

# Mathematical Modeling and Simulation of a Non-Ideal Plug Flow Reactor in a Saponification Pilot Plant

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## Abstract

*This paper proposes a mathematical model for the operation of a non-ideal plug flow reactor in a saponification pilot plant of a typical process industry in Lagos, Nigeria. The residence time distribution (RTD) analysis technique involving tracer experiments was used. The model also gives a prediction of the number of ideal continuous stirred tank reactors (CSTR) that could represent the non-ideal plug flow reactor (PFR) in question. Simulated results reveals that 8.18 number of ideal stirred tanks in series would represent the non-ideal plug flow reactor under study.*

**Keywords:** model, simulation, PFR, RTD, CSTR, NaOH,  $C_{17}H_{35}COOH$

## 1. Introduction

The ideal plug flow reactor is one in which fluid flows in a tubular constriction (unidirectional) at constant velocity with no axial mixing. This ensures that each material or element have the same residence time in the reactor. Most of the chemical reactors in the industries have non-ideal regime. The non-ideal plug flow reactor (PFR) is one whose attributes deviate from that of the ideal plug flow reactors. Therefore, an in-depth knowledge of the residence time distribution (RTD) of materials in the reactors is necessary for its analysis. The residence time distribution indicates how much time each fraction of a charged material spends in the vessel. The residence time distribution of reactants or tracers in a flow vessel is a key datum for determining reactor performance (Perry and Green 1997).

This paper aims at developing a mathematic model and simulates the operation of a non-ideal plug flow reactor. The model should enhance easy prediction of the outlet concentration, extent of conversion of the reactants and the number of ideal stirred tanks in series that will be equivalent to non-ideal plug flow reactor. This work is however limited to a second order isothermal reaction.

## 1.1 Residence Time Distribution (RTD)

The time an atom spends in a reactor is called the residence time, while the distribution of residence times for a stream of fluid leaving a vessel or reactor is called the exit age distribution function  $E$ , which is synonymous to the residence time distribution or RTD (Coulson and Richardson 1994). The RTD is determined experimentally by injecting an inert chemical molecule or atom called tracer, into the reactor at some time  $t = 0$  and then measuring the tracer concentration  $C$ , in the effluent stream as a function of time. The tracer is normally colored with physical properties similar to those of the reacting mixture, so that its behavior will reflect that of the material flowing through the reactor. The tracer must not disturb the flow pattern of the system. The analysis of the output concentration with time, gives the desired information about the system and helps to determine the residence time distribution function  $E(t)$  (Meyer 1992; Smith, *et al.* 1996; Fogler 1997).

## 2. Mathematical Model Development

### 2.1 One parameter model

In this model the RTD data otherwise known as tracer data, was obtained from a pulse

tracer experiment carried out on a non-ideal plug flow reactor. The result was used to determine the number of equal sized ideal continuous stirred tank reactor (CSTR) arranged in series. The number of ideal stirred tanks that will fit the RTD data of the non-ideal plug flow reactor simply means the number of ideal CSTR in series that will be equivalent to the non-ideal PFR. This one parameter model, for specificity can be regarded as “tank in series model”. And, the only adjustable parameter to be extracted from the residence time distribution (RTD), data is the number of tank n.

In developing this model, let consider three equal sized ideal CSTRs in series (Fig. 1). If a pulse tracer experiment is carried out on these three tanks in series, then from RTD function (Levenspiel 1972), the fraction of tracer material leaving the last tank between time t and t+Δt will be

$$E(t) = \frac{C_3(t)}{\int_0^\infty C_3(t)dt} \dots\dots\dots 1$$

where C<sub>3</sub> is the concentration of tracer material exiting the system (3<sup>rd</sup> tank); E(t) is the RTD function. The outlet concentration of tracer material, C<sub>3</sub>(t) as a function of time, can be obtained by carrying out material balance around each of the tanks. From the principle of conservation of mass;

$$\text{Input} = \text{Output} + \text{Disappearance} + \text{Accumulation} \dots\dots\dots 2$$

