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Mathematical Modeling and Simulation of a Non-Ideal Continuous Stirred Tank Reactor in a Saponification Pilot Plant

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Abstract

This paper attempts to develop a mathematical model for a non-ideal continuous stirred tank reactor (CSTR) commonly used in process industry. The mathematical model was developed for a saponification reaction in a continuous stirred tank reactor. The model can be used to predict the extent of conversion of reactant at different operating conditions; concentration, temperature, flow rate and residence time. Comparative analysis of the extent of conversion results from the developed model and pilot plant showed a mean deviation less than 5.0%.

Keywords

CSTR, $C_{17}H_{35}COOH$, NaOH, model, simulation

1. Introduction

The continuous stirred tank reactor (CSTR) has continuous input and output of material. It is well mixed with no dead zone or bypass in ideal operations. The assumptions made during the simulation of the ideal CSTR equations are: (a) composition and temperature are uniform everywhere in the tank, (b) the effluent composition is the same as that in the tank and (c) the tank operates at steady state. Deviation from ideality (Fig. 1) assumed in developing the basic reactor design operations are present in practical reactors, and the extent of the non-ideality often varies considerably depending on the scale and type of reactor. Deviation from back-mixed reactor is due to: (a) short circuiting and bypassing of the reaction fluid i.e. certain portions of fluid may proceed directly from the feed inlet to the product discharge without proper mixing, (b) internal recycling of the fluid and, (c) the presence of stagnant fluid pockets (dead volume). A model continuous stirred tank is as presented in Fig. 2.

