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Performance Evaluation of Batch Reactor for Sodium Benzoate Production

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The performance of the Batch Reactor for the production of sodium benzoate from the reaction of sodium hydroxide and benzoic acid were investigated. The performance equation for the operation of batch reactor was developed for the analysis of the reactor's functional dimensions and parameters. The analysis of the reactor's functional parameters was performed at molar ratio of benzoic acid to sodium hydroxide of 1.5 to 3.0 at intervals of 0.5 and at the same reactor operating conditions. The set of reactors' performance equations were solved simultaneously and then, simulated with the aid of MATLAB R2015a computer program. The results of the analysis obtained for the batch reactor, although, showed that conversion, temperature and heat generated per reactor volume increases with increase in molar feed ratio, conversion and temperature increased with time, while the heat generated per reactor volume decreases with time. Following the results obtained from the analysis, the production of sodium benzoate from sodium hydroxide and benzoic acid can be executed in either of batch reactor depending on the capacity of production and conditions of operation. Finally, the optimum performance was observed at molar feed ratio of 3.0.

INTRODUCTION

Nowadays, the chemical and process industries highly depend on crude oil as feed stock to produce almost every chemical or material. However, some products can be synthesized without the use of crude oil feed stock, and one of such products is sodium benzoate. According to Kralj (2012), Sodium benzoate as an aromatic hydrocarbon is among the most important raw materials in the chemical industry and is obtained exclusively from fossil resources. Sodium benzoate is a salt derived from a weak acid and a strong base, so its aqueous solution is alkaline. One major route of sodium benzoate production is by the neutralization reaction of benzoic acid with sodium hydroxide.

Although, benzoic acid, one of the raw materials for the production of sodium benzoate, is majorly obtained from petrochemical industries, it is also found naturally in fruits like berries, apples, plums, cinnamon, and several other natural foods. Therefore, when benzoic acid from these natural fruits and spices are used in sodium benzoate production, it implies that it has a naturally containing ingredient. Thus, sodium benzoate produced from benzoic acid extracted from fruits and spices is commonly found in carbonated sodas, fruit juice products, salad dressings, and fermented foods such as vinegar, wine, and pickles (Mitchell, 2016).

Srour, (1998) estimated the global sodium benzoate production to about 55,000 - 60,000 tons per year, while in 2001, the Worldwide production capacity was estimated at 100,000 tons per year with an average maximum operating rate at 75%, representing 75,000 tons sodium benzoate production per year (SIDS Initial Assessment Report, 2001) and the largest producers of sodium benzoate are the Netherlands, Estonia, the U.S.A. and China. The production capacity is expected to rise as far as its application increases, which will in turn increase the demand.

Preservation of perishable products and foods is a common practice to avoid wastages. However, one preservative may be suited at a particular purpose than the other, based on side effect. This is justified by the used of sodium benzoate as preservative for foods, despite benzoic acid proven to be more effective preservative, because it does not dissolve well in water (Kralj, 2012).

Sodium benzoate is used widely as chemical additives, preservatives and flavouring agents especially in food, cosmetics and pharmaceutical industries (Dudley *et al*., 2006; Ankudovich *et al*., 2007). It is also used as a corrosion inhibitor and in technical systems as additive to automotive engine antifreeze coolants (Bozzini *et al*., 2007). Also, according to Mitchell, (2016), sodium benzoate is also added to health and beauty products such as mouthwash, shampoo, body lotions, and deodorant to prevent contamination by bacteria.

The US Food and Drug Administration (FDA) and the Canadian Health Protection Branch have pronounced this chemical preservative to be acceptable when consumed in low amounts (0.1 percent by weight in food and 5ppb in water) (Mitchell, 2016). The International Programme on Chemical Safety found no adverse effects in humans at doses of 647–825 mg/kg of body weight per day (Cosmetic Ingredient Review, 2000). However, on health perspective, the consumption of foods or drinks with sodium benzoate preservative beyond acceptable limit could be detrimental. Consumption by hypersensitive patient could result to asthmatic attacks, hives, or other allergic reactions, while the combination of sodium benzoate and citric acid and or ascorbic acid (vitamin C) lead to the formation of benzene, a cancer-causing chemical associated with leukemia and other blood cancers (Mitchell, 2016).