For a steady state system, there is no accumulation, therefore;

$$\text{Input} = \text{Output} + \text{Disappearance} \dots\dots\dots 3$$

Equation 3 can be expressed in rate form. Taking a material balance around a continuous stirred tank;

$$v_{in} C_{in} = v_{out} C_{out} + V \frac{dC_{out}}{dt} \dots\dots\dots 4$$

where V is the volume of the tank; v is the volumetric flow rate and C is the tracer concentration. From the three identical tanks in series, the volumetric flow rate v<sub>1</sub> is constant i.e. v<sub>in</sub>=v<sub>out</sub> for each of the tanks. The volume V of each of the tanks is also identical i.e. V<sub>1</sub>=V<sub>2</sub>=V<sub>i</sub>. Therefore, the space time τ<sub>1</sub> of the individual reactors is also identical, since the

space time for ideal CSTR is the ratio of volume to volumetric flow rate, i.e. τ<sub>1</sub>=τ<sub>2</sub>=τ<sub>i</sub>. Where the subscript 1,2 and i represents the first, second and i<sup>th</sup> tank respectively. Taking the material balance round tank 1 (Fig. 2) gives;

$$vC_o = vC_1 + V \frac{dC_1}{dt} \dots\dots\dots 5$$

where C<sub>o</sub> is the inlet concentration to tank 1; C<sub>1</sub> is the out let concentration from tank 1. For a pulse tracer experiment, C<sub>o</sub> as a function of time is zero. Therefore, equation 5 becomes;

$$V_1 \frac{dC_1}{dt} = -vC_1 \dots\dots\dots 6$$

$$C_1 = C_o e^{-vt/v_1} \dots\dots\dots 7$$

For ideal CSTR, the space time is given as;

$$\tau = V/v \text{ or } \tau_1 = V_1/v \dots\dots\dots 8$$

$$C_1 = C_o e^{-t/\tau_1} \dots\dots\dots 9$$

The material balance on tracer around tank 2 will be;

$$vC_1 = vC_2 + V_i \frac{dC_2}{dt} \dots\dots\dots 10$$

Dividing through by V<sub>i</sub> and then substituting equation 7 and 8 into equation 10 gives a first order ordinary differential equation;

$$\frac{dC_2}{dt} + \frac{C_2}{\tau_i} = \frac{C_o}{\tau_i} e^{-t/\tau_i} \dots\dots\dots 11$$

Using an integrating factor, e<sup>-t/τ<sub>i</sub></sup> along with the initial condition C<sub>2</sub>=0 ant t=0 gives;

$$C_2 = \frac{C_o t}{\tau_i} e^{-t/\tau_i} \dots\dots\dots 12$$

By taking material balance on tracer around tank 3, we have

$$vC_2 = vC_3 + V_i \frac{dC_3}{dt} \dots\dots\dots 13$$

or

$$\frac{dC_3}{dt} + \frac{C_3}{\tau_i} = \frac{C_o}{\tau_i^2} e^{-t/\tau_i} \dots\dots\dots 14$$

or

$$C_3 = \frac{C_o t^2}{2\tau_i^2} e^{-t/\tau_i} \dots\dots\dots 15$$

Substituting equation 15 into 1 we obtain;

$$E(t) = \frac{\frac{C_o t^2}{2\tau_i^2} e^{-t/\tau}}{\int_0^\infty \frac{C_o t^2}{2\tau_i^2} e^{-t/\tau} dt} \dots\dots\dots 16a$$

$$E(t) = \frac{t^2 e^{-t/\tau}}{\int_0^\infty t^2 e^{-t/\tau} dt} \dots\dots\dots 16b$$

By applying integration by part (Stroud 1995), equation 16b becomes;

$$E(t) = \frac{t^2}{2\tau_i^3} e^{-t/\tau} \dots\dots\dots 17$$

This is the RTD function for three tanks in series. Generalizing this method for a series of n CSTR gives the RTD function as;

$$E(t) = \frac{t^{n-1}}{(n-1)! \tau_i^n} e^{-t/\tau} \dots\dots\dots 18$$

The RTD function can be normalized by expressing in dimensionless time scale as (Levenspiel 1972; Coulson and Richardson 1994);

$$\theta = t / \tau \dots\dots\dots 19$$

Equation 18 becomes;