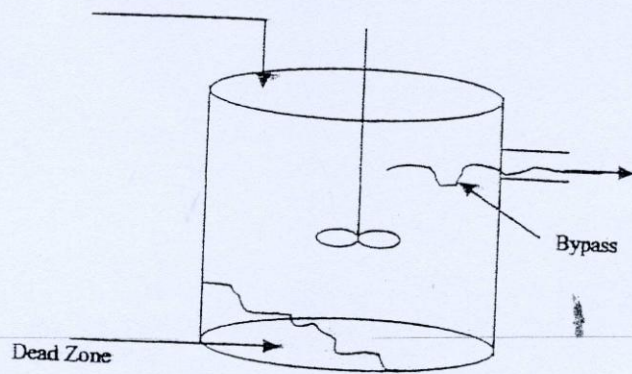


Fig. 1: A Continuous stirred tank reactor

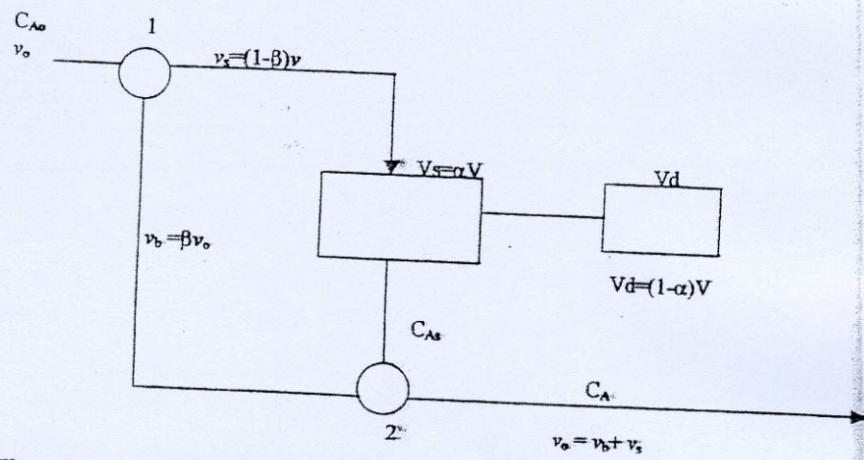


Fig. 2: The model for the continuous stirred tank reactor

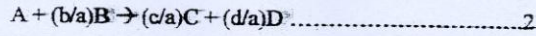
These various types of behaviors listed imply that different portions of the reacting fluid follow separate flow patterns through the reaction vessel, resulting in a wide distribution of residence time. Such deviations from ideality represent inefficiency in the reactor performance and cause reduction in production capacity. To alleviate these conditions, there are various methods often used to characterize the magnitude of deviation. One of such is the stimulus response technique that utilizes a tracer. Three typical techniques of introducing a tracer into the reaction vessel presently documented are the step input, the pulse input and the cyclic input. Information thus obtained can be used to determine the reactants conversion in a reactor, either directly or in combination with one of the several mathematical models. It will also show the extent of non-ideality of the reactor (Fogler, 1997; Levenspiel, 1972).

The equations that describe a chemical reactor must be solvable and without an inordinate expenditure of either human or computer time. It obviously does no good to have a situation described very accurately by a set of integral-differential equations with much boundary conditions if the solution to this system is virtually unobtainable. For this reason, it is the usual practice to assure mathematical tractability by modeling a non-ideal reactor as a combination of ideal reactor. The following process limitations were employed in this work; liquid-phase homogeneous reactions, isothermal operation, single-phase and irreversible steady state operation reactions.

2.0 Development Of The Model Equation

A type of reactor used very commonly in industrial processing is the continuous stirred tank reactor (CSTR). The CSTR is normally run at steady state and is usually ensures a well-mixed condition of the reactants. As a result of the latter quality, the CSTR is generally moderated as no spatial variations in concentration, temperature or reaction rate throughout the vessel. Since the temperature and concentration are identical everywhere within the reaction vessel, they are the same at the exit point as they are elsewhere in the tank (Smith et-al, 1996; Meyer, 1992; Paynes, 1982). Thus the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. In systems where mixing is highly non-ideal the well mixed model is inadequate and other modeling techniques must be sort for, that can adequately represent the residence time distribution. Consider a model chemical equation:





Reactant A is taken as the basis. For a flow system, the concentration C_A at a given point is given as (Luyben, 1990):

$$C_A = F_A / v \quad \dots\dots\dots 3$$

Where F_A is the molar flow rate of reactant A and v is the volumetric flow rate. Writing the concentration of A, B, C and D for the general reaction given by equation 2 in terms of the entering molar flow rates:

$$C_A = F_A / v = F_{A0} / v (1-X) \quad \dots\dots\dots 4$$

$$C_B = F_B / v = F_{B0} - (b/a) F_{A0} X \quad \dots\dots\dots 5$$

$$C_C = F_C / v = F_{C0} + (c/a) F_{A0} X \quad \dots\dots\dots 6$$

$$C_D = F_D / v = F_{D0} + (d/a) F_{A0} X \quad \dots\dots\dots 7$$

Where X is the conversion of reactant A; a, b, c and d are stoichiometric coefficients of A, B, C and D respectively; F_{A0} and F_A are entering and exit flow rate of A and the same applies to B, C and D. For liquids, volume (V) change with reaction is negligible when no phase change is taking place thus:

$$V = v_0 \quad \dots\dots\dots 8$$

$$C_A = F_{A0} / v_0 (1-X) = C_{A0} \quad \dots\dots\dots 9$$

$$C_B = C_{A0} [\theta_B - (b/a)X] \quad \dots\dots\dots 10$$

Where $\theta_B = F_{B0} / F_{A0}$. The molar flow rate at which A leaves the system is given by (Luyben, 1990; Perry and Green, 1997; Richardson and Peacock, 1994)

$$F_A = F_{A0} (1-X) \quad \dots\dots\dots 11a$$

$$F_{A0} - F_A = F_{A0} X \quad \dots\dots\dots 11b$$

The design equation for a CSTR (Luyben, 1990), is given by:

$$V = (F_{A0} - F_A) / -r_A \quad \dots\dots\dots 12a$$

$$F_{A0} - F_A = -V r_A \quad \dots\dots\dots 12b$$

Where $-r_A$ is the disappearance of A. Equating equations 11b and 12b:

