6H_5Cl	99.16
Hydrochloric Acid	HCl	– 95.30
1,4-Dichlorobenzene	$C_6H_4Cl_2$	77.15

$$\ln \frac{K_{313}}{3.659 \times 10^{20}} = -2.343$$
$$K_{313} = 3.514 \times 10^{19}$$

Because the value of $K_{313} > 1$, thus, the second reaction (side reaction) is irreversible.

Therefore, the production of monochlorobenzene through gas-liquid phase benzene chlorination is preferred. This chlorination process involves reacting benzene (C_6H_6) with chlorine (Cl_2) to produce chlorobenzene ($C_6H_5Cl_2$) along with by-products dichlorobenzene ($C_6H_4Cl_2$) and HCl [6]. Process flow diagram of chlorination benzene without modification is shown in Figure 1.

3.2. Modified Process Flowsheet and Simulation

To maximize the chlorobenzene yield, a process modification is carried out by adding a recycle from the top product chlorination reactor so that it returns to the chlorination reactor. Recycling the top products can occur by adding one distillation unit and one mixer unit. The distillation unit is added as an HCl remover, with the input consisting predominantly of HCl from the output of the chlorination reactor. Meanwhile, the mixer unit is added to combine the bottom stream from the distillation unit (HCl remover) and the top stream from the purification unit into the recycling loop. Subsequently, the recycled flow carries the dominant benzene reactant (C_6H_6) from the mixer to the chlorination reactor. This process modification can enhance chlorobenzene production by minimizing the use of raw materials and energy. Simulation of chlorination benzene with modification is shown in Figure 2.

Flowsheet modifications can be seen in the units located in the blue line. The modification consists of adding one distillation unit and one mixer unit. The modified flowsheet can be seen in Figure 3.

3.3. Improvement of Product Yield Due to The Process Modification

The results of the process modification show an improvement in the yield of chlorobenzene by recycling the output from the chlorination reactor back into the chlorination reactor. The process modification applied to the simulation of chlorobenzene production involves adding one distillation unit and one mixer unit. The distillation unit is added as an HCl remover, with the input consisting predominantly of HCl from the output of the chlorination reactor. Meanwhile, the mixer unit is added to combine the bottom stream from the distillation unit (HCl remover) and the top stream from the purification unit into the recycling loop. Subsequently, the recycled flow carries the dominant benzene reactant (C_6H_6) from the mixer to the chlorination reactor. The purpose of this process modification is to enhance chlorobenzene production by minimizing the use of raw materials and energy. Table 3 compares the processes with and without modification in terms of chlorobenzene yield. The simulation results using Aspen HYSYS, it is obtained mass balances and energy balances for processes with and without modification. These results are presented in Table S1 and Table S2 (Supporting Information).

3.4. Sensitivity Analysis of Reactor Operating Conditions

Sensitivity analysis was conducted by varying the independent variable, which is the benzene pressure, with the goal of targeting the dependent variable, the liquid chlorobenzene mole fraction, using the Case Study tool. The case study was executed with pressure variations of 12.5 psia, 13 psia, 13.5 psia, 14 psia, and 14.5 psia. Table 4 presents the results of the sensitivity analysis of reactor operating conditions by varying benzene pressure which affect on the mole fraction of chlorobenzene at effluent reactor.

The results of the case study indicate that the higher the benzene pressure, the lower the yield of the liquid product coming out of the reactor. Chlorobenzene is the main product that certainly requires high yield after leaving the reactor to facilitate the separation process [15]. Therefore, to alleviate the burden on the separation unit, the process can use lower benzene pressure. High reactant pressure also requires expensive treatment and storage facilities [16]. By using lower benzene pressure, energy efficiency can be achieved as it lightens the load on the separation unit. Figure 5 illustrates the relationship between benzene pressure and the mole fraction of chlorobenzene.

The sensitivity analysis was also conducted by varying the independent variable, which is the ratio of benzene mass flow to chlorine gas mass flow, with the goal of targeting the dependent variable, the liquid chlorobenzene mole fraction, using the case study tool. The case study was executed with variations in the benzene mass flow to chlorine gas mass flow ratio: 0.87, 0.88, 0.89, 0.90, and 0.91. The following table presents the results of the sensitivity analysis of the benzene mass flow to chlorine gas mass flow ratio on the mole fraction of chlorobenzene.