$$E(\theta) = \frac{n(n\theta)^{n-1}}{(n-1)!} e^{-n\theta} \dots\dots\dots 20$$

The variance,  $\sigma^2$ , of the RTD data from tracer experiment is given by (Levenspiel 1972);

$$\sigma^2 = \int_0^\infty (t - tm)^2 E(t) dt \dots\dots\dots 21$$

Expressing this variance as dimensionless variance,  $\sigma^2\theta$ , gives;

$$\sigma^2\theta = \frac{\sigma^2}{\tau^2} = \int_0^\infty (\theta - 1)^2 E(\theta) d\theta \dots\dots 22$$

Expanding equation 22 gives;

$$\sigma^2\theta = \int_0^\infty \theta^2 E(\theta) d\theta - 2 \int_0^\infty \theta E(\theta) d\theta + \int_0^\infty E(\theta) d\theta \dots\dots\dots 23$$

$$\int_0^\infty E(\theta) d\theta = 1 \dots\dots\dots 24$$

Since the fraction of all the materials that has resided for a period of time, t, in the reactor between t = 0 and t =  $\infty$  is 1 (Kreyszig 1996; Stroud 1995). Therefore;

$$\sigma^2\theta = \int_0^\infty \theta^2 E(\theta) d\theta - 1 \dots\dots\dots 25$$

Substituting equation 20 into 25 gives;

$$\sigma^2\theta = \int_0^\infty \theta^2 \frac{n(n\theta)^{n-1}}{(n-1)!} e^{-n\theta} d\theta - 1 \dots\dots 26a$$

$$\sigma^2\theta = \frac{n^n}{(n-1)!} \int_0^\infty \theta^{n+1} e^{-n\theta} d\theta - 1 \dots\dots 26b$$

Integrating will give;

$$\sigma^2\theta = \frac{n^n}{(n-1)!} \left[ \frac{(n+1)!}{n^{n+2}} \right] - 1 \dots\dots 27a$$

$$\sigma^2\theta = \frac{1}{n} \dots\dots\dots 27b$$

Taking the dimensionless variance back to time gives;

$$\frac{\sigma^2}{\tau^2} = \frac{1}{n} \dots\dots\dots 28$$

$$n = \frac{\tau^2}{\sigma^2} \dots\dots\dots 29$$

The number of tanks in series is given by n, where  $\tau$  is the space-time in the combined tanks in series, but it is equivalent to the mean residence time,  $t_m$ , in the non-ideal plug flow reactor.

### 2.2 Chemical Reaction Model

This model is basically used for the chemical reaction taking place in the non-ideal plug flow reactor. With this model it is possible to predict the outlet concentration, and then the conversion of a particular reactant taking part in the chemical reaction in the PFR. Unlike the first model, this model is not too general, because it is dependent on the order of reaction. But, its flexibility is that, it can be developed for any order of reaction depending on which reaction is taking place in the non-ideal PFR.

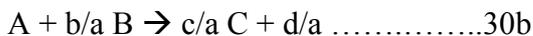
Having determined the number of tanks in a series performing a sequential mole balance around each of the tanks to obtain the outlet concentration. For a steady state ideal CSTR, there is no accumulation therefore, equation 3 will still hold for the material balance around the tanks (Luyben 1990; Aweh 2002). For a second order reaction, taking place in the n ideal tanks in series, of the form;



The rate expression is;

$$-r_A = K C_A C_B \dots\dots\dots 31a$$

where a, b, c, and d are the stoichiometric coefficients, and if reactant A is taken as reference, equation 30 can be written as;



Taking a mole balance on reactant A around tank 1 will be;

$$F_{A0} = F_{A1} + V_1(-r_A)_1 \dots\dots\dots 32$$

Where  $F_{A0}$  is the molar flow rate of reactant A into the reactor, tank 1(moles/time);  $F_{A1}$  is the molar flow rate of reactant A out of tank 1(moles/time);  $V_1$  is the volume of tank;  $(-r_A)_1$  is the rate of disappearance of reactant A in tank 1 [moles/(volume x time)];  $K$  is the specific rate constant;  $C_A$ ,  $C_B$  are the concentrations of reactants A and B respectively (moles/volume); and  $-r_A$  is the rate of disappearance of reactant A [moles/(volume x time)].

