

Design and Evaluation of Millireactor to Perform Reactions at Small Scale

V Kalyan

Department of Chemical Engineering

Anurag Group of Institutions (Autonomous), Venkatapur (v), Ghatkesar (M), Hyderabad – 500088

Sk Shaheda

Department of Chemical Engineering

Anurag Group of Institutions (Autonomous), Venkatapur (v), Ghatkesar (M), Hyderabad – 500088

AVS Prasad

B. Tech. Student, Department of Chemical Engineering

Anurag Group of Institutions (Autonomous), Venkatapur (v), Ghatkesar (M), Hyderabad – 500088

Abstract - The present research activity lays emphasis on designing, fabrication and evaluation of Millireactor-Prototype experimental device to perform chemical reactions of 1. Saponification reaction system of ethyl acetate and sodium hydroxide was studied for which reaction kinetics were obtained. 2. Equilibrium limited esterification reaction involving Butanol and Propionic acid was performed to validate the MilliReactor design. N-butyl propionate ester obtained from experimental MilliReactor was compared with Alfa Aesar manufactured N-butyl Propionate and the absorbance values of both samples at wavelengths of 200nm, 265nm, 330nm, are found to be 0.8, 0.26, and 0.019

Key Words: Millireactor, Butanol, Propionic acid, Saponification reaction, Prototype device

I. INTRODUCTION

Glass Microreactors involve microfabricated structures to allow flow chemistry to be performed at a microscale. Applications include Compound Library Generation, Process Development and Compound Synthesis. Developing a Millireactor based on the principles of reaction engineering, heat and mass transfer and its performance was demonstrated by performing esterification and saponification reactions. Esterification of propionic acid with Butanol was performed and was optimized for achieving an improved conversion. This kind work has been demonstrated by Yukako Asano et al [1] through the development of a Microreactor for the separation of water through a T-type zeolite membrane by pervaporation, which was employed for esterification of oleic acid.

For the better heat and mass transfer during the reaction course, thermal exchanger was specifically designed to provide uniform temperature distribution throughout the reactor length i.e. from Millimixer T-Junction to end of Millireactor outlet. Amol A. Kulkarni et al [8] for the analysis of homogeneous and heterogeneous acid-catalyzed esterification of acetic acid with 1-butanol developed a miniaturized Microreactor plant. The plant configuration includes a micromixer followed by an isothermal microreactor. For the case of homogeneously catalyzed esterification, a long