$$F_{A0} X = -V r_A \quad \dots\dots\dots 13$$

The conversion for a second order reaction of this form is:

$$r_A = -K C_A C_B \quad \dots\dots\dots 14$$

Substituting equation 14 into 13:

$$F_{A0} X - K C_A C_B V = 0 \quad \dots\dots\dots 15$$

From equation 8 and 9:

$$F_{A0} = C_{A0}v_0 / (1-X) \text{ and } C_A = C_{A0} \dots\dots\dots 16$$

Substituting equations 10, 16 into 15;

$$C_{A0}v_0 X / (1-X) - KC_{A0} \cdot C_{A0}[\theta_B - (b/a)X]V = 0 \dots\dots\dots 17a$$

$$C_{A0}v_0 X - KC_{A0}(1-X) \cdot C_{A0}[\theta_B - (b/a)X]V = 0 \dots\dots\dots 17b$$

Dividing equation 17b by $C_{A0}v_0$;

$$X - KC_{A0}(1-X)[\theta_B - (b/a)X]V / v_0 = 0 \dots\dots\dots 18$$

The residence time is given by;

$$\tau = V / v_0 \dots\dots\dots 19$$

$$X - K\tau C_{A0}(1-X)[\theta_B - (b/a)X] = 0 \dots\dots\dots 20$$

$$\text{Let } D = K\tau C_{A0} \dots\dots\dots 21$$

Equation 21 is dimensionless and substituting it into 20 gives;

$$X - D(1-X)[\theta_B - (b/a)X] = 0 \dots\dots\dots 22$$

$$(b/a)DX^2 - [(b/a)D + D\theta_B + 1]X + D\theta_B = 0 \dots\dots\dots 23$$

Equation 23 is a quadratic equation, which can be solved by the general formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \dots\dots\dots 24$$

$$X = \frac{[(b/a)D + \theta_B D + 1] \pm \sqrt{[(b/a)D + \theta_B D + 1]^2 - 4(b/a)\theta_B D^2}}{2(b/a)D} \dots\dots\dots 25$$

A test was conducted to find out which of the roots of the above equation will be proper for the conversion (Kreyszig, 1996; Stroud, 1995). The negative root was found suitable for our conversion and the appropriate model is;

$$X = \frac{[(b/a)D + \theta_B D + 1] - \sqrt{[(b/a)D + \theta_B D + 1]^2 - 4(b/a)\theta_B D^2}}{2(b/a)D} \dots\dots\dots 26$$

A non-ideal CSTR is modeled by using a combination of an ideal CSTR of volume V_r , a dead zone of volume V_d and a bypass with a volumetric flow rate v_b . A tracer data obtained from experiment (Fig. 3) was used to evaluate the necessary model parameters. From the model system (Fig. 2), the concentration of A leaving the reaction zone can be calculated. Taking material balance at point 2 (Fig. 2);

$$C_A(v_b + v_r) = C_{A0}v_b + C_{A0}v_r \dots\dots\dots 27$$

$$C_A = (C_{A0}v_b + C_{A0}v_r) / (v_b + v_r) = (C_{A0}v_b + C_{A0}v_r) / v_0 \dots\dots\dots 28$$

$$\text{Since } v_0 = v_b + v_r; \text{ then } v_r = v_0 - v_b \text{ and } \beta = v_b/v_0 \dots\dots\dots 29$$

Substituting equation 29 into 28;

$$C_A = \beta C_{A0} + (1-\beta)C_{AS} \dots\dots\dots 30$$

Conversion, X, is given by (Himmelblau, 1996);

$$X = (C_{A0} - C_A) / C_{A0} = 1 - C_A / C_{A0} \dots\dots\dots 31a$$

$$C_A / C_{A0} = 1 - X \dots\dots\dots 31b$$

Substituting equation 26 into 31b;

$$\frac{C_s}{C_{s0}} = 1 - \frac{[(b/a)D + \theta_s D + 1] - \sqrt{[(b/a)D + \theta_s D + 1]^2 - 4(b/a)\theta_s D^2}}{2(b/a)D} \dots\dots\dots 32$$