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The knowledge of the chemical reaction kinetic in complex chemical systems is essential for the accurate and reliable design of reactors. It has a significant impact on the equipment needed in chemical production plants (Vas Bhat, 2000; Simmie, 2003; Elliott *et al*., 2004).The aim of this study is to investigate the performance of batch reactor in the production of sodium benzoate from the reaction of benzoic acid and sodium hydroxide.

MATERIALS AND METHODS

The model equations for batch reactor as well as the equations relating their functional dimensions and parameters are developed in this paper. The resulting respective reactor equations were used for the simulation of the functional parameters, implemented with MATLAB simulink.

Expression of the Rate Kinetics

The rate equation for the production of sodium benzoate via the reaction of sodium hydroxide and benzoic acid was obtained from the reaction mechanism presented in equation (1) and (2). Thus, from equation (2), the reaction mechanism of the process is expressed thus:

$$NaOH + C_6H_5COOH \xrightarrow{k} C_6H_5COONa + H_2O \qquad (1)$$

Or for simplicity, equation (2.1) can be re-written as

$$A + B \xrightarrow{k} C + D \qquad (2)$$

Where, $A = NaOH$, $B = C_6H_5COOH$, $C = C_6H_5COONa$ and $D = H_2O$

The rate equation with respect to sodium hydroxide is expressed as

$$-r_A = -\frac{dC_A}{dt} = kC_AC_B \qquad (3)$$

Expressing equation (3) in terms of sodium hydroxide conversion and following the relationship between instantaneous concentration and the initial concentration of reactants expressed by Levenspiel (2004), we obtained as follows.

$$C_A = C_{Ao} - C_{Ao}X_A$$

$$C_A = C_{Ao}(1 - X_A) \qquad (4)$$

$$C_B = C_{Bo} - C_{Ao}X_A$$

$$C_B = C_{Ao}(\alpha - X_A) \qquad (5)$$

Where α is the ratio of the initial concentration of benzoic acid to that of sodium hydroxide in the reaction $\left(\alpha = \frac{C_{Bo}}{C_{Ao}}\right)$.

Substitution of equations (4) and (5) into (3) yields

$$-r_A = kC_{Ao}^2(1 - X_A)(\alpha - X_A) \qquad (6)$$

But for temperature dependent rate, the specific rate is expressed according to Arrhenius equation given as

$$k = k_o \exp\left(-\frac{Ea}{RT}\right) \qquad (7)$$

Thus equation (6) becomes

$$-r_A = k_o \exp\left(-\frac{Ea}{RT}\right)C_{Ao}^2(1 - X_A)(\alpha - X_A) \qquad (8)$$

Development of Reactor Performance Equations

The performance equations for batch, continuous stirred-tank and plug flow reactors are developed in this section by applying the principle of conservation of mass and energy as presented in equations (9) and (24) respectively.

$$\left\{\begin{array}{c}\text{Rate of}\\ \text{input of}\\ \text{material}\\ \text{into reactor}\end{array}\right\} = \left\{\begin{array}{c}\text{Rate of}\\ \text{output of}\\ \text{material from}\\ \text{reactor}\end{array}\right\} + \left\{\begin{array}{c}\text{Rate of}\\ \text{depletion}\\ \text{due to}\\ \text{reaction}\end{array}\right\} + \left\{\begin{array}{c}\text{Rate of}\\ \text{accumulation}\\ \text{of material}\\ \text{within reactor}\end{array}\right\} \quad (9)$$

Mass Balance on Batch Reactor

A schematic diagram of batch reactor is presented in Figure 1, where the raw materials are charged into the reactor at once and allowed to react until reaction is completed before withdrawing the product. However, the performance equation is developed following equation (9) as follow.