$$(-r_A)_1 = K C_{A1} C_{B1} \dots\dots\dots 31b$$

The molar flow rate is;

$$F_{A0} = vC_{A0} \text{ and } F_{A1} = vC_{A1} \dots\dots\dots 33$$

Substituting equation 31b and 33 into 32, we have;

$$vC_{A0} = vC_{A1} + V_1 K C_{A1} C_{B1} \dots\dots\dots 34$$

where  $v$  is the volumetric flow rate (volume/time) and  $C_{A1}$ ,  $C_{B1}$  are the concentrations of reactants A and B respectively in tank 1 (moles/volume). Substituting equation 8 ( $\tau_1 = V_1/v$ ) into 34 gives;

$$\tau_1 K C_{A1} C_{B1} = C_{A0} - C_{A1} \dots\dots\dots 35$$

From the principle of chemical engineering, conversion of reactant A,  $X_A$ , is given by (Himmelblau 1996);

$$X_A = (C_{A0} - C_A) / C_{A0} \dots\dots\dots 36$$

$$C_{A1} = C_{A0} - C_{A0} X_{A1} \dots\dots\dots 37$$

and  $C_{B1} = C_{B0} - b/a C_{A0} X_{A1} \dots\dots\dots 38$

Where  $C_{A0}$ ,  $C_{B0}$  are the inlet concentrations of A and B. equation 37 can be rearranged as;

$$C_{A0} X_{A1} = C_{A0} - C_{A1} \dots\dots\dots 39$$

Substituting equation 39 into 38 gives;

$$C_{B1} = C_{B0} - b/a C_{A0} + b/a C_{A1} \dots\dots 40a$$

$$C_{B1} = \Delta C_o + b/a C_{A1} \dots\dots\dots 40b$$

Where  $\Delta C_o = C_{B0} - b/a C_{A0} \dots\dots\dots 41$

Substituting equation 40b into 35 gives;

$$K \tau_1 C_{A1} (\Delta C_o + b/a C_{A1}) = C_{A0} - C_{A1} \dots\dots 42a$$

$$b/a K \tau_1 C_{A1}^2 + (K \tau_1 \Delta C_o + 1) C_{A1} - C_{A0} = 0 \dots\dots\dots 42b$$

Equation 42b is a quadratic equation of the form

$$ax^2 + bx + c = 0 \dots\dots\dots 43$$

This can be solved by the general formula;

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

.....44

Therefore,  $C_{A1}$ ,  $C_{A2}$  and  $C_{An}$  can be solved. It can be generalized that for n tanks in series, the outlet concentration of reactant A from the nth tank is;

$$C_{An} = \frac{-(K\tau_1 \Delta C_o + 1) \pm \sqrt{(K\tau_1 \Delta C_o + 1)^2 - 4(b/a)K\tau_1 C_{An-1}}}{2(b/a)K\tau_1} \dots\dots\dots 45$$

Using the overall conversion of reactant A in the n tanks in series (Himmelblau, 1996);

$$X_{An} = (C_{A0} - C_{An}) / C_{A0} \dots\dots\dots 46$$

Equation 29 and combination of equations 45 to 46 forms the mathematical model of the non-ideal plug flow reactor in which a second order reaction is taking place.

### 3. Results and Discussion

The mathematical model developed so far is for a second order liquid phase chemical reaction-taking place in a non-ideal plug flow reactor. To verify these model equations, the simulated result from the model was compared with practical / experimental data of a second order neutralization reaction taking place in a non-ideal plug flow reactor of a saponification pilot plant, in a typical process industry in Lagos. In the saponification plant, two distinct chemical reactions take place in two different reactors. The hydrolysis of fat (glyceryl stearate) to give fatty acid (stearic acid) and the



10.000	9.5000	0.0000	5.00
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Table 3. Simulated concentrations at 363 K (variation in stearic acid) in the PFR