Introducing the concept of Gibb's free energy change $\Delta G = -RT \log K$, so that $K = 10^{(-\Delta G/RT)}$ and substituting this into equation 21, then $D^* = 10^{(-\Delta G/RT)} \tau C_{A0}$. Equation 32 becomes;

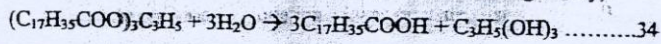
$$\frac{C_s}{C_{s0}} = 1 - \frac{[(b/a)D^* + \theta_s D^* + 1] - \sqrt{[(b/a)D^* + \theta_s D^* + 1]^2 - 4(b/a)\theta_s D^{*2}}}{2(b/a)D^*} \dots\dots\dots 33$$

Equation 33 is the expected model equation

3.0 Results and Discussion

3.1 Experimental Results

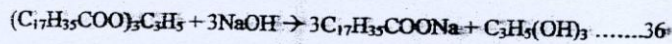
In the continuous flow process of the saponification process, two major reactions occur at different reaction vessel. The first occurs in the hydrolyser and is given by;



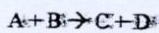
and the second takes place at the neutralizer and given by;



The net saponification reaction equation can be represented as (Austin, 1984; Aweh 2002; Nwokoro 2002):



The neutralization reaction (35) is known to proceed with second order reaction. Equation 35 can be model as:



Where A is stearic acid ($C_{17}H_{35}COOH$); B is sodium hydroxide ($NaOH$); C is the sodium stearate ($C_{17}H_{35}COONa$); and D is water (H_2O). The CSTR has a volume of 100 litres ($0.1m^3$), volumetric flow rate of 98 L/hr ($0.098 m^3/hr$) and the data collected were at various temperatures as presented in Table 1.

Table 1: Influence of temperature on saponification reaction

Temperature (K)	Inlet concentration of A (kmol/m ³)	Outlet concentration of A (kmol/m ³)	Conversion of A %
348	0.0100	0.0058	42.00
348	2.5075	2.1750	13.26
363	0.0100	0.0046	54.00
363	2.5075	2.1400	14.66
383	0.0100	0.0039	61.00
383	2.5075	2.1600	13.86

The kinetic data were used to determine the specific rate constant for the neutralization reaction with known second order reaction (Fig. 3). The results obtained for the rate constants are; 1.956 m³/kmol.hr (at 348 K), 3.012 m³/kmol.hr (at 363 K) and 4.074 m³/kmol.hr (at 383 K).

3.2 Simulated Results

The simulated results are presented in Tables 2-7. Tables 2-5 present the simulated results with variation in initial concentration of stearic acid at the three different temperatures while Tables 5-7 present results with variation in initial concentration of sodium hydroxide for the same conditions. Equation 33 was simulated using Visual Basic program.

Table 2: Simulated concentration and conversion at 348 K (variation in C₁₇H₃₅COOH)

Initial concentration of A (kmol/m ³)	Outlet concentration of A (kmol/m ³)	Outlet concentration of B (kmol/m ³)	Conversion of A %
0.01	0.0054	0.4954	46.05
1.009	0.7304	0.2214	27.61
2.008	1.6388	0.1308	18.39
3.007	2.5983	0.0913	13.59
4.006	3.5758	0.0698	10.74
5.005	4.5614	0.0564	8.86
6.004	5.5513	0.0473	7.54
7.003	6.5437	0.0407	6.56
8.002	7.5377	0.0357	5.80
9.001	8.5328	0.0318	5.20
10.00	9.5287	0.0287	4.71

Table 3: Simulated concentration and conversion at 363 K (variation in $C_{17}H_{35}COOH$)