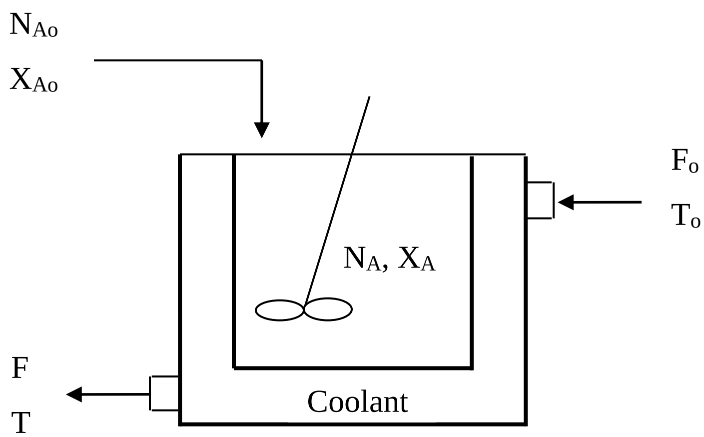

Figure 1 Batch Reactor

$$Input\, of\ material \quad = N_{Ao} \qquad (10)$$

$$Output\, of\ material \quad = N_{A} \qquad (11)$$

$$Rate\, of\ depletion \quad = -r_A V_{Batch} \qquad (12)$$

$$Rate\, of\ accumulation = \frac{dN_A}{dt} \qquad (13)$$

Substituting equations (10) through equation (13) into equation (9) yields:

$$N_{Ao} = N_A + (-r_A)V_{Batch} + \frac{dN_A}{dt}$$

But for batch reactor, $N_{Ao} = N_A = 0$

Hence,

$$-\frac{dN_A}{dt} = (-r_A)V_{Batch} \tag{14}$$

Expressing equation (14) in terms of degree of conversion, we have:

$$N_A = N_{Ao}(1 - X_A) \tag{15}$$

$$\frac{N_{Ao}}{V_{Batch}}\frac{dX_A}{dt} = (-r_A) \tag{16}$$

Substituting the rate term in equation (8) into (16) gives:

$$\frac{N_{Ao}}{V_{Batch}}\frac{dX_A}{dt} = C_{Ao}^2(1 - X_A)(\alpha - X_A)k_o \exp\left(-\frac{Ea}{RT}\right) \tag{17}$$

But $C_{Ao} = \dfrac{N_{Ao}}{V_{Batch}}$ (18)

$$C_{Ao}\frac{dX_A}{dt} = C_{Ao}^2(1 - X_A)(\alpha - X_A)k_o \exp\left(-\frac{Ea}{RT}\right)$$

$$\frac{dX_A}{dt} = C_{Ao}(1 - X_A)(\alpha - X_A)k_o \exp\left(-\frac{Ea}{RT}\right) \tag{19}$$

Heat Generation per unit Volume of Reactor

Heat generation per unit volume of reactor is expressed as

$$q_{Batch} = \frac{Q}{V_{Batch}} \tag{20}$$

Where: $Q = (-\Delta H_r)F_{Ao}X_A$ (21)

But for batch reactor, there is no flow of materials thus,

$$Q = (-\Delta H_r)\frac{N_{Ao}}{t}X_A \tag{22}$$

Substituting equation (22) into (20) gives

$$q_{Batch} = \frac{(-\Delta H_r)N_{Ao}X_A}{tV_{Batch}} \tag{23}$$

Energy Balance on Batch Reactor

$$\left\{\begin{array}{c}\text{Rate of}\\ \text{energy}\\ \text{input into}\\ \text{reactor}\end{array}\right\} = \left\{\begin{array}{c}\text{Rate of}\\ \text{energy}\\ \text{output}\end{array}\right\} + \left\{\begin{array}{c}\text{Heat}\\ \text{production}\\ \text{rate due to}\\ \text{reaction}\end{array}\right\} + \left\{\begin{array}{c}\text{Heat}\\ \text{removal}\\ \text{rate by}\\ \text{coolant}\end{array}\right\} + \left\{\begin{array}{l}\text{Accumulation}\\ \text{of energy}\\ \text{within reactor}\end{array}\right\} \quad (24)$$

