

Thermal Exchanger Integrated Millifluidic Reactor for Esterification Reactions

V.Kalyan¹, Sk.Shaheda²

Department of Chemical Engineering,
Anurag Group Of institutions, Hyderabad,
Telangana state

ABSTRACT—Current work emphasis on the development of Thermal Exchanger Integrated Millifluidic Reactor (TEIMR) to carry out esterification reactions involving methanol & 1-propanol with propionic acid. When performed under millimetre channel diameter of 1.1mm. Two factors greatly influenced the results. First, upon increasing the concentration of the acid [limiting reactant], there was a drop in reaction kinetics. Conversions for methanol reaction system were of range 97.02% to 99.02% and its activation energy at 303°k, 313°k, and 323°k for 3.23moles/L and 4.26mol/L of propionic acid are found to be 14965.2 KJ/Kmole and 16628 KJ/Kmole. Conversions for 1-propanol reaction system 94.51% to 99.1% and its activation energy at 303°k, 313°k, and 323°k for 4.53moles/L are found to be 41570KJ/Kmole. The results indicated 1-propanol is temperature sensitive than methanol reaction system. Second, Peristaltic pumps rely on silicon tubing to pump reactants into the millimeter reactor, due to the variations in elastic modulus of silicon tubing uncertainties in residence times resulted which influenced reaction rate.

Key words—Chemical process, MillifluidicReactor (TEIMR), Rate kinetics, methanol & 1-propanol esterification reactions

Corresponding Author: V. Kalyan

INTRODUCTION

Development of miniature devices for conducting experiments at small scale requires kinetic study and its performance can be evaluated by obtaining reaction yields or conversions. Performing kinetics is always been most sought aspect in microfluidics as reported by [1], [2], [3], [4]. It is noted that when extreme reactions of exothermic in nature are conducted in batch or cstr reactors there are high cases of hot spots forming inside, which decreases product yields, milli and microreactors are capable of producing better yields as reported by [5]. Glass milli and micro structured device structures allow flow chemistry to be performed at a millimeter and micrometer scale. Applications include Process intensification, Compound Synthesis. This is due to the attributes of small volumes, high surface area, and small size, low energy consumption present in micro-domain enhances the driving forces i.e. diffusional flux per unit volume or unit area. Other effects include viscosity variation near the solid surface [6], [7], slip flow at the boundary, and micro polar fluid effects mentioned. Reynolds number indicates whether the flow is laminar or turbulent. In micro fluidics, it is often Reynolds number < 2000 [8]. Our study involves development of thermal exchanger coupled millifluidic reactor of dimension 1.1mm internal diameter and length of 500mm made of borosilicate glass and reactor channel of straight sections fitted in Teflon bar structure containing circular discs into which holes of internal diameter 3mm are drilled. The entire reactor channel coupled Teflon bar structures are inserted into thermal exchanger where in hot water is circulated to maintain reaction temperature.

MATERIALS AND METHODS

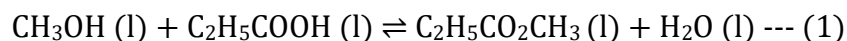
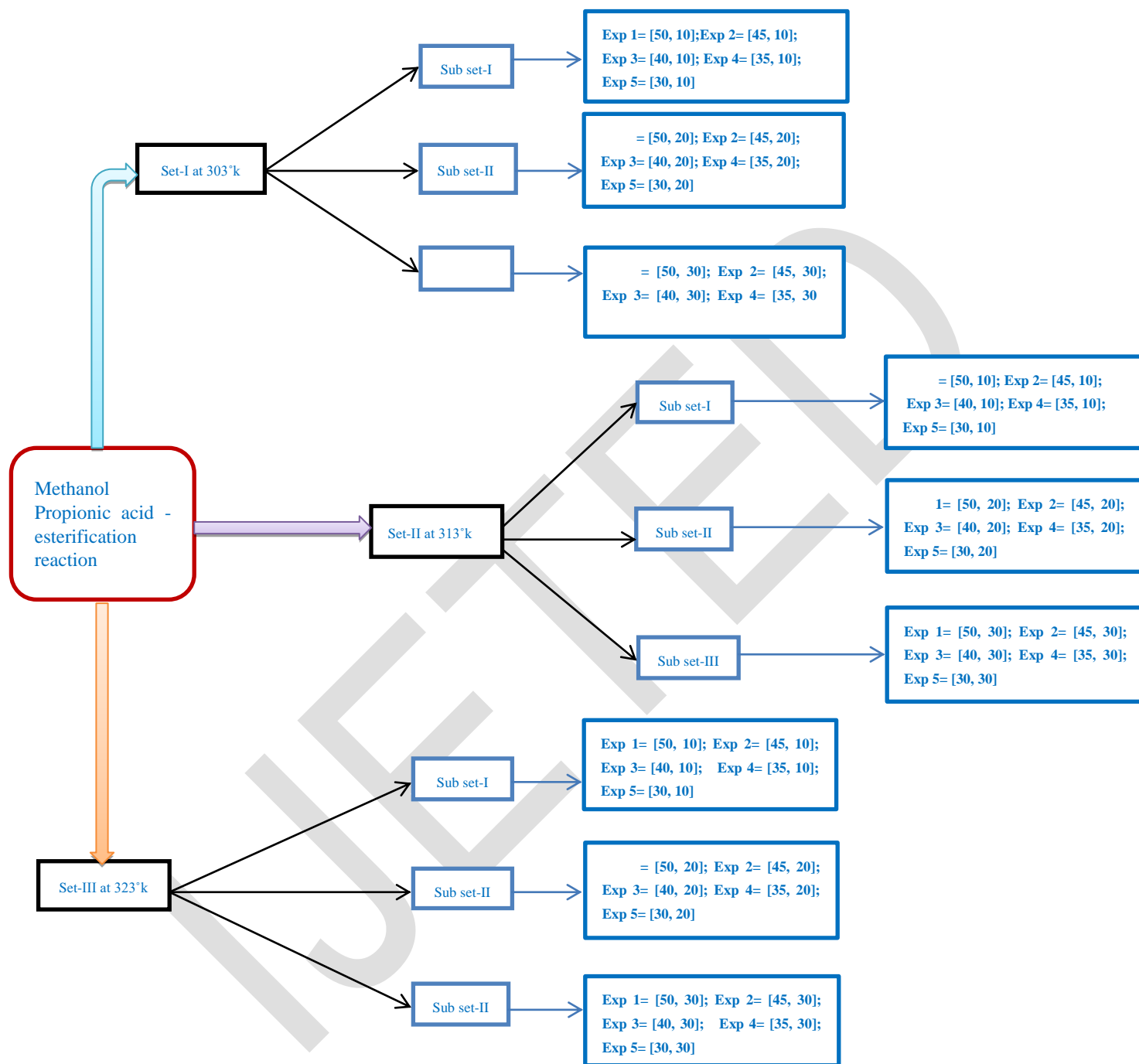
Methanol, 1-propanol and Propionic acid were analytical grade (99.6 %) and sulphuric acid (98%). Two precision peristaltic pumps. TEIMR - prototype experimental device.

Two reactants i.e., Propionic acid and Alcohol were pumped using peristaltic pumps. At T-junction two were brought into contact as the angle between two inlets is 90° mixing occurs due to collisions causing micro mixing. The reaction progresses along length of reactor. Each Pump rpm were set manually to obtain required flow rates. These two reactants were fed by maintaining different rpm's to the Millifluidic Reactor. Both flowrates of Alcohol and Propionic acid was adjusted as per molar ratio and its total combined flowrate was measured. H_2SO_4 acid catalyst (1.3ml/200ml of alcohol) is added to reactant. The esterification reaction initiates at T-junction and continues along length. Hot water is circulated in thermal exchanger to maintain required temperatures of (303°k, 313°k, and 323°k). Residence times, Pump rpm and temperatures affected the reaction rate. The outlet liquid was collected for a predetermined volume and analytically conversions were calculated for propionic acid.