Initial concentration of A ($kmol/m^3$)	Outlet concentration of A ($kmol/m^3$)	Outlet concentration of B ($kmol/m^3$)	Conversion of A %
0.01	0.0043	0.4943	56.74
1.009	0.6862	0.1772	31.99
2.008	1.6032	0.0952	20.16
3.007	2.5709	0.0639	14.50
4.006	3.5639	0.0479	11.28
5.005	4.5433	0.0383	9.22
6.004	5.5359	0.0319	7.80
7.003	6.5303	0.0273	6.75
8.002	7.5258	0.0238	5.95
9.001	8.5222	0.0212	5.32
10.00	9.5190	0.0190	4.81

Table 4: Simulated concentration and conversion at 383 K (variation in $C_{17}H_{35}COOH$)

Initial concentration of A ($kmol/m^3$)	Outlet concentration of A ($kmol/m^3$)	Outlet concentration of B ($kmol/m^3$)	Conversion of A %
0.01	0.0036	0.4936	63.92
1.009	0.6578	0.1488	34.81
2.008	1.5828	0.0748	21.17
3.007	2.5561	0.0491	14.99
4.006	3.5425	0.0365	11.57
5.005	4.5339	0.0289	9.41
6.004	5.5280	0.0240	7.93
7.003	6.5235	0.0205	6.85
8.002	7.5199	0.0179	6.03
9.001	8.5168	0.0158	5.38
10.00	9.5142	0.0142	4.86

Table 5: Simulated concentration and conversion at 348 K (variation in NaOH)

Initial concentration of B ($kmol/m^3$)	Outlet concentration of A ($kmol/m^3$)	Outlet concentration of B ($kmol/m^3$)	Conversion of A %
0.01	4.9910	0.0010	0.18
1.009	4.1157	0.1247	17.69
2.008	3.2929	0.3009	34.14
3.007	2.5504	0.5574	48.99
4.006	1.9228	0.9288	61.54
5.005	1.4357	1.4407	71.29
6.004	1.0865	2.0905	78.27
7.003	0.8461	2.8491	83.08
8.002	0.6807	3.6827	86.39
9.001	0.5639	4.5649	88.72
10.00	0.4789	5.4749	90.42

Table 6: Simulated concentration and conversion at 363 K (variation in NaOH)

Initial concentration of B (kmol/m ³)	Outlet concentration of A (kmol/m ³)	Outlet concentration of B (kmol/m ³)	Conversion of A %
0.01	4.9907	0.0007	0.19
1.009	4.0764	0.0854	18.47
2.008	3.2034	0.2114	35.93
3.007	2.4010	0.4080	51.98
4.006	1.7155	0.7215	65.69
5.005	1.1950	1.2000	76.10
6.004	0.8461	1.8501	83.08
7.003	0.6267	2.6297	87.47
8.002	0.4874	3.4894	90.25
9.001	0.3948	4.3958	92.10
10.00	0.3302	5.3302	93.40

Table 7: Simulated concentration and conversion at 383 K (variation in NaOH)

Initial concentration of B (kmol/m ³)	Outlet concentration of A (kmol/m ³)	Outlet concentration of B (kmol/m ³)	Conversion of A %
0.01	4.9905	0.0050	0.19
1.009	4.0563	0.0653	18.87
2.008	3.1559	0.1639	36.88
3.007	2.3176	0.3246	53.65
4.006	1.5936	0.5996	68.13
5.005	1.0501	1.0551	79.00
6.004	0.7049	1.7089	85.90
7.003	0.5033	2.5063	89.93
8.002	0.3826	3.3846	92.35
9.001	0.3057	4.3067	93.89
10.00	0.2534	5.2534	94.93