The energy balance on batch reactor can be expressed as follows using equation (24).

$$\textit{Energy input} = F_{Ao}C_{Po}T_{Ao} \quad (25)$$

$$\textit{Energy output rate} = F_A C_P T_A \quad (26)$$

$$\textit{Heat production rate} = (-\Delta H_r)(-r_A)V_{Batch} \quad (27)$$

$$\textit{Rate of heat removal by coolant} = Q_{rev} \quad (28)$$

$$\textit{Accumulation of energy} = \frac{dH_A}{dt} \quad (29)$$

Inserting equations (25) through (29) into the energy equation (24) yields

$$F_{Ao}C_{Po}T_{Ao} = F_A C_P T_A + (-\Delta H_r)(-r_A)V_{Batch} - Q_{rev} + \frac{dH_A}{dt} \quad (30)$$

For batch reactor, there is no inflow and outflow of energy, therefore, equation (30) reduces to

$$(-\Delta H_r)(-r_A)V_{Batch} - Q_{rev} = \frac{dH_A}{dt} \quad (31)$$

But $H_A = N_A C_P T$ while $Q_{rev} = UA(T_A - T_o) = \frac{\pi D^2 U}{4}(T_A - T_o)$

Where $A = \frac{\pi D^2}{4}$ = Cross sectional area of the batch reactor

Upon substitution, equation (31) into becomes:

$$\frac{dT_A}{dt} = \frac{(-\Delta H_r)(-r_A)V_{Batch}}{N_{Ao}C_P} + \frac{\pi D^2 U}{4N_{Ao}C_P}(T_A - T_o) \quad (32)$$

Again, $\frac{N_{Ao}}{V_{Batch}} = C_{Ao}$ thus, $\frac{V_{Batch}}{N_{Ao}} = \frac{1}{C_{Ao}}$

Therefore, $$\frac{dT_A}{dt} = \frac{(-\Delta H_r)(-r_A)}{C_{Ao}C_P} + \frac{\pi D^2 U}{4N_{Ao}C_P}(T_A - T_o) \quad (33)$$

Inserting the value of the rate of reaction $(-r_A)$ in equation (8) into equation (33) we have:

$$\frac{dT_A}{dt} = \frac{(-\Delta H_r)k_o \exp\left(-\frac{Ea}{RT}\right)C_{Ao}^2(1-X_A)(\alpha - X_A)}{C_{Ao}C_P} + \frac{\pi D^2 U}{4N_{Ao}C_P}(T_A - T_o)$$

$$\frac{dT_A}{dt} = \frac{(-\Delta H_r)k_o \exp\left(-\frac{Ea}{RT}\right)C_{Ao}(1-X_A)(\alpha - X_A)}{C_P} + \frac{\pi D^2 U}{4N_{Ao}C_P}(T_A - T_o) \quad (34)$$

Equations (19) and (34) are system of ordinary differential equations which must be solved simultaneously since conversion and temperature of the batch reactor are depending on time of the reaction.

Simulation Parameters

The inputs parameters used to perform the calculation and evaluation of the reactor functional parameters and dimensions are presented in Table 1.

Table 1 Summary of Input Parameters

Parameter	Value	Reference
Initial concentration, C_{Ao} (mol/m^3)	23.9	Kralj (2012)
Volumetric flow rate (m^3/hr)	2.125	Assumed
Heat of reaction, ΔH_r (kJ/mol)	303.92	Kralj (2012)
Coefficient of Heat transfer, U (kJ/m^2.K)	140	Assumed
Mean specific heat capacity, C_p(kJ/mol.K)	150	Assumed
Density, (kg/m^3)	1530	Linstrom and Mallard (2014)
Mean viscosity, μ (Ns/m^2)	1.8722 x 10^{-5}	Linstrom and Mallard (2014)
Molar flow rate, F_{Ao} (kmol/hr)	40.0	Assumed
Activation energy, Ea (kJ/kmol)	35082.59	Kralj (2012)
Pre-exponential factor, k_o (m^3/kmol.hr)	788588.57	Kralj (2012)

RESULTS AND DISCUSSION

The performance of batch reactor at various molar feed ratios, for the production of sodium benzoate was presented in this research work. The heat generated per reactor volume for the batch reactors was analysed.