1. Methanol and propionic acid reaction system

Example: **Exp 1 = [50, 10]** == Experiment 1 = [Pump-1 maintained at 50 Rpm, Pump-2 at 10 Rpm]

Experiment Tree Diagram



The reaction is reversible and common method of operating equilibrium limited reactions is to use an excess of one reactant i.e. alcohols in order to increase the conversion of the limiting reactant (propionic acid) ^[9]. The above reaction can be denoted as

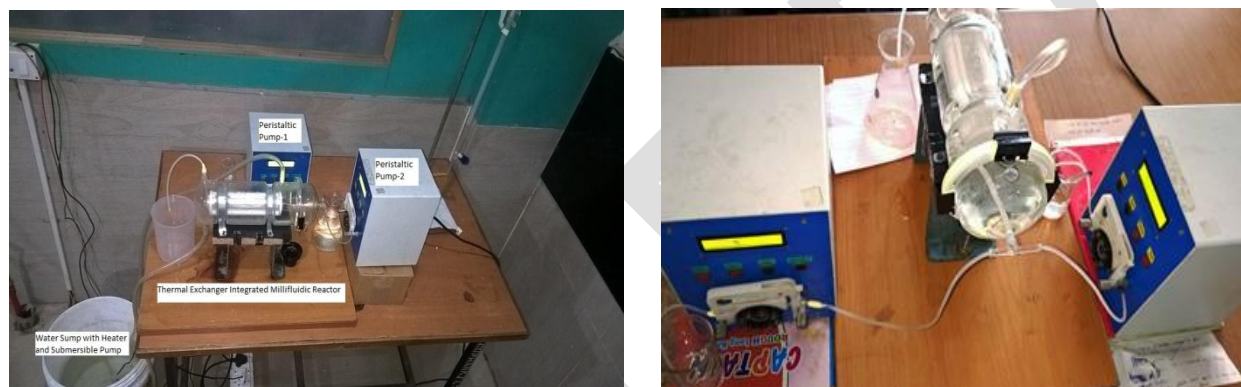


Since C_{B0} is much larger than C_{A0} , C_B , remains approximately constant at all times, the second order reaction equation (1), described as pseudo first-order reaction ^[10] as below

$$-\ln(1-X_A) = K \cdot t.$$

Residence time is varied by varying speed of pump-1 i.e. by changing flow rate of methanol while keeping pump-2 flow rate constant.

For which molar ratio M , changes due to change in residence time. The rate kinetics was determined as shown in figure 1 and values are listed in table 1.



Exp setup: a).Thermal Exchanger integrated Millifluidic Reactor. b) Front view of TEIMR

SET-I

SUB-SET-I

Table 1: Methanol concentration $[C_{B0}] \gg C_{A0}$ at 303°k

Pump-1 Rpm	Pump-2 Rpm	$M=C_{B0}/C_{A0}$	C_{A0} moles/ L	C_{B0} moles/L	Residence time(sec)	Conversion X_A	$-\ln(1-X_A)$
50	10	12.15	1.76	21.4	75	0.9759	3.725543438
45	10	11.86	1.76	20.89	82	0.9799	3.907035464
40	10	11.65	1.76	20.52	119	0.9837	4.116590171
35	10	11.55	1.76	20.33	122	0.9844	4.160484365
30	10	11.26	1.76	19.83	125	0.985	4.199705078

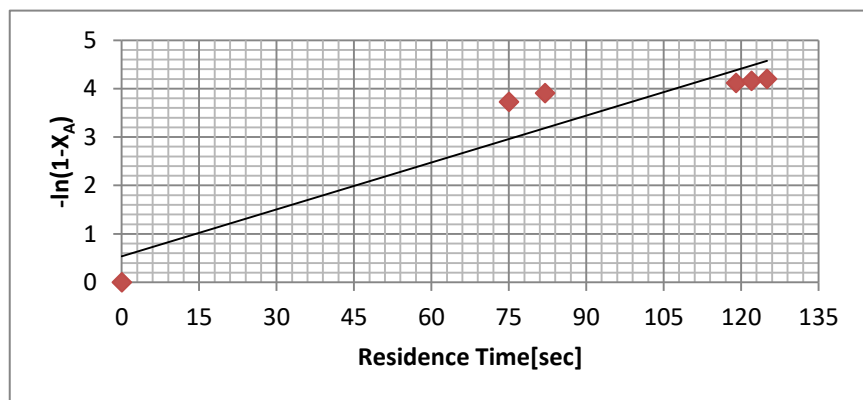


Figure 1: plot of $-\ln(1-X_A)$ vs. Residence time [sec]

Slope $k=0.034$ [L/moles. sec] from figure 1.

For molar ratios values less than that of 7.0 2nd order kinetics were performed. At 303°k pump-2 flow rate is maintained constant at 20 rpm i.e. 3.23mol/L, where methanol flow rate is varied from (18.68, 17.78, 17.31, 17.03, 16.3 moles/L) by adjusting pump-1 rpm. These are presented in table 2 and a plot of $\ln((M-X_A)/(M^*(1-X_A)))$ vs. residence time X is plotted to determine slope and rate constant.

SUB SET-II

Table 2: Methanol reaction system at 303°k

Pump-1 Rpm	Pump-2 Rpm	Conversion X_A	C_{AO} moles/L	C_{BO} moles/L	$M=C_{BO}/C_{AO}$	$-[C_{BO}-C_{AO}]$	$Y=\ln((M-X_A)/(M^*(1-X_A)))$	Residence time X[sec]
50	20	0.9705	3.23	18.68	5.7832	15.45	3.3396	63
45	20	0.9718	3.23	17.78	5.5046	14.55	3.3741	71
40	20	0.9799	3.23	17.31	5.3591	14.08	3.7051	98
35	20	0.9885	3.23	17.03	5.2724	13.8	4.2577	103
30	20	0.9902	3.23	16.3	5.0464	13.07	4.4069	110

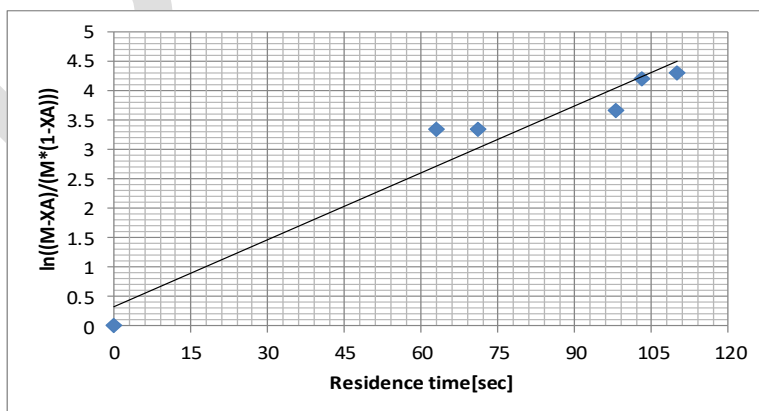


Figure 2: plot of $\ln((M-X_A)/(M^*(1-X_A)))$ vs. Residence time

Rate constants at respective molar ratios when $C_{AO}=3.23$ moles/L, using 2nd order kinetics rate constants are determined by the following procedure

$$\ln \frac{M-X_A}{M*(1-X_A)} = (C_{AO}-C_{BO}) * k * T$$

From figure 2: slope of the line passing through the origin= 0.04125

$$0.04125 = (C_{AO}-C_{BO}) * k * T$$

$$\frac{0.04125}{(C_{AO} - C_{BO}) * T} = k$$

At time=63 sec of residence time & $C_{AO}-C_{BO}=15.45$ moles/L.

The rate constant for above conditions are determined by using above kinetics of 2nd order.

$k_{63, 15.45} = 0.0026$ L/ [moles. sec]. Similarly at other residence times, rate constant values[k] were determined and tabulated in table 3.

Table 3: Second order kinetics for molar ratios at 303°k

$M=C_{BO}/C_{AO}$	$Y = \ln((M-X_A)/(M*(1-X_A)))$	k, Rate constant[L/moles.sec]	Residence time X[sec]
5.7832	3.3396	0.00266	63
5.5046	3.3741	0.00283	71
5.3591	3.7051	0.00292	98
5.2724	4.2577	0.00298	103
5.0464	4.4069	0.00315	110

The mean rate constant value for the entire subset is $k_{avg}=0.0029$ L/moles.sec

SUB SET-III

Table 5: Conversions generated for sub set-III conditions

Temp °k	Pump-1 RPM	Pump-2 RPM	Residence time, sec	X_A	C_{AO} moles/L	C_{BO} moles/L	$M=C_{BO}/C_{AO}$	$C_{BO}-C_{AO}$
303	50	30	62	0.9625	4.26	16.78	3.938967	12.52
303	45	30	74	0.9734	4.26	15.84	3.71831	11.58
303	40	30	86	0.9755	4.26	15.2	3.568075	10.94
303	35	30	91	0.9778	4.26	14.8	3.474178	10.54
303	30	30	101	0.9787	4.26	14.07	3.302817	9.81

Propionic acid is maintained at constant concentration of 4.26moles/L whereas methanol is varied from [16.78, 15.84, 15.2, 14.8, and 14.07] moles/L.