Initial concentration of A (kmol/m <sup>3</sup> )	Outlet concentration of A (kmol/m <sup>3</sup> )	Outlet concentration of B (kmol/m <sup>3</sup> )	Conversion of A (%)
0.0100	0.0028	0.4928	71.57
0.5095	0.2287	0.2193	55.12
1.0090	0.5966	0.0876	40.87
1.5085	1.0433	0.0348	30.84
2.0080	1.5224	0.0144	24.18
2.5075	2.0139	0.0064	19.69
3.0070	2.510	0.0030	16.53
3.5065	3.0080	0.0015	14.22
4.0060	3.5068	0.0008	12.46
4.5055	4.0059	0.0004	11.09
5.0050	4.5052	0.0002	9.99
5.5045	5.0046	0.0001	9.08

Table 4. Simulated concentrations at 348 K (variation in NaOH) in the PFR

Initial concentration of B (kmol/m <sup>3</sup> )	Outlet concentration of A (kmol/m <sup>3</sup> )	Outlet concentration of B (kmol/m <sup>3</sup> )	Conversion of A (%)
0.0100	4.9900	0.0000	0.20
0.5095	4.4923	0.0018	10.15
1.0090	3.9962	0.0052	20.08
1.5085	3.5032	0.0117	29.94
2.0080	3.0158	0.0238	39.69
2.5075	2.5379	0.0454	49.24
3.0070	2.0762	0.0832	58.48
3.5065	1.6405	0.1470	67.19
4.0060	1.2443	0.2503	75.11
4.5055	0.9019	0.4074	81.96
5.0050	0.6247	0.6297	87.51
5.5045	0.4158	0.9203	91.68

Table 5. Simulated concentrations at 363 K (variation in NaOH) in the PFR

Initial concentration of B (kmol/m <sup>3</sup> )	Outlet concentration of A (kmol/m <sup>3</sup> )	Outlet concentration of B (kmol/m <sup>3</sup> )	Conversion of A (%)
0.0100	4.9900	0.0000	0.20
0.5095	4.4907	0.0002	10.19
1.0090	3.9918	0.0008	20.16
1.5085	3.4936	0.0021	30.13
2.0080	2.9970	0.0050	40.06
2.5075	2.5039	0.0114	49.92
3.0070	2.0183	0.0253	59.63
3.5065	1.5488	0.0553	69.02
4.0060	1.1116	0.1176	77.77
4.5055	0.7323	0.2378	85.35
5.0050	0.4385	0.4435	91.23

5.5045	0.2414	0.7459	95.17
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These simulated results show the effect of varying initial concentration of the reactants at the different operating temperatures, on the outlet concentration and the extent of conversion of reactants (Fig. 4-5).

Table 6. Comparison of Experimental with simulated results.

S/No	Temperature (K)	Inlet conc. of A (kmol / m <sup>3</sup> )	Outlet conc. of A (kmol / m <sup>3</sup> )		Conversion of A (%)	
			Practical	Simulated	Practical	Simulated
1	348	0.0100	0.0049	0.0043	51.00	56.82
2	348	2.5075	2.0551	2.0295	18.04	19.06
3	363	0.0100	0.0032	0.0028	63.00	71.57
4	363	2.5075	2.0511	2.0139	18.20	19.69
5	383	0.0100	0.0025	0.0019	75.00	80.93
6	383	2.5075	2.0454	2.0097	18.43	19.85

Comparative analysis of the results based on the absolute difference between the simulated and practical conversions of A, and their percentage error is presented in Table 7.

Table 7. Accuracy table

S /No	Conversion of A (%)		Absolute deviation, D	Error (%)
	Practical	Simulated		
1	51.00	56.82	5.82	11.41
2	18.04	19.06	1.02	5.65
3	68.00	71.57	3.57	5.25
4	18.20	19.69	1.49	8.19
5	75.00	80.93	5.93	7.91
6	18.43	19.85	1.42	7.71

The comparison of the simulated and practical results shows that the experimental outlet concentration and conversion of A were lower than those of the simulated (Table 6). This deviation was consistent. The percentage error from Table 8 ranges from 5.25-11.41%. The causes of the observed errors might be associated with the fact that the model did not take into account the nature of the reactants, their concentration activeness, viscosity and other parameters that have effects on the reaction.