Batch Reactor Analysis

The mass and energy balance equations were coupled into a system of ordinary differential equations and solved simultaneously with respect to batch time. The simulated results obtained from the analysis were presented in Figures 2 to 7. Time is a major measuring index in the operation of batch reactor, therefore, the degree of conversion of sodium hydroxide to sodium benzoate as well as the temperature required to achieve the desired product were investigated at time ranges of zero to 2 hours at varying molar feed ratio of benzoic acid to sodium hydroxide. Also, the rate of heat generation per the batch reactor volume was investigated at different molar feed ratios of benzoic acid to sodium hydroxide charged into the reactor, with respect to time, degree of sodium hydroxide conversion and operating temperature. It is worthy of note however, that the batch reactor size was kept constant throughout the simulation since in batch reactor, the reactants are fed into the reactor at once and the product withdrawn only after the completion of reaction.

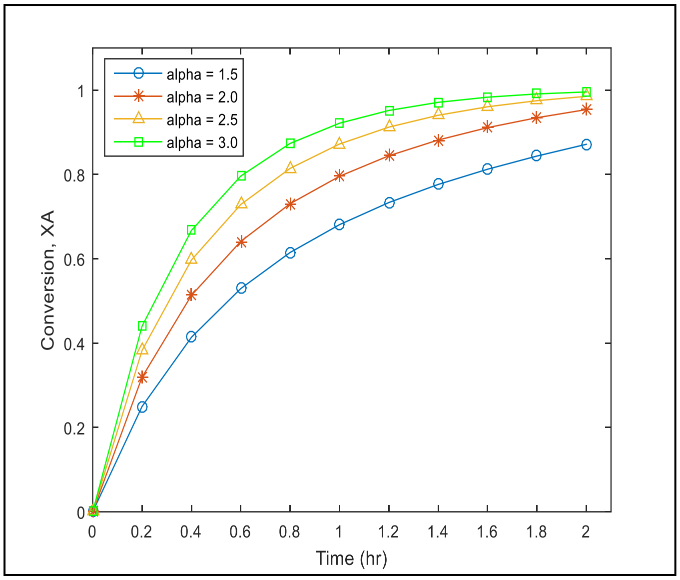

Figure 2 Influence of Molar Feed Ratio on Degree of Conversion Against Time

The degree of sodium hydroxide conversion against time in batch reactor at different molar feed ratios and constant reactor volume is shown in Figure 2. Although, increase in the time of reaction increases the degree of sodium hydroxide conversion at all molar feed ratios as shown in the figure, but the degree of sodium hydroxide conversion in the batch reactor at a given reaction time increase further with increase in molar feed ratio. Thus, the high molar feed ratio implies that the amount of benzoic acid in the reaction mixture must be relatively higher than that of sodium hydroxide to obtain a higher conversion at any time in the batch reactor for the production of sodium benzoate from sodium hydroxide and benzoic acid. However, degrees of sodium hydroxide obtained at 2 hours batch time were 87.15, 95.38, 98.53 and 99.57% at molar feed ratios (α) of 1.5, 2.0, 2.5 and 3.0 respectively. This implies that to produce sodium benzoate in a batch reactor with conversion of sodium hydroxide greater than 95%, the amount of benzoic acid must be at least twice or thrice the amount of sodium hydroxide in the reaction mixture. Though, Kralj (2012) used a molar feed ratio of 1.5 while experimentally investigating the rate kinetics of sodium benzoate production from the reaction of sodium hydroxide and benzoic acid.