Table 6: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

Residence time X[sec]	$M=C_{BO}/C_{AO}$	$Y = \ln((M-X_A)/(M^*(1-X_A)))$	k, Rate constant[L/moles.sec]
0	0	0	0
62	3.9389	3.003227366	0.00413
74	3.7183	3.323322133	0.00446
86	3.568	3.389699608	0.00473
91	3.4741	3.477137173	0.00491
101	3.3028	3.49761048	0.00527

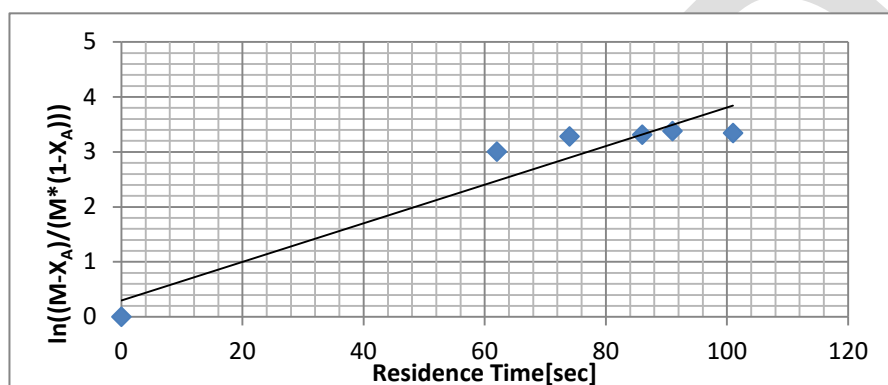


Figure 3: plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

SET-II

SUB SET-I

Table 7: Conversions generated for sub set-I conditions

S.No	Temp °k	Pump-1 RPM	Pump-2 RPM	Residence Time Sec	Conversion X_A	C_{AO} moles/L	C_{BO} moles/L	$M=C_{BO}/C_{AO}$
16	313	50	10	79	0.9584	1.76	21.4	12.1590
19	313	45	10	103	0.9967	1.76	20.89	11.8693
22	313	40	10	140	0.9982	1.76	20.52	11.6590
25	313	35	10	150	0.9812	1.76	20.33	11.5511
28	313	30	10	154	0.9916	1.76	19.83	11.2670

Propionic acid is maintained at constant concentration of 1.76moles/L whereas methanol is varied from [21.4, 20.89, 20.52, 20.33, and 19.73] moles/L.

Table 8: Conversions and Pseudo 1st order kinetics

Residence time, sec	X_A	$Y = -\ln(1-X_A)$
0	0	0
79	0.9584	3.1796
103	0.9812	3.9738
140	0.9916	4.7795
150	0.9967	5.7138
154	0.9982	6.3199

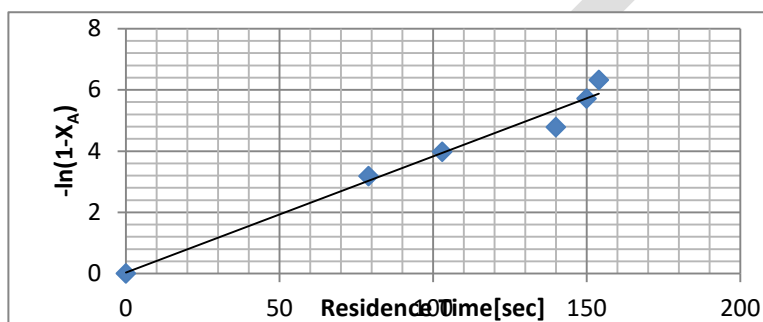


Figure 4: plot of conversion vs. $-\ln(1-X_A)$

SUB SET-II

Table 9: Conversions generated for sub set-II conditions

S.no	Temp °K	Pump-1 RPM	Pump-2 RPM	Residence time, sec	Conversion , X_A	C_{AO} moles/ L	C_{BO} moles/ L	$M = C_{BO}/C_{AO}$	$C_{BO} - C_{AO}$
17	313	50	20	65	0.9803	3.23	18.68	5.783282	15.45
20	313	45	20	72	0.9755	3.23	17.78	5.504644	14.55
23	313	40	20	98	0.9918	3.23	17.31	5.359133	14.08
26	313	35	20	102	0.9962	3.23	17.03	5.272446	13.8
29	313	30	20	115	0.9994	3.23	16.3	5.04644	13.07

Propionic acid is maintained at constant concentration of 3.23 moles/L whereas methanol is varied from [18.68, 17.78, 17.31, 17.03, and 16.3] moles/L.

Table 10: Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$

Residence Time, sec	X_A	M	$Y=\ln((M-X_A)/(M*(1-X_A)))$	k, Rate constant[L/moles.sec]
0	0	0	0	0
65	0.9803	5.7832	3.741399383	0.003489
72	0.9755	5.5046	3.514021299	0.003704
98	0.9918	5.3591	4.598970043	0.003828
102	0.9962	5.2724	5.36333331	0.003906
115	0.9994	5.0464	7.197881651	0.004124

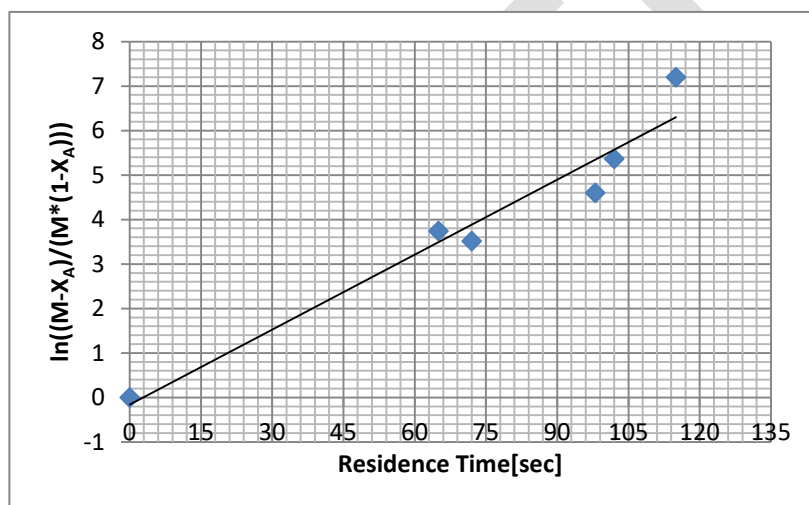


Figure 5: plot of Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$

Slope of the line from the figure 5 is 0.0539.

SUB SET-III

Table 11: Conversions generated for sub set-III conditions

S.No	Temp °k	Pump-1 Rpm	Pump-2 Rpm	Residence time, sec	Conversion, X_A	C_{AO} moles/L	C_{BO} moles/L	$M=C_{BO}/C_{AO}$	$C_{BO}-C_{AO}$
18	313	50	30	60	0.97	4.26	16.78	3.938967	12.52
21	313	45	30	69	0.9726	4.26	15.84	3.71831	11.58
24	313	40	30	95	0.9829	4.26	15.2	3.568075	10.94
27	313	35	30	106	0.9904	4.26	14.8	3.474178	10.54
30	313	30	30	113	0.9926	4.26	14.07	3.302817	9.81

Propionic acid is maintained at constant concentration of 4.26moles/L whereas methanol is varied from [16.78, 15.84, 15.2, 14.8, and 14.07] moles/L.

Table 12: Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$

Residence Time, sec	X_A	M	$Y=\ln((M-X_A)/(M*(1-X_A)))$	k, Rate constant[L/moles.sec]
0	0	0	0	0
60	0.97	3.9389	3.223848	0.003282748
69	0.9726	3.7183	3.293982	0.003549223
99	0.9829	3.568	3.746436	0.003756856
106	0.9904	3.4741	4.310406	0.003899431
113	0.9926	3.3028	4.548839	0.004189602