From the tables of simulated result, it can be seen that for a fixed initial concentration of B, increasing initial concentration of A leads to decreasing conversion for the different temperatures of operation. At increased temperature however, the conversion increases. Conversely, for a fixed initial concentration of

A, increasing initial concentration of B leads to increased conversion for the different operating

temperature. Increased operating temperature also, leads to increasing conversion (Fogler 1997). Fig. 4 gives the simulated result of the conversion of C<sub>17</sub>H<sub>35</sub>COOH at the three operating temperature of 348, 363, and 383 K while varying the concentration of C<sub>17</sub>H<sub>35</sub>COOH. The result shows a decrease in conversion of A (C<sub>17</sub>H<sub>35</sub>COOH) meaning that the reactant (A) is being used up. Conversion was highest at 383 K and lowest at 348 K. Fig. 5 on the other hand shows the conversion of A with variation in concentration of NaOH. This result shows an increase in conversion with increase in concentration of NaOH (Awah 2002; Nwokoro 2002). The observed results might be connected with the fact that NaOH is

a strong base while  $C_{17}H_{35}COOH$  is a weak acid.

The model developed also gives a prediction of the number of serially arranged ideal stirred tank reactors,  $n$ , that will have an equivalent performance as a non-ideal plug flow reactor the size of which would be equal to that of the combined tanks. Simulation of equation 29 shows that the number of tanks in series would be 8.18. The significance of 8.18 tanks, means that this non-ideal plug flow reactor under study could be represented by nine ideal stirred tanks arranged in series with the same flow rate of  $0.098m^3 / hr$ . The first eight tanks are of the same size (identical) and the 9<sup>th</sup> tank is 0.18 of the 8<sup>th</sup> tank in size (Aweh 2002; Luyben 1990). The combined volume (size) of the nine tanks must however, be equal to that of the plug flow reactor. From this analysis it would be more economical to use a single PFR than using about nine tanks of the CSTR for the given reaction.

#### 4. Conclusion

The mathematical model for the operation of a non-ideal plug flow reactor has been developed. The model was used to generate simulated results for a non-ideal plug flow reactor of a saponification pilot plant. In the process of simulation, it was found out that 8.18 identically sized ideal stirred tanks operating in series would have an equivalent performance with the non-ideal plug flow reactor.

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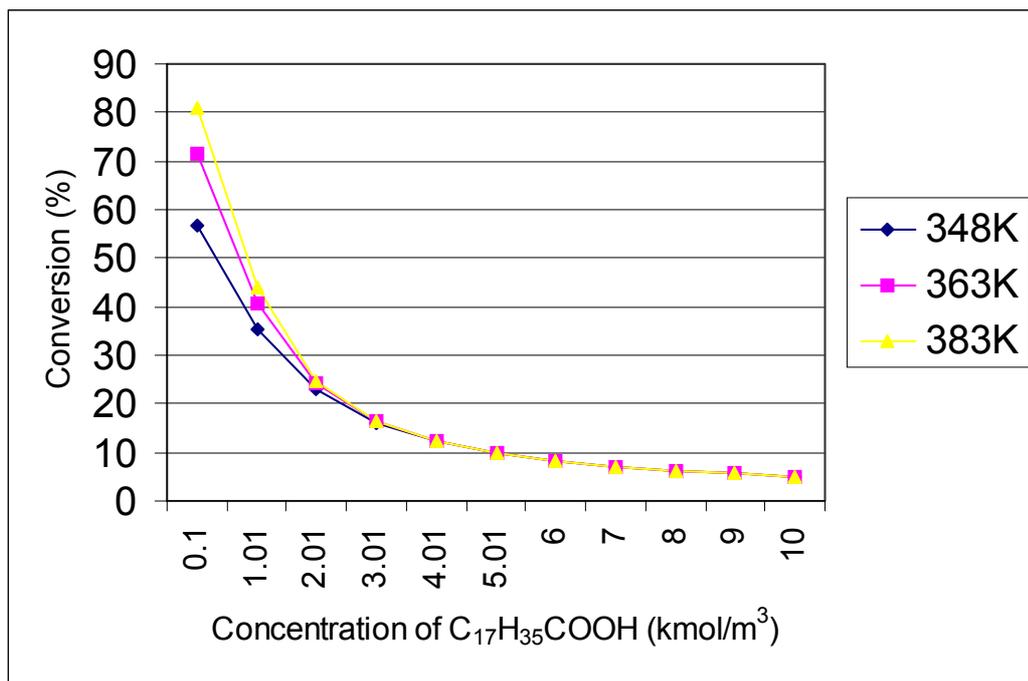