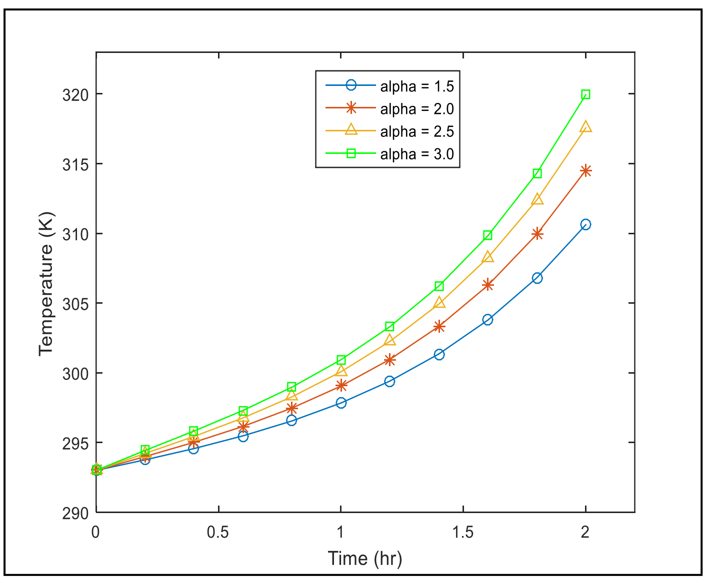

Figure 3 Influence of Molar Feed Ratio on Temperature of Reaction

Similarly, the reaction temperature against time in the batch reactor at different molar feed ratios and constant reactor volume is shown in Figure 3. Again, as shown in the figure, increasing the reaction time increases the temperature of the reaction at all molar feed ratios. However, when the molar feed ratio was increased, the reaction temperature also increases at any given time. This therefore, implies that higher amount of benzoic acid to sodium hydroxide in the reaction mixture favours the reaction temperature at any time, which in turn resulted in higher yield of sodium benzoate. The corresponding reaction temperature obtained at 2 hours batch time from the initial reaction temperature of 293K (20 ºC) were 302.52, 304.46, 305.98 and 307.19K at molar feed ratios (α) of 1.5, 2.0, 2.5 and 3.0 respectively.

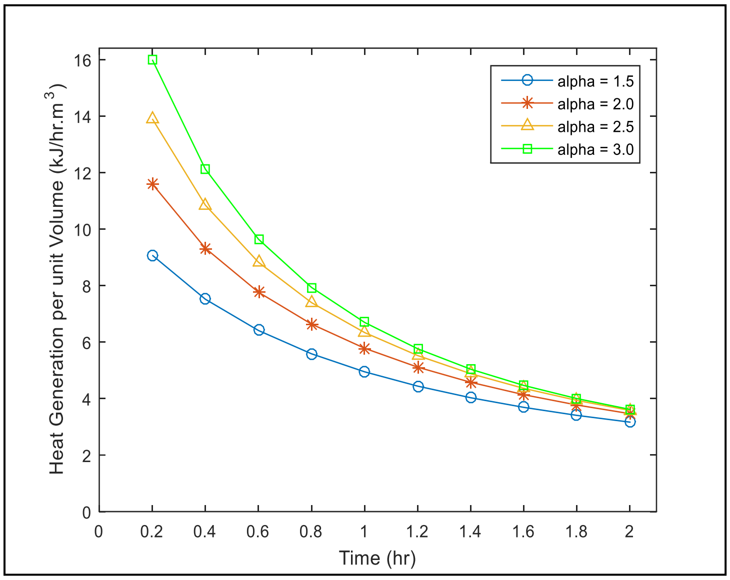

Figure 4 Influence of Molar Feed Ratio on Heat Generated per unit Volume

The heat generated per volume of batch reactor against batch time of 2 hours, evaluated at different molar feed ratios and constant volume was shown in Figure 4. The result showed that increasing the molar feed ratio also, increases the heat generation of the batch reactor. On the contrary, the heat generated per volume of batch reactor decreases as time of the reaction is increased. However, the heat generated per volume of the batch reactor after 2 hours were given as 3.17kJ/hr.m^3, 3.46kJ/hr.m^3, 3.58kJ/hr.m^3 and 3.62kJ/hr.m^3 at molar feed ratios (α) of 1.5, 2.0, 2.5 and 3.0 respectively. It follows therefore that, the heat generated per volume of the batch reactor in 2 hours increased by 12.43% between molar feed ratio of 1.5 and molar feed ratio of 3.0.