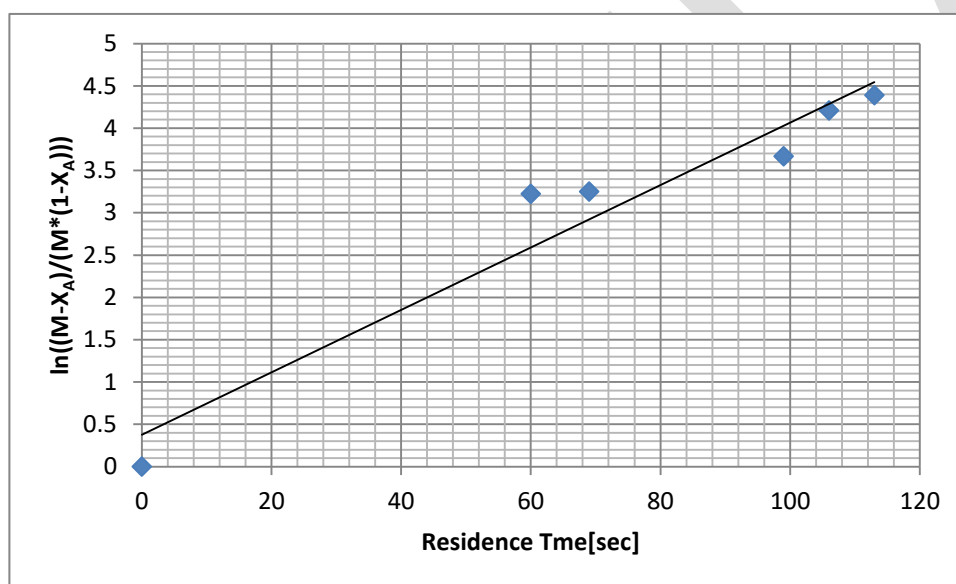


Figure 6: plot of Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$

Slope of the line from the figure 6 is 0.0411

SET-III

SUB SET-I

Table 13: Conversions generated for sub set-I conditions

S.No	Temp °k	Pump-1 RPM	Pump-2 RPM	Residence time, sec	Conversion, X_A	C_{AO} moles/L	C_{BO} moles/L	$M=C_{BO}/C_{AO}$
31	323	50	10	90	0.929	1.76	21.4	12.15909
34	323	45	10	142	0.975	1.76	20.89	11.86932
37	323	40	10	148	0.979	1.76	20.52	11.65909
40	323	35	10	153	0.9846	1.76	20.33	11.55114
43	323	30	10	158	0.989	1.76	19.83	11.26705

Propionic acid is maintained at constant concentration of 1.76moles/L whereas methanol is varied from [19.83, 20.33, 20.52, 20.89, and 21.4] moles/L.

Table 14: Conversions and Pseudo 1st order kinetics

Residence time,sec	X_A	$Y=-\ln(1-X_A)$
0	0	0
90	0.929	2.645075402
142	0.975	3.688879454
148	0.979	3.863232841
153	0.9846	4.17338777
158	0.989	4.509860006

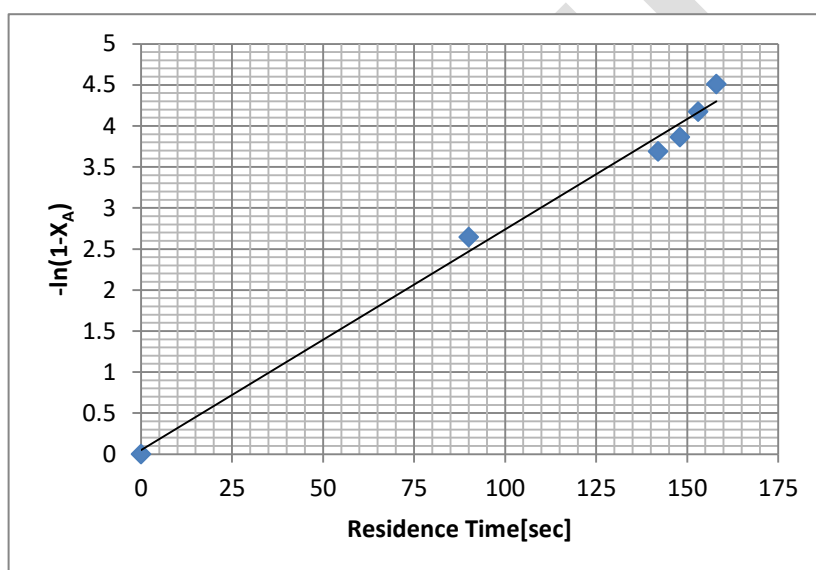


Figure 7: plot of conversion vs. $-\ln(1-X_A)$

SUB SET-II

Table 15: Conversions generated for sub set-II conditions

S.No	Temp °k	Pump-1 RPM	Pump-2 RPM	Residence time, sec	Conversion, X_A	C_{AO} moles/L	C_{BO} moles/L	M	$C_{BO}-C_{AO}$
32	323	50	20	77	0.9767	3.23	18.68	5.783282	15.45
35	323	45	20	89	0.9804	3.23	17.78	5.504644	14.55
38	323	40	20	115	0.9829	3.23	17.31	5.359133	14.08
41	323	35	20	132	0.9872	3.23	17.03	5.272446	13.8
44	323	30	20	142	0.9905	3.23	16.3	5.04644	13.07

Propionic acid is maintained at constant concentration of 3.23moles/L whereas methanol is varied from [18.68, 17.78, 17.31, 17.03, and 16.3] moles/L.

Table 16: Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$

Residence time, sec	X_A	M	$Y=\ln((M-X_A)/(M*(1-X_A)))$	k, Rate constant [L/moles.sec]
0	0	0	0	0
77	0.9767	5.7832	3.5743	0.00362
89	0.9804	5.5046	3.7162	0.00384
115	0.9829	5.3591	3.8719	0.00397
132	0.9872	5.2724	4.15099	0.00405
142	0.9905	5.0464	4.45099	0.00428

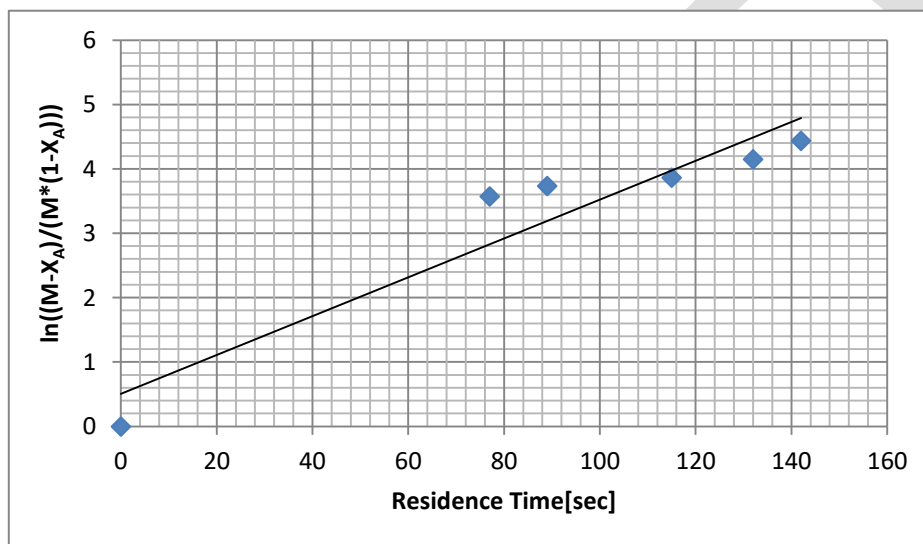


Figure 8: plot of Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$

Slope of the line in figure 8 is 0.056

SUB SET-III

Table 17: Conversions generated for sub set-III conditions

S.No	Temp °k	Pump-1 RPM	Pump-2 RPM	Residence time, sec	Conversion, X_A	C_{AO} moles/L	C_{BO} moles/L	$M=C_{BO}/C_{AO}$	$C_{BO}-C_{AO}$
33	323	50	30	78	0.9748	4.26	16.78	3.938967	12.52
36	323	45	30	128	0.9804	4.26	15.84	3.71831	11.58
39	323	40	30	134	0.9818	4.26	15.2	3.568075	10.94
42	323	35	30	138	0.9827	4.26	14.8	3.474178	10.54

Propionic acid is maintained at constant concentration of 4.26moles/L whereas methanol is varied from [16.78, 15.84, 15.2, and 14.8] moles/L.