The results of the case study indicate that the higher the ratio of benzene mass flow to chlorine gas mass flow, the higher the yield of the liquid product coming out of the reactor. Sadeghi and Ahangar [17] state that an increase in mass flow can enhance the yield of the main product. On the

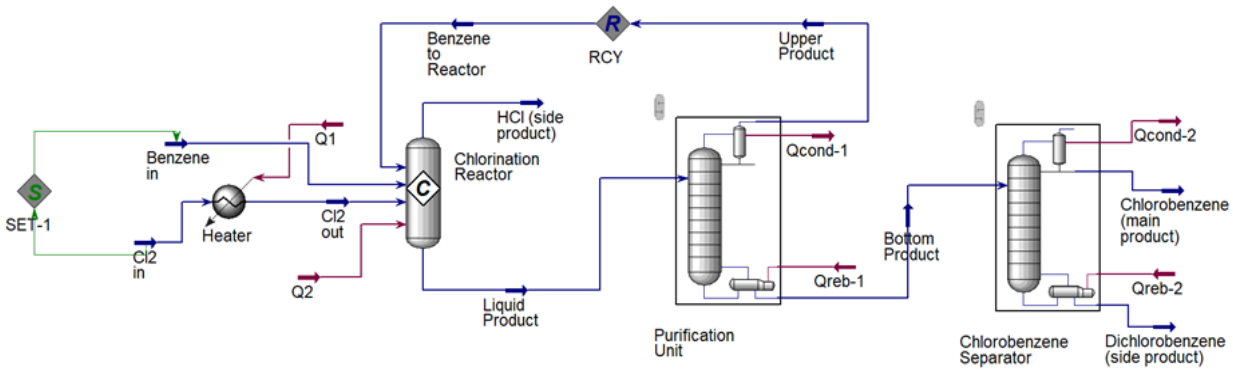

Figure 1. Basic process flow diagram benzene chlorination

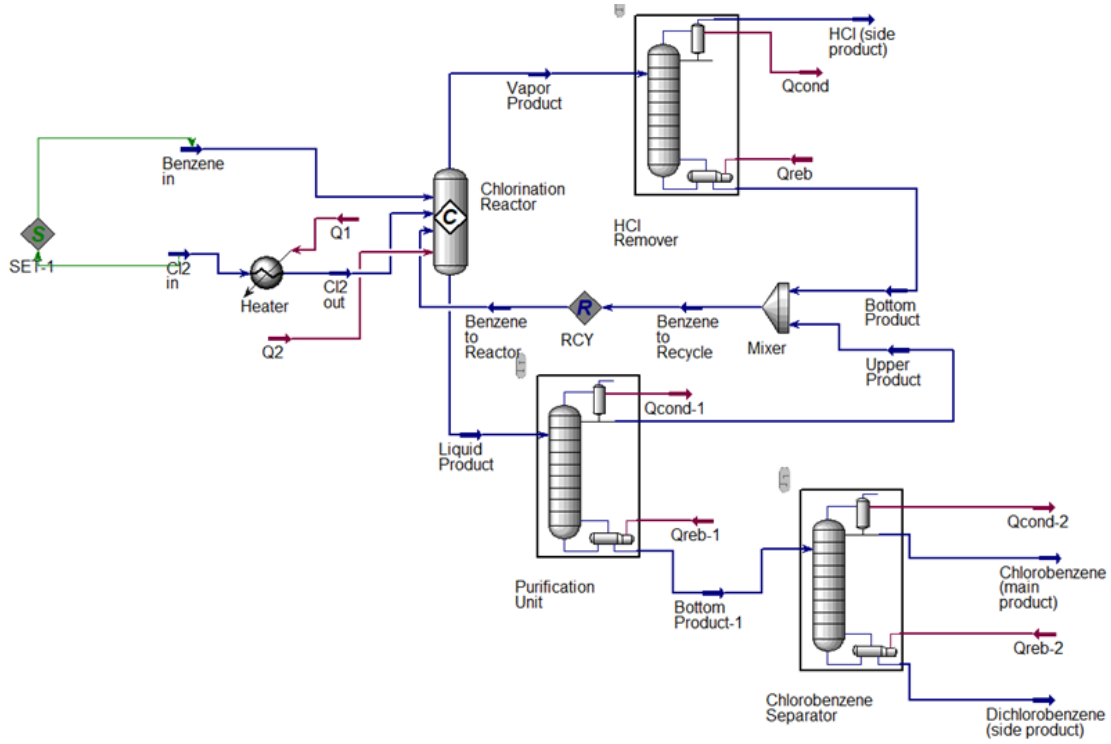

Figure 2. Modified process flow diagram benzene chlorination

Table 3. Comparison process without modification and with modification

Process	Chlorobenzene Yield (%)
Without modification	83
With modification	98

Table 4. Sensitivity analysis of operating condition of reactor by varying pressure of benzene

Pressure of benzene entering reactor (psia)	Chlorobenzene mole fraction leaving the reactor
12.5	0.6427
13	0.6408
13.5	0.6389
14	0.6371
14.5	0.6353