Table 8: Comparison in terms of conversion

S/N	Temp. K	Concentration of A kmol/m ³	Industrial Result X _A %	Simulated result X _A %	Deviation %
1	348	0.0100	42.00	46.05	4.05
2	348	2.5075	13.26	15.65	2.39
3	363	0.0100	54.00	56.74	2.74
4	363	2.5075	14.66	16.89	2.23
5	383	0.0100	61.00	63.92	2.92
6	383	2.5075	13.86	17.57	3.71

The developed model was simulated at the same operating conditions as presented in Tables 2-7. A table of comparison of conversion is shown in Table 8. Conversions evaluation results are also presented in Fig. 4-5. Fig. 4 shows a progressive decrease in conversion of A as the initial concentration of A increases. Fig. 5 on the other hand shows a progressive increase in A as the concentration of B increases. These figures show the same type of patterns for the

three different temperature used and it is noticeable that higher conversion was achieved at higher temperature.

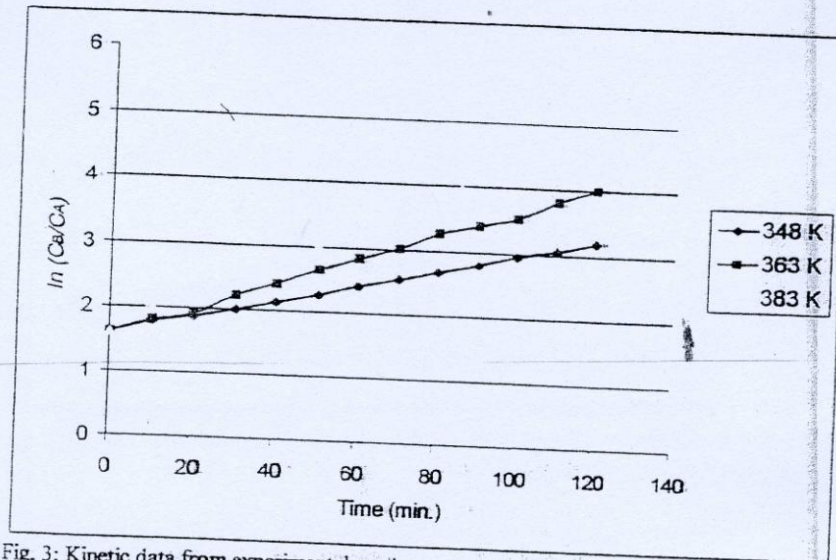


Fig. 3: Kinetic data from experimental results

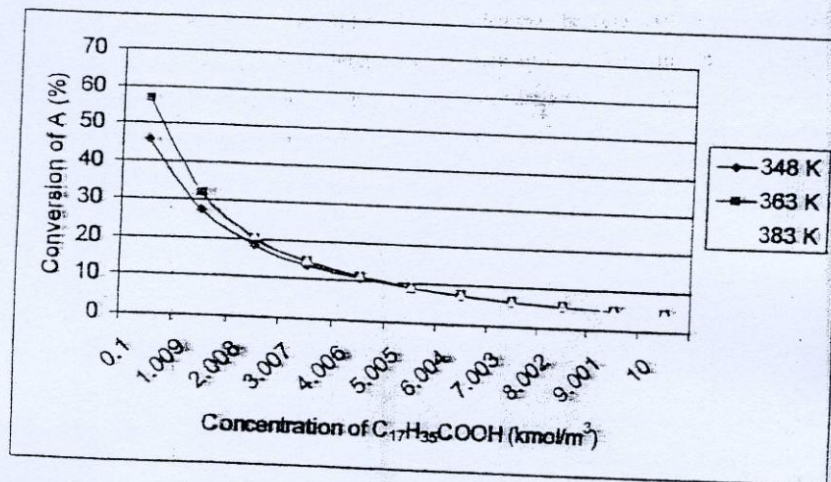


Fig. 4: Simulated result of the conversion of A (C₁₇H₃₅COOH) at three different operating temperature and variation in initial concentration of A (C₁₇H₃₅COOH).