Table 18: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

M	$Y=\ln((M-X_A)/(M^*(1-X_A)))$	k, Rate constant [L/moles.sec]
0	0	0
3.9389	3.396583233	0.002635783
3.7183	3.626150341	0.002849741
3.568	3.684518087	0.003016453
3.4741	3.724558126	0.00313093

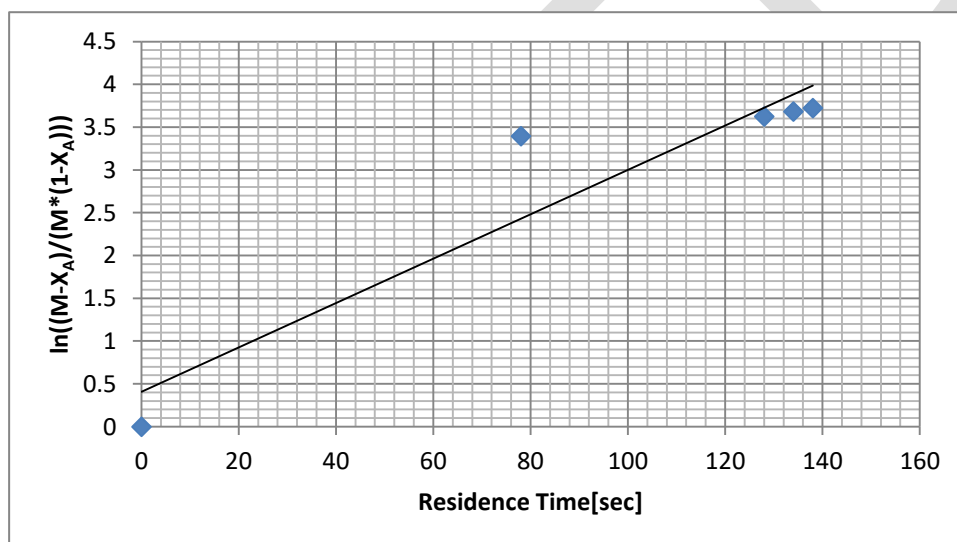


Figure 9: plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

Slope of the line from the figure 9 is 0.033

Arrhenius plots were plotted to temperatures of 303 °k, 313°k & 323°k to estimate Activation energy E and frequency factor K_0 .

Tables 19: Arrhenius data for $C_{AO} = 3.23$ moles/L at 303,313, and 323°k

C_{AO} [moles/L]	Temp°K	lnk	1/T
3.23	303	-5.83754	0.00330
3.23	313	-5.57013	0.00319
3.23	323	-5.53404	0.00309

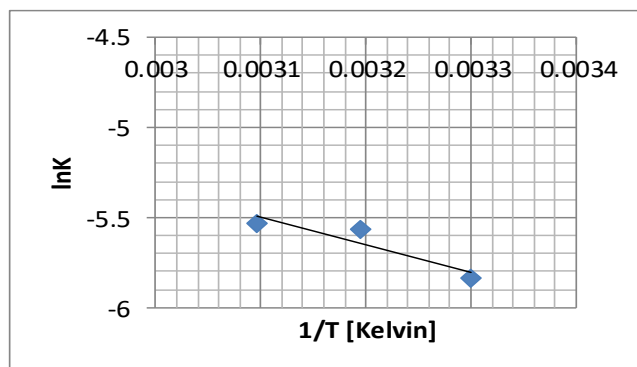


Figure 10: $\ln k$ vs. $1/T$ at temperatures of 303, 313, and 323° kelvin when $C_{AO} = 3.23 \text{ mol/L}$

From figure 10 Intercept $K_0 = 0.0045$, Activation energy $E = 14965.2 \text{ KJ/Kmole}$.

The experiment when conducted at $C_{AO} = 4.26 \text{ moles/L}$ and its temperature dependency is calculated as below in table 5.

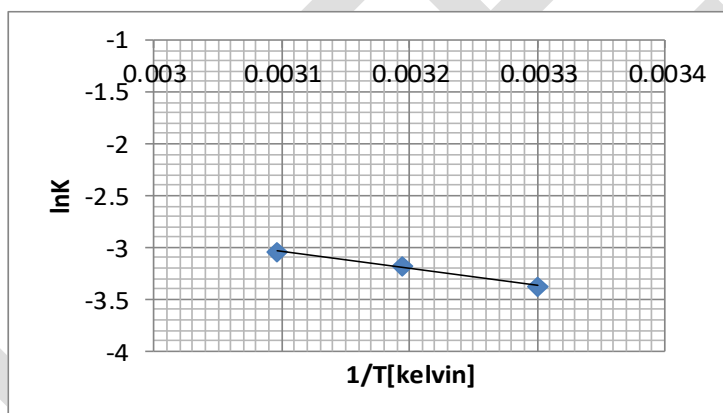


Figure 11: plot of $\ln k$ vs. $1/T$ at temperatures of 303, 313, and 323° kelvins for $C_{AO} = 4.26 \text{ moles/L}$.

Frequency factor $K_0 = 0.0523$, Activation energy $E = 16,628 \text{ KJ/Kmole}$ was found from figure 11

Table 20: Arrhenius data for $C_{AO} = 4.26 \text{ moles/L}$ at 303, 313, and 323°k

$C_{AO} [\text{moles/L}]$	Temp °K	$\ln k$	$1/T$
4.26	303	-5.36041	0.0033
4.26	313	-5.59001	0.003195
4.26	323	-5.84304	0.003096

The activation energy data indicates that methanol propionic acid esterification reaction is temperature insensitive. The experiment is repeated in multiple sets. The method was performed as described in experiment tree diagram.

In each set, propionic acid concentration were increased which resulted in increase of conversion, due to large surface area to volume ratio of millimeter reactor and with increase in

temperature. These findings were listed below in the table 6, where for $C_{AO} = 1.76$ & 3.23 moles/L with increase in temperature, the rate constant increased. For $C_{AO} = 4.26$ moles/L increase in temperatures resulted in decrease in the rate constant as shown in Table 21

Table 21: Rate constant data vs. limiting reactant concentration.

Temp, °k	C_{AO} , moles/L	k_{avg} , L/moles.sec
303	1.76	0.034
	3.23	0.0029
	4.26	0.0046
313	1.76	0.0417
	3.23	0.0038
	4.26	0.0037
323	1.76	0.0478
	3.23	0.0039
	4.26	0.0029

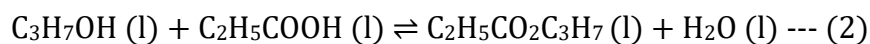
Another major effect was due to silicon tubing which is used in precision peristaltic pumps to pump reactant contents. With prolonged usage, these silicon tubes imparted uneven and prolonged residence times even though the sets are repeated with same revolution speeds. To make reaction system reliable for experimentation 30minutes of time gap for every 1 hour of operation is practiced because of elasticity nature of silicontubing. This effect was observed in times taken for pumps to pump fluid into reactor system as shown in table 22.

Table 22: Variance resulted in times for different temperatures.

S. No	Pump-1 Rpm	Pump-2 Rpm	Time taken to collect 5 ml of product sample[seconds]		
			At 303°k	At 313°k	At 323°k
1.	50	10	75	79	90
2.	45	10	82	103	142
3.	40	10	119	140	148
4.	35	10	122	150	153
5.	30	10	125	154	158

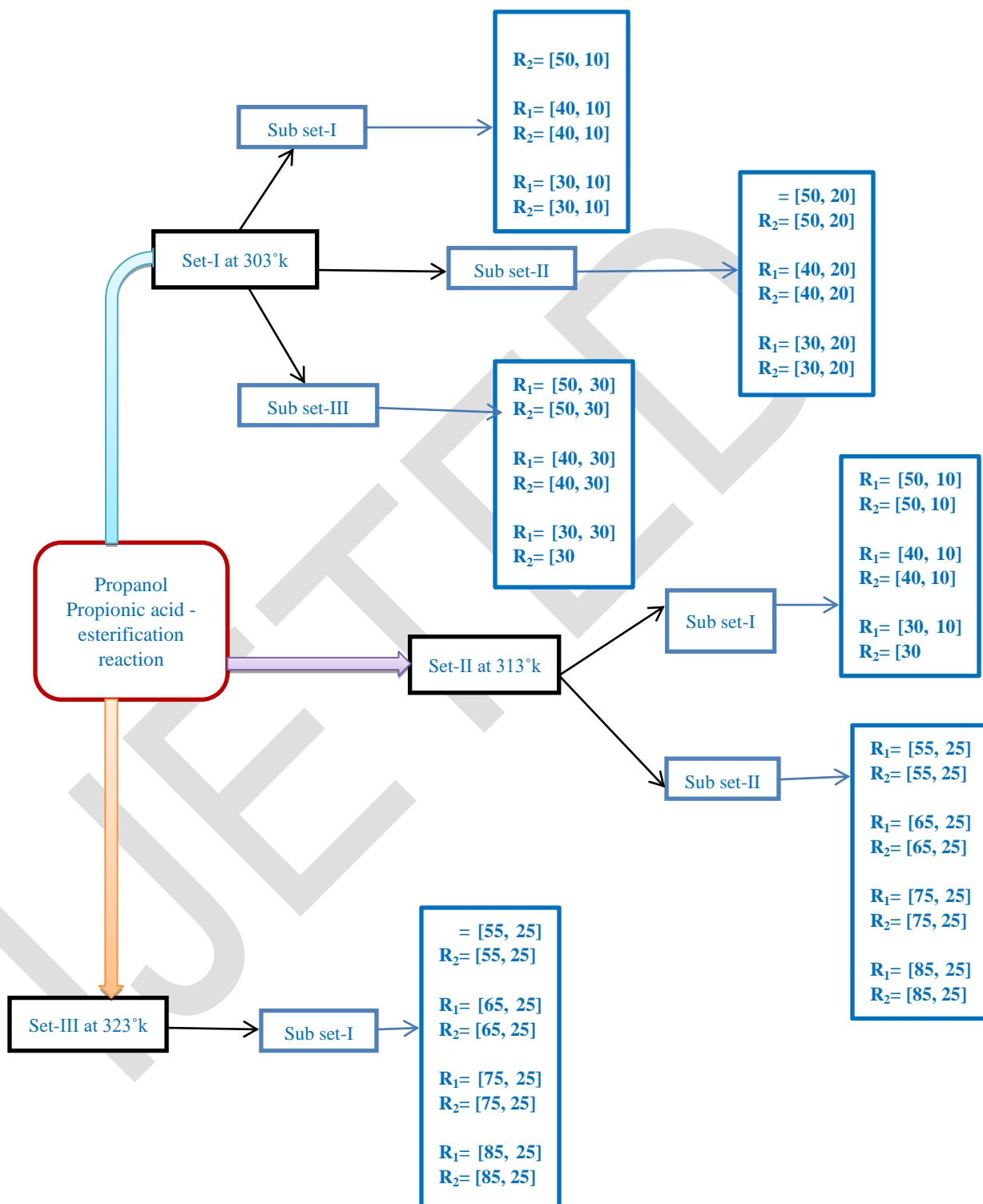
2. 1-Propanol and Propionic acid reaction system.