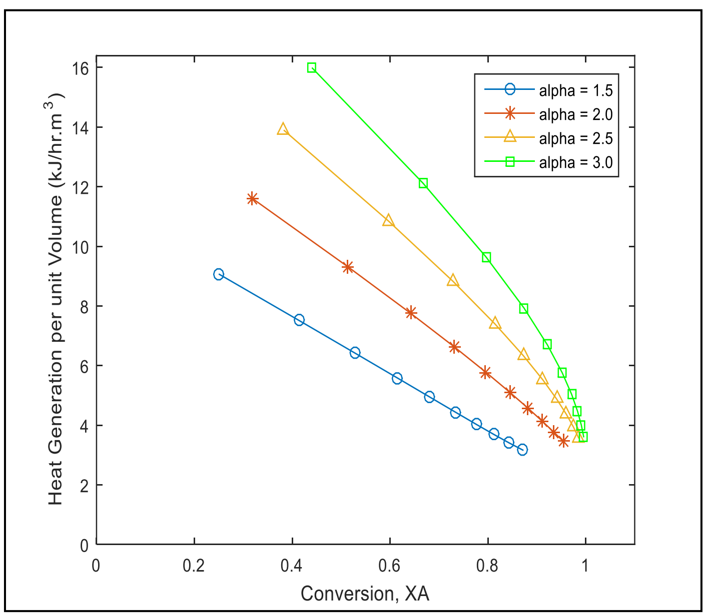

Figure 5 Heat Generated per Reactor Volume Against Conversion at Varying Feed Ratio

Figure 5 showed the heat generated per volume of the batch reactor against the degree of sodium hydroxide conversion, evaluated at different molar feed ratios and constant reactor volume. Although, the rate of heat generation per the batch reactor volume increases as the molar feed ratio is increased, heat generation per the reactor volume decreases as sodium hydroxide conversion increases. The corresponding values of the heat generated per volume of the batch reactor and sodium hydroxide conversion in 2 hours were given as 3.17kJ/hr.m^3 and 87.15%; 3.46kJ/hr.m^3 and 95.38%; 3.58kJ/hr.m^3 and 98.53%; and 3.62kJ/hr.m^3 and 99.57% at molar feed ratios (α) of 1.5, 2.0, 2.5 and 3.0 respectively. This implies that, to achieve higher conversion of sodium hydroxide, more heat will be generated per volume of the reactor.