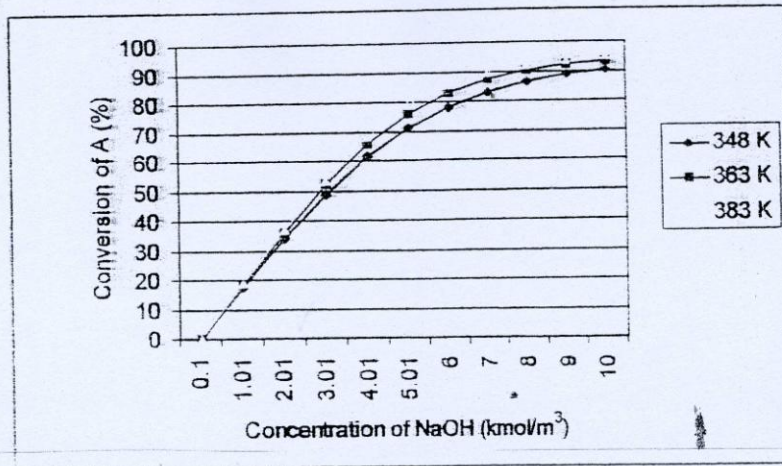


Fig. 5: Simulated result of the conversion of A ($C_{17}H_{35}COOH$) at three different operating temperature and variation in initial concentration of B (NaOH).

Tables 2-4 was simulated using variations in the initial concentration of A ($C_{17}H_{35}COOH$) with the initial concentration of B (NaOH) fixed at 0.5 kmol/m^3 . The concentration of A reduces at the outlet stream indicating the consumption of reactants A in the reaction. At 348K with an initial concentration of A as 0.01 kmol/m^3 gives an output concentration of 0.0054 kmol/m^3 representing a conversion of 46.05 % of A. Also at the same temperature an initial concentration of 10.0 kmol/m^3 gives a conversion of 4.71% of A. From Tables 2-4 it is noticeable that the conversion of A increases with increase in temperature (Nwokoro, 2002.; Fogler, 1997; Levenspiel, 1971).

Table 5-7 was simulated using variations in the initial concentration of B (NaOH) with the initial concentration of A fixed at 5.0 kmol/m^3 and a volumetric flow rate of $0.098 \text{ m}^3/\text{hr}$. It was observed that the concentration of A increases with increase in concentration of B. There exist the same pattern in the conversion of A from Tables 1-7, that is, at lower concentration there was higher conversion and at higher concentrations there was lower conversion (Aweh; 2002; Nwokoro, 2002). It is observable that at higher flow rate there was a drop in the conversion of A, showing that the reactant particles spend less time in the reactors. From Table 7, an initial concentration of B 0.01 kmol/m^3 gives an outlet concentration of A as

4.9905 kmol/m³ indicating a 0.19% conversion of A. In all these tables the conversion has been based on reactant A and not B, thus one can easily predict the conversion of B by the same process.

A comparison based on conversion deviation is presented in Table 8, these deviation are close and give a mean deviation of 3%. Variations in initial concentration of A for a fixed initial concentration of B at the three different operating conditions are presented. As the initial concentration of A increases, conversion decreases indicating drop in yield of product irrespective of the value of temperature and flow rate. However for a fixed initial value of A and B, at different temperature and flow rates, the conversion of A decreases indicating decreasing yield of products.

For a fixed value of initial concentration A (0.01 kmol/m³) and B (0.5 kmol/m³) and temperature of 363 K, conversion decreases as the volumetric flow rate increases indicating the reactant particles spend less time in the reaction vessel. At a constant flow rate and increasing temperature, conversion of A also increases.

4. Conclusion

A mathematical model was developed for a saponification reaction in a continuous stirred tank reactor. The model can be used to predict the extent of conversion of reactant at different operating conditions; concentration, temperature, flow rate and residence time. Comparative analysis of the extent of conversion results from the developed model and pilot plant showed a mean deviation less than 5.0%.

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