It was decided to conduct propanol propionic esterification reaction experiments with fewer variations in speeds with two replicates. The experiment is carried out in sets.



The above reaction (2) kinetics is estimated as reaction (1) and all conditions are valid as in previous case.

Experiment Tree Diagram



SET-I

Sub set-I

Table 23: Experiment at 303°k

S.No	Replicate	Temp °k	Pump-1 RPM	Pump-2 RPM	Residence time, sec	C _{AO} moles/L	C _{BO} moles/L	C _{BO} -C _{AO}
1	1	303	50	10	95	1.8	11.54	9.74
2	2	303	50	10	92	1.8	11.54	9.74
3	1	303	40	10	100	1.8	10.8	9
4	2	303	40	10	101	1.8	10.8	9
5	1	303	30	10	109	1.8	10.6	8.8
6	2	303	30	10	113	1.8	10.6	8.8

Propionic acid concentration is maintained at 1.8 moles/L while 1-Propanol is varied as [11.54, 10.8, and 10.6] moles/L. Each combination is replicated twice too ascertain its accuracy.

Table 24: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

M=C _{BO} /C _{AO}	X _A	Y=ln((M-X _A)/(M*(1-X _A)))	Residence time, sec
6.41	0.9451	2.742758	55
6.41	0.9706	3.362601	52
6	0.9729	3.431305	100
6	0.9645	3.162976	101
5.88	0.995	5.113237	109
5.88	0.991	4.526268	113

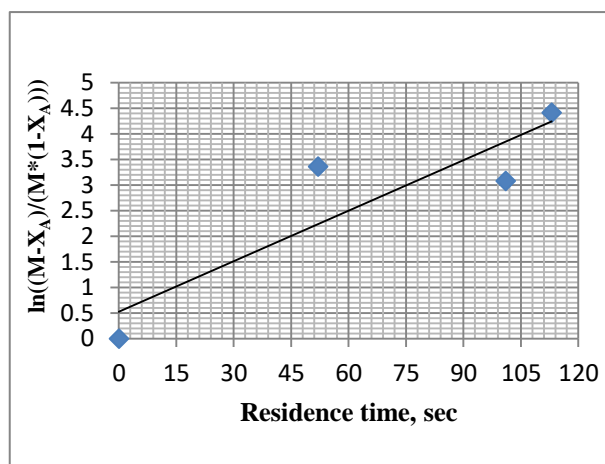
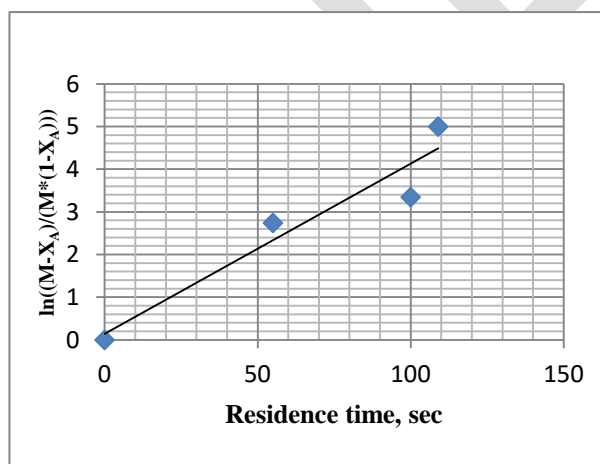


Figure 12: Plot of Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$ Replicate-1
Figure 13: Plot of Residence time vs. $\ln((M-X_A)/(M*(1-X_A)))$ Replicate-2

Sub set-II

Table 25: Experiment at 303°k

S.no	Replicate	Temp °k	Pump-1	Pump-2	Residence time, sec	C _{AO} moles/L	C _{BO} moles/L	C _{BO} -C _{AO}
1	1	303	50	20	80	2.93	10.94	8.01
2	2	303	50	20	85	2.93	10.94	8.01
3	1	303	40	20	88	2.93	9.36	6.43
4	2	303	40	20	83	2.93	9.36	6.43
5	1	303	30	20	70	2.93	9.1	6.17
6	2	303	30	20	71	2.93	9.1	6.17

Propionic acid concentration is maintained at 2.93moles/L while 1-Propanol is varied as [10.94, 9.36, and 9.1] moles/L. Each combination is replicated twice too ascertain its accuracy.

Table 26: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

M=C _{BO} /C _{AO}	X _A	Y= $\ln((M-X_A)/(M^*(1-X_A)))$	Residence time, sec
3.733	0.9723	3.284669	70
3.733	0.976	3.426707	71
3.194	0.998	5.840048	80
3.194	0.9965	5.281115	83
3.105	0.9917	4.406858	85
3.105	0.9814	3.604812	89

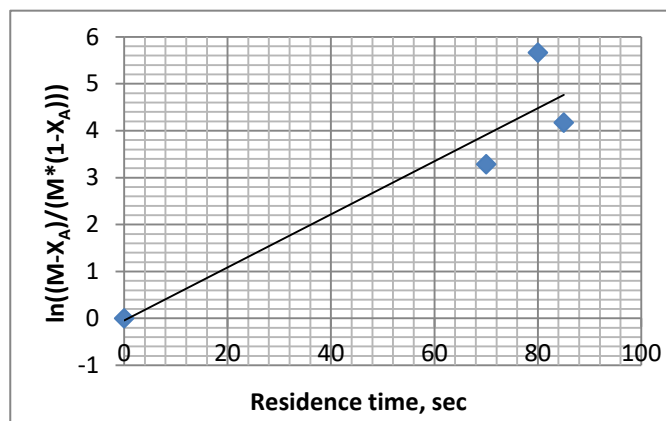
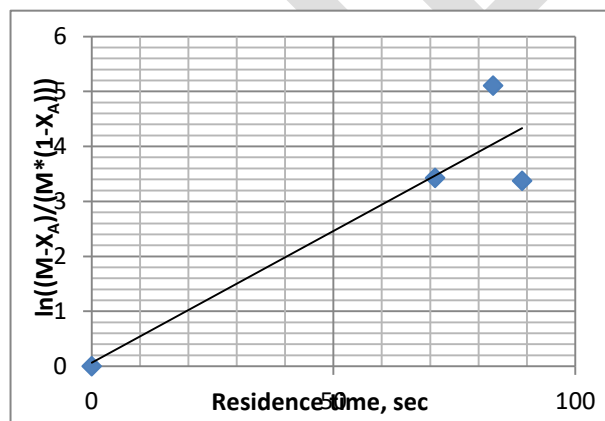


Figure 14: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-1
Figure 15: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-2

Sub set-III

Table 27: Experiment at 303°k

S.no	Replicate	Temp °k	Pump-1	Pump-2	Residence time, sec	C _{AO} moles/L	C _{BO} moles/L	C _{BO} -C _{AO}
1	1	303	50	30	55	4.53	9.28	4.75
2	2	303	50	30	52	4.53	9.28	4.75
3	1	303	40	30	80	4.53	8.03	3.5
4	2	303	40	30	85	4.53	8.03	3.5
5	1	303	30	30	50	4.53	7.93	3.2
6	2	303	30	30	56	4.53	7.93	3.2

Propionic acid concentration is maintained at 4.53moles/L while 1-Propanol is varied as [9.28, 8.03, and 7.93] moles/L. Each combination is replicated twice too ascertain its accuracy.