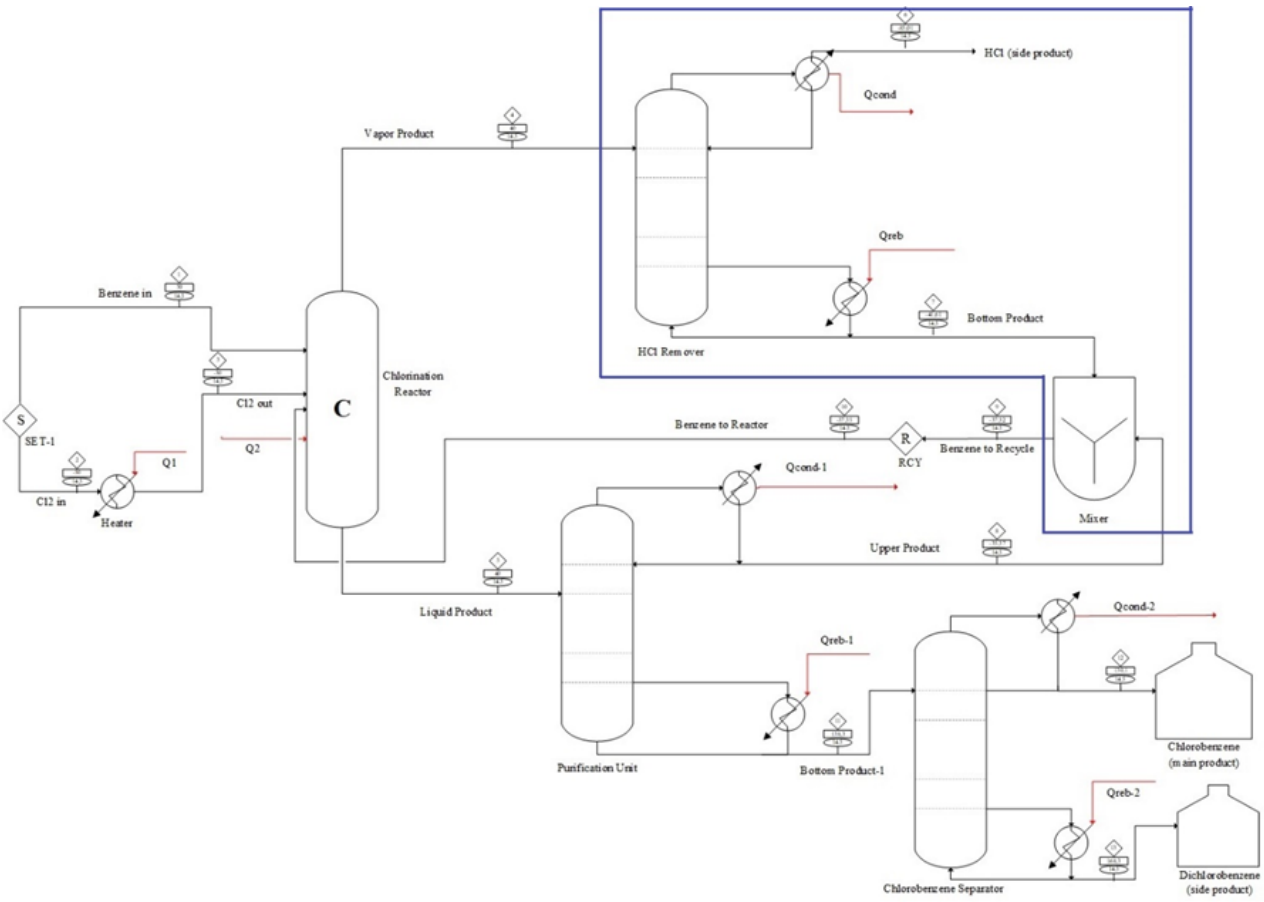

Figure 3. Flow diagram of modified process of benzene chlorination

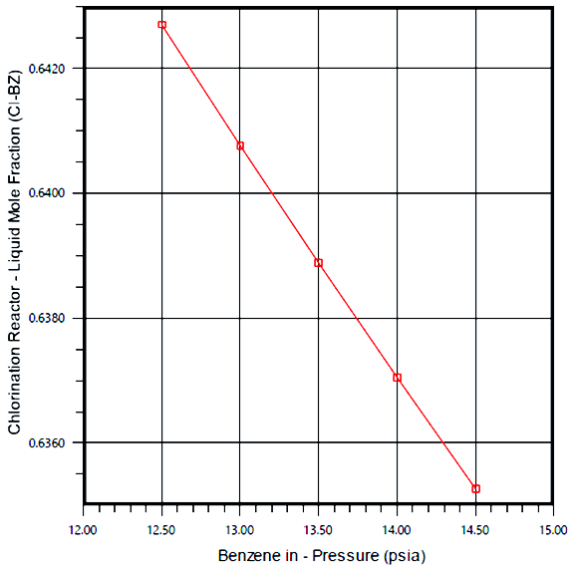

Figure 4. Sensitivity analysis of benzene pressure graph

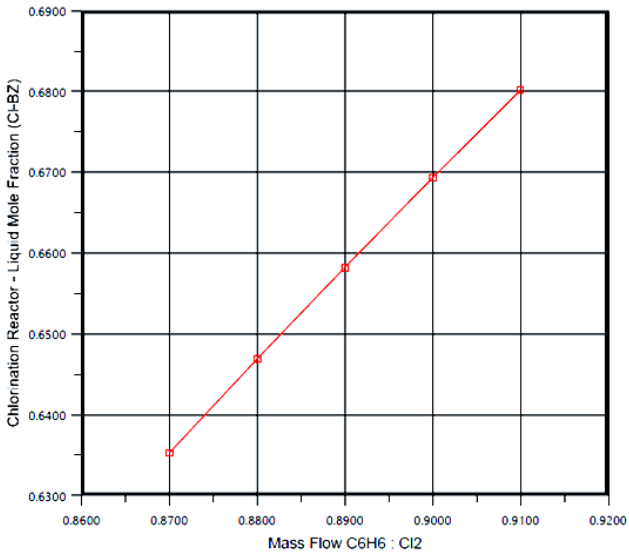

Figure 5. Sensitivity analysis of the ratio of benzene mass flow to chlorine gas mass flow graph

contrary, reducing mass flow can lead to an increase in yield towards by-products. Figure 5 depicts the relationship between the benzene pressure and the mole fraction of chlorobenzene.

4. Conclusions

Process modifications in chlorobenzene production must be undertaken to achieve increased energy and mass efficiency. Through process modifications, factories can optimize raw material and energy usage, reduce environmental impact, enhance product yield, and improve operational efficiency. Based on the implemented process modifications, there has been an increase in the yield of the produced chlorobenzene from 83% to 98%. Further studies regarding the benzene chlorination process are still needed. In particular, economic analysis for developing the benzene chlorination process to be more energy efficient and also economical in the use of raw materials. Apart from that, analyzing the impact on the environment is also very important, considering that in this decade, the world is starting to take environmental problems seriously. Pollution due to production is of course a serious problem which is currently regulated and stipulated in regulations.

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