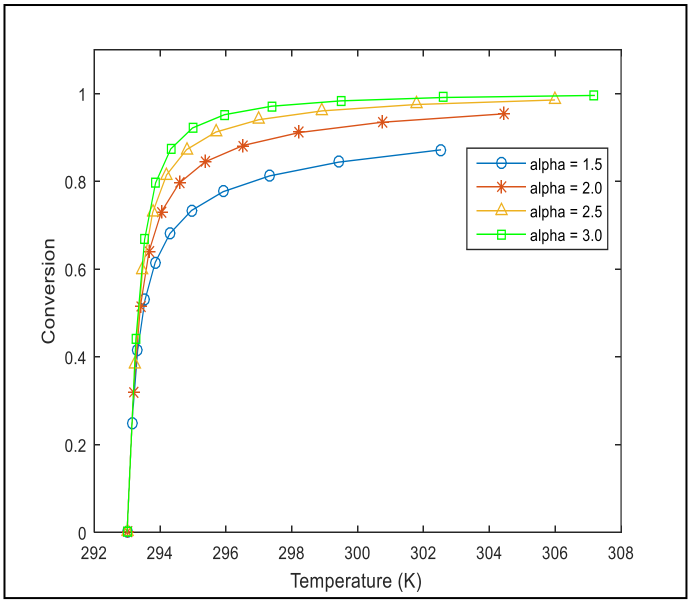

Figure 6 Conversion against Temperature at Varying Feed Ratios

Similarly, Figure 6 shows the profiles of sodium hydroxide degree of conversion against the reaction temperature in the batch reactor at different molar feed ratios and constant reactor volume. From Figure 6, the degree of conversion of sodium hydroxide increases as reaction temperature is increased at all molar feed ratios. Initially, there was tremendous increase in conversion with slow increase in temperature, but the reverse was the case after 1 hour of reaction as conversion slowly increases at faster increase in the reaction temperature. This again showed that, high conversion is favoured by temperature increase which will facilitate the completion of the reaction in the batch reactor to produce the sodium benzoate from the reaction mixture of sodium hydroxide and benzoic acid. However, the corresponding values of sodium hydroxide conversion and temperature in 2 hours were given as 87.15% and 302.52K; 95.38% and 304.46K; 98.53% and 305.98K; and 99.57% and 307.19K at molar feed ratios (α) of 1.5, 2.0, 2.5 and 3.0 respectively.

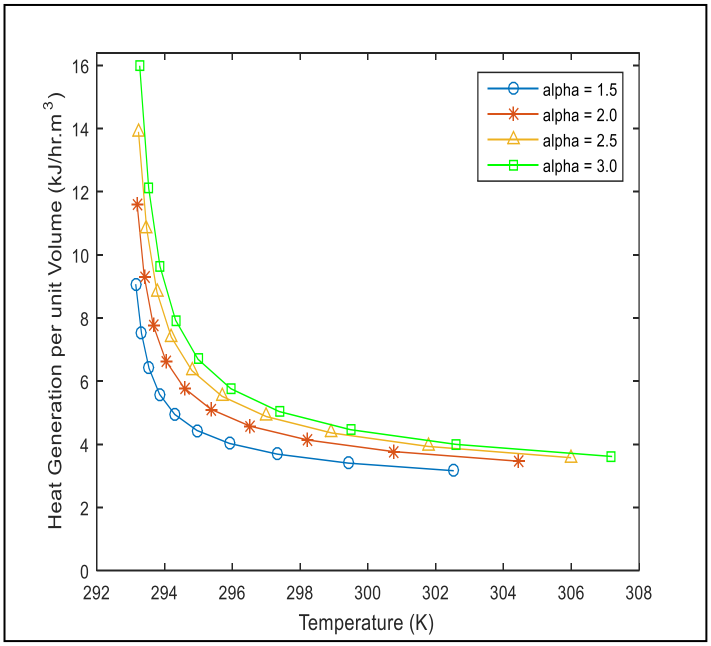

Figure 7 Heat Generated per Volume against Temperature at Varying Feed Ratio

Figure 7 showed the heat generated per volume of the batch reactor against the reaction temperature, evaluated at different molar feed ratios and constant reactor volume. Again, the rate of heat generation per the batch reactor volume increases as the molar feed ratio is increased, but the heat generation per the reactor volume decreases as reaction temperature increases. The corresponding values of the heat generated per volume of the batch reactor and reaction temperature in 2 hours were 3.17kJ/hr.m^3 and 302.52K; 3.46kJ/hr.m^3 and 304.46K; 3.58kJ/hr.m^3 and 305.98K; and 3.62kJ/hr.m^3 and 307.19K at molar feed ratios (α) of 1.5, 2.0, 2.5 and 3.0 respectively.

CONCLUSION

Performance equations for batch reactor have been modelled in this research work for the production of sodium benzoate from the reaction of sodium hydroxide and benzoic acid. The performance equations were solved and simulated using MATLAB R2015a, to facilitate the analysis of the reactors parameters. The analysis was performed at different molar feed ratios and at same operational parameters. From the result analysis of the batch reactor, it was observed that at 2 hours, conversion, temperature and heat generated per reactor volume increases as molar feed ratio was increased. The molar feed ratio influenced the reactor parameters performance, as well as increase in molar feed ratio causes improvement in the conversion of sodium hydroxide. Especially, at molar feed ratio of 3.0, the conversion in the batch reactor was a few fractions above 99%. Following the results obtained from the analysis demonstrates the production of sodium benzoate from sodium hydroxide and benzoic acid depending on the capacity of production and conditions of operation.

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