Table 28: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

M=C _{BO} /C _{AO}	X _A	Y= $\ln((M-X_A)/(M^*(1-X_A)))$	Residence time, sec
2.048565	0.9631	2.664413	90
2.048565	0.9868	3.670332	92
1.772627	0.9716	2.767043	88
1.772627	0.9699	2.711027	85
1.706402	0.8862	1.440721	50
1.706402	0.926	1.821357	56

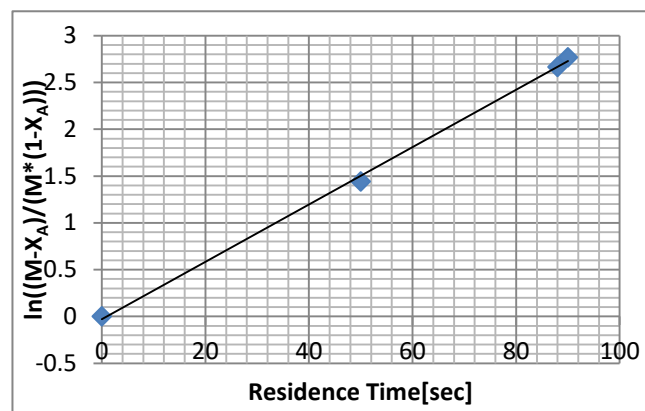
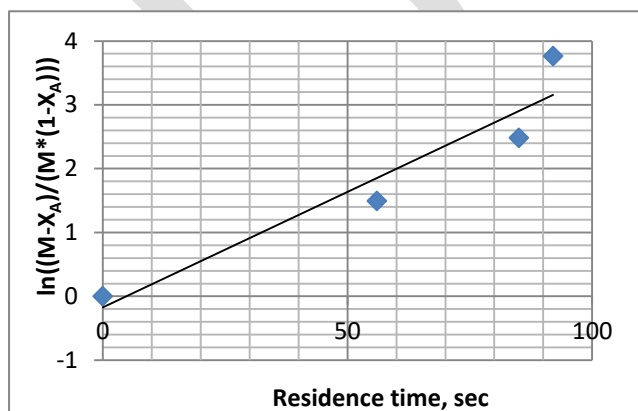


Figure 16: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-1
Figure 17: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-2

SET-II

Sub set-I

Table 29: Experiment at 313°k

S.No	Replicate	Temp °k	Pump-1	Pump-2	Residence time, sec	C _{AO} moles/L	C _{BO} moles/L	C _{BO} -C _{AO}
1	1	313	50	10	36	1.8	11.54	9.74
2	2	313	50	10	42	1.8	11.54	9.74
3	1	313	40	10	53	1.8	10.8	9
4	2	313	40	10	57	1.8	10.8	9
5	1	313	30	10	88	1.8	10.6	8.8
6	2	313	30	10	83	1.8	10.6	8.8

Propionic acid concentration is maintained at 1.8moles/L while 1-Propanol is varied as [11.54, 10.8, and 10.6] moles/L. Each combination is replicated twice too ascertain its accuracy.

Table 30: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

M=C _{BO} /C _{AO}	X _A	Y= $\ln((M-X_A)/(M^*(1-X_A)))$	Residence time, sec
6.411	0.9725	3.42906	36
6.411	0.9763	3.577072	42
6	0.9901	4.434877	53
6	0.9969	5.594651	57
5.888	0.9981	6.080188	88
5.888	0.9996	7.638026	83

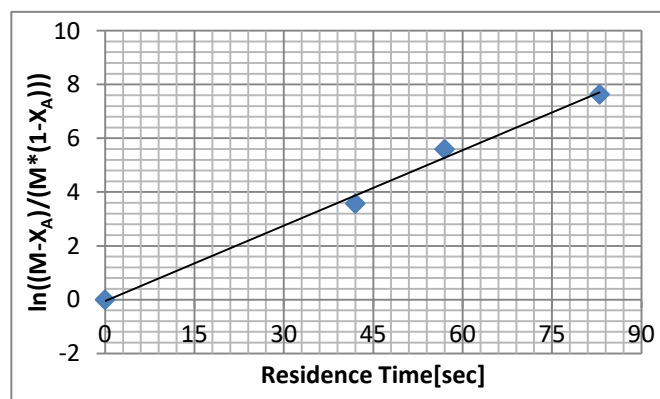
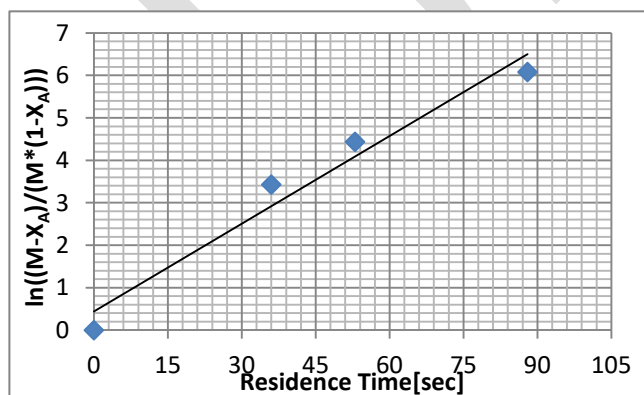


Figure 18: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-1
Figure 19: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-1

Sub set-II

Table 31: Experiment at 313°k

S.No	Replicate	Temp °k	Pump-1	Pump-2	Residence time, sec	C _{AO} moles/L	C _{BO} moles/L	C _{BO} -C _{AO}
1	1	313	55	25	44	4.53	8.801	4.271
2	2	313	55	25	46	4.53	8.801	4.271
3	1	313	65	25	38	4.53	9.46	5.26
4	2	313	65	25	43	4.53	9.46	5.26
5	1	313	75	25	30	4.53	9.3	5.27
6	2	313	75	25	32	4.53	9.3	5.27
7	1	313	85	25	24	4.53	8.25	4.9
8	2	313	85	25	27	4.53	8.25	4.9

Propionic acid concentration is maintained at 4.53moles/Lwhile 1-Propanol is varied as [8.801, 9.46, 9.3, &8.25] moles/L. Each combination is replicated twice too ascertain its accuracy.

Table 32: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

X _A	M=C _{BO} /C _{AO}	Y= $\ln((M-X_A)/(M^*(1-X_A)))$	Residence time, sec
0.9956	1.942826	4.707789	44
0.9964	1.942826	4.907615	46
0.9982	2.252381	5.734463	38
0.9958	2.252381	4.889077	43
0.9969	2.307692	5.210737	30
0.9879	2.307692	3.855776	32
0.9768	2.462687	3.258362	24
0.9717	2.462687	3.063079	27

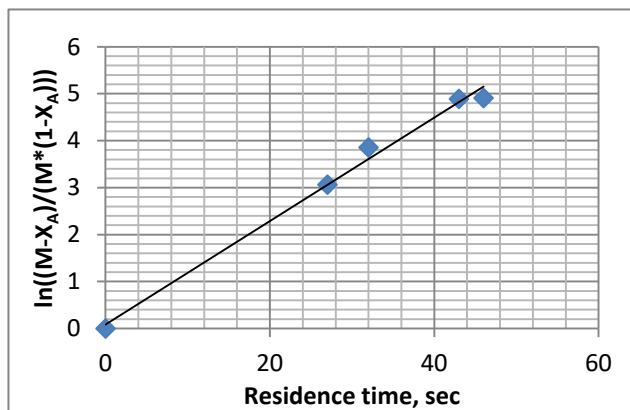
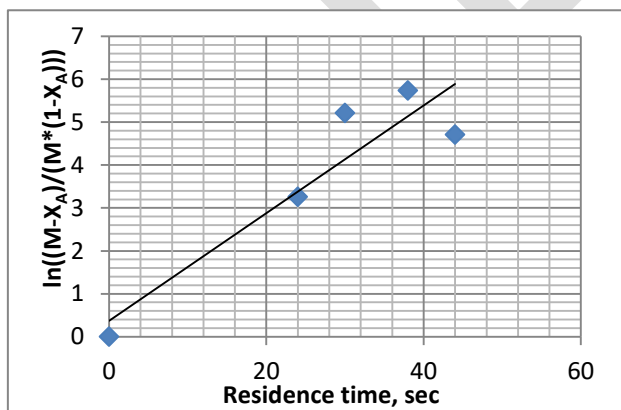


Figure 20: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-1
Figure 21: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-2

SET-III

Sub set-I

Table 33: Experiment at 323°k

S.No	Replicate	Temp °k	Pump-1	Pump-2	Residence time, sec	C _{AO} moles/L	C _{BO} moles/L	C _{BO} -C _{AO}
9	1	323	55	25	41	4.53	8.801	4.271
10	2	323	55	25	39	4.53	8.801	4.271
11	1	323	65	25	35	4.53	9.46	4.93
12	2	323	65	25	36	4.53	9.46	4.93
13	1	323	75	25	29	4.53	9.3	4.77
14	2	323	75	25	31	4.53	9.3	4.77
15	1	323	85	25	26	4.53	8.25	3.72
16	2	323	85	25	27	4.53	8.25	3.72

Propionic acid concentration is maintained at 4.53moles/Lwhile 1-Propanol is varied as [8.801, 9.46, 9.3, and 8.25] moles/L. Each combination is replicated twice too ascertain its accuracy.