Fig. 4. Simulated Result of conversion of A (C<sub>17</sub>H<sub>35</sub>COOH) at three different operating temperature and variation in initial concentration of A (C<sub>17</sub>H<sub>35</sub>COOH).

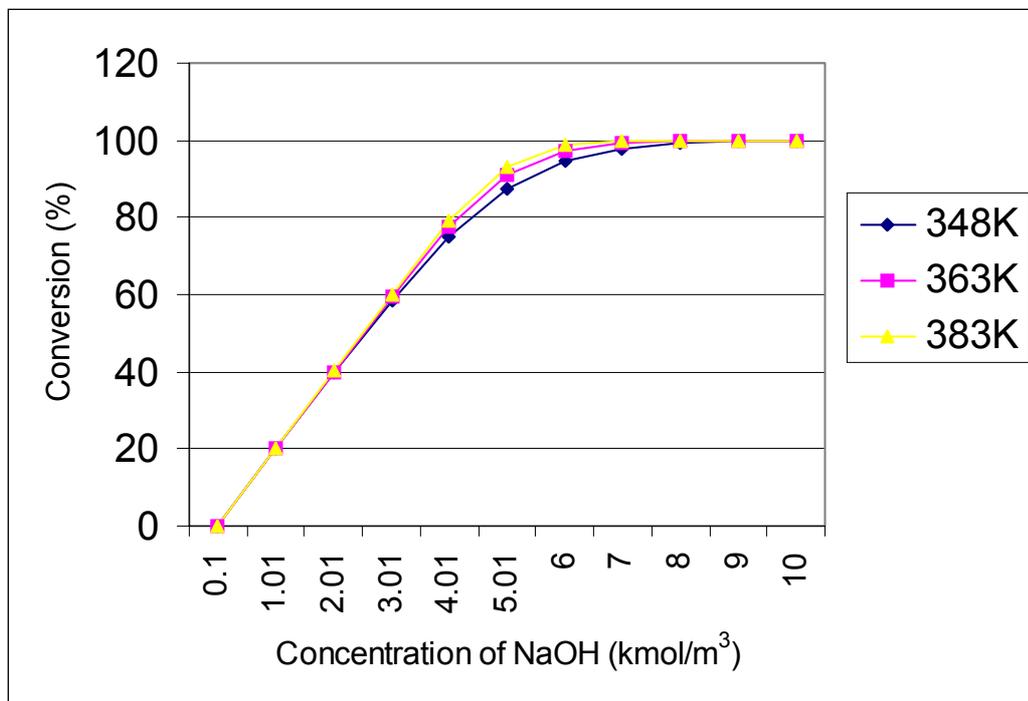


Fig. 5. Simulated Result of conversion of A (C<sub>17</sub>H<sub>35</sub>COOH) at three different operating temperature and variation in initial concentration of B (NaOH).