Table 34: Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$

X _A	M=C _{BO} /C _{AO}	Y= $\ln((M-X_A)/(M^*(1-X_A)))$	Residence time, sec
0.9995	1.942826	6.878415	41
0.9999	1.942826	8.487429	39
0.9968	2.252381	5.160215	35
0.9947	2.252381	4.65733	36
0.9961	2.307692	4.981773	29
0.9942	2.307692	4.586339	31
0.9958	2.462687	4.95456	26
0.9928	2.462687	4.417607	27

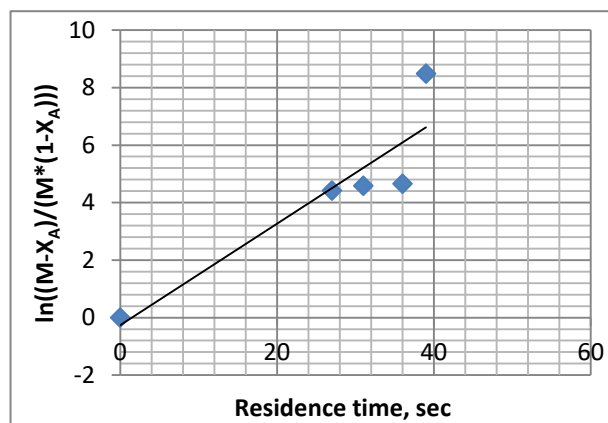
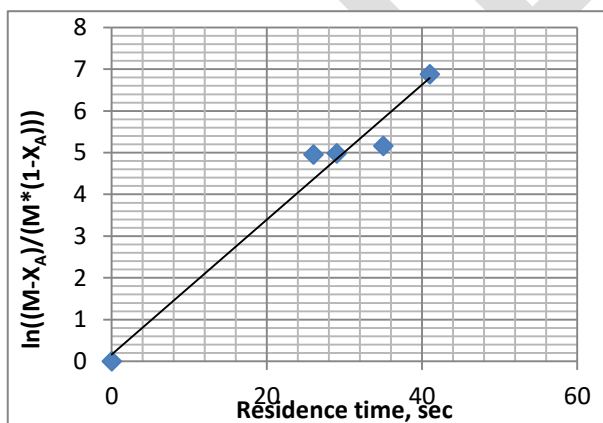


Figure 22: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-1
Figure 23: Plot of Residence time vs. $\ln((M-X_A)/(M^*(1-X_A)))$ Replicate-2

Propanol Propionic acid esterification reaction on temperature dependency is determined by Arrhenius equation. Experimental data are obtained at 303,313, and 323 Kelvin for $C_{AO}=4.53$ moles/L listed below in the table 9.

Table 9: Arrhenius data for $C_{AO} = 4.53$ moles/L at 303,313, and 323°k

Temp °K	C_{AO} ,moles/L	$Y = \ln k$	$X = 1/T$
303	4.53	-4.4828	0.0033
313	4.53	-3.869	0.00319
323	4.53	-3.4842	0.00309

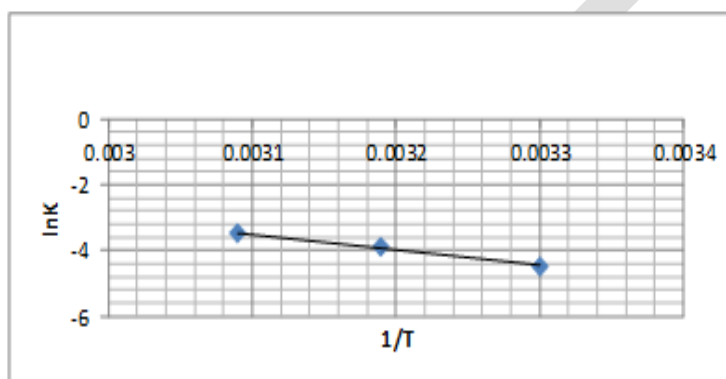


Figure 24: plot of $\ln k$ vs. $1/T$ at 303, 313, and 323 kelvins for $C_{AO} = 4.53$ mol/L

From the figure 6 frequency factor, $k_0=0.0497$, Activation energy, $E=41,570$ KJ/Kmole are estimated. Higher activation energy shows the propanol propionic acid is temperature sensitive.

CONCLUSIONS

The prototype TEIMR was able to perform satisfactorily for the production of esters on continuous basis. The primary constraint is that of silicon tubing which induced uncertainties in residence times. However, the design was satisfactory for both methanol and propanol ester reactions obtaining 90% conversions.

NOMENCLATURE

- A- Alcohols
- B- Propionic acid
- C_{AO} - Propionic acid feed concentration.
- C_{BO} - Alcohol feed concentration.
- E- Activation energy.
- k- Rate constant.
- k_{avg} - Average rate constant.
- K_0 - Frequency factor
- M- Molar ratio C_{BO}/C_{AO}
- R_1 -Replicate 1 [Pump-1 RPM, Pump-2 RPM]
- R_2 -Replicate 2 [Pump-1 RPM, Pump-2 RPM]
- X_A - Limiting reactant conversion.

REFERENCES

- [1] Yukako Asano, Shigenori Togashi, Yoshishige Endo .Improvement in the Yield of an Equilibrium Esterification Reaction Using a Micro reactor for Water Separation. *Journal of Chemical Engineering of Japan*, 2013, Vol. 46, No. 4 pp. 313-318.
- [2] Romain Richard, Sophie Thiebaud-Roux, Laurent E. Prat. Modeling the kinetics of transesterification reaction of sunflower oil with ethanol in microreactors. *Chemical Engineering Science*, Elsevier, 2013, vol. 87, pp. 258-269.
- [3] T. Sankarshana¹, V. Kalyan², Usha Virendra², and C.E. Alemayehu¹. Reaction Performance in Micro and Milli Tubes. *Proceedings of the World Congress on Engineering and Computer Science 2012 Vol II WCECS 2012*.
- [4] Shigenori Togashi, Tetsuro Miyamoto, Yukako Asano, Yoshishige Endo. Yield Improvement of Chemical Reactions by Using a Microreactor and Development of a Pilot Plant Using the Numbering-Up of Microreactors .*Journal Of Chemical Engineering of Japan* Vol. 42, 2009.
- [5] D.M.Roberge, N.Bieler, M.Mathier, M.Eyholzer, B.Zimmermann, P.Barthe, C.Guermeur, O. Lobet, M.Moreno, P.Woehl. Development of an Industrial Multi-Injection Microreactor for Fast and Exothermic Reactions – Part II, *Chemical Engineering & Technology* ,Volume 31, Issue 8, Pages 1155–1161, 2008.
- [6] Maris Teresa Sanz, JurgenGmehling, “Esterification of acetic acid with isopropanolcoupled with pervaporation part 1 (Kineticsand pervaporation studies)”, *Chem. Eng.Journal*, 123, 1-8, 2006.
- [7] Joshua D. Tice, Adam D. Lyon, Rustem F. Ismagilov. Effects of viscosity on droplet formation and mixing in microfluidic channels, *AnalyticaChimicaActa*, Volume 507, Issue 1, Pages 73–77, 2004.
- [8] Junemo Koo and Clement Kleinstreuer. Liquid flow in microchannels: experimental observations and computational analyses of microfluidics effects,*Journal of Micromechanics and Microengineering*, Volume 13, Number 5, 2003.
- [9] Z.J.Hua, W.G.Zhanga, K.J.Hüttingera, B.Reznikb, D.Gerthsenb. Influence of pressure,temperature and surface area/volume ratio on the texture of pyrolytic carbon deposited from methane, *Carbon* Volume 41, Issue 4, 2003, Pages 749–758, 2003.
- [10] Levenspiel.O “Chemical reaction engineering” 3rd edition, JohnWiley&Sons, 1999.