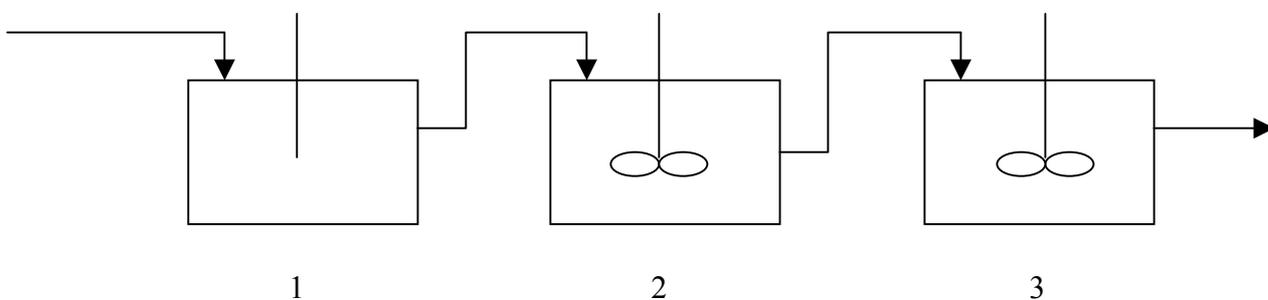


Fig. 1. Continuous Stirred Tank Reactor (CSTR) in series

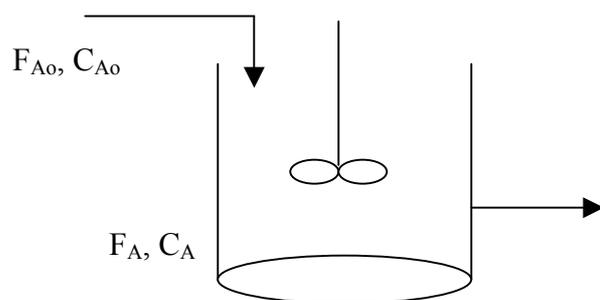


Fig. 2. Material balance around the CSTR

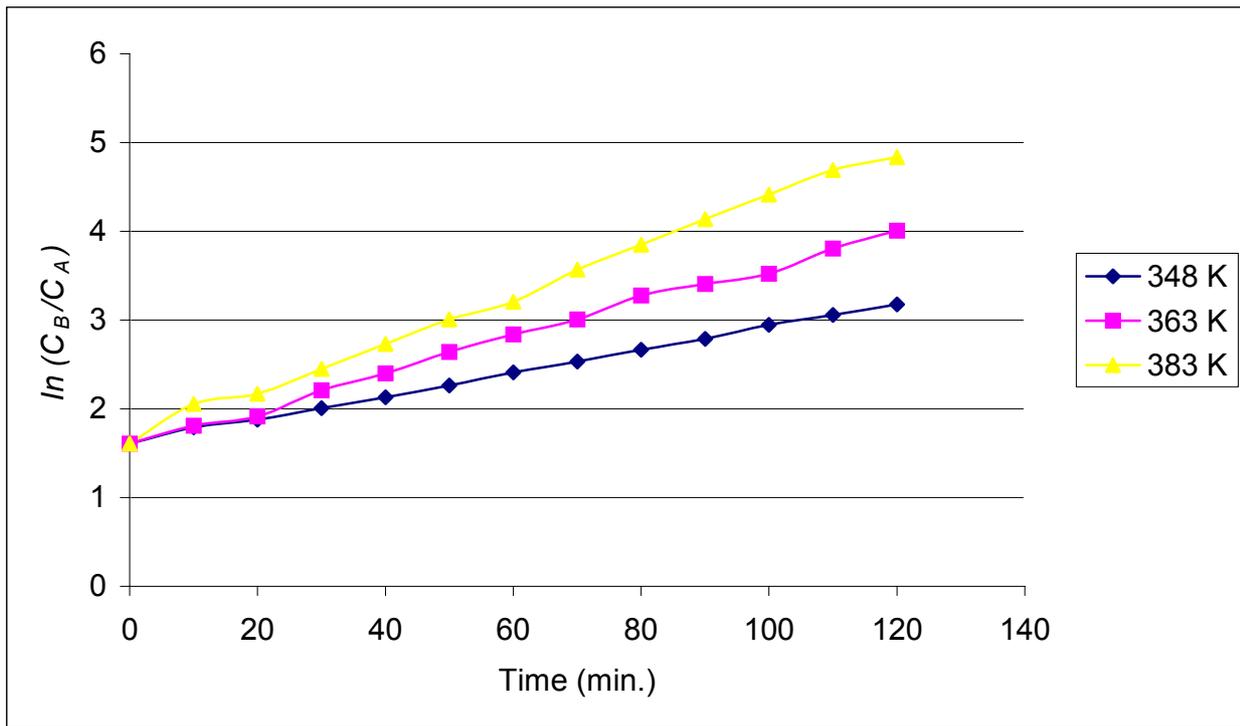


Fig. 3. Kinetic data showing time versus  $\ln(C_B/C_A)$  dependency obtained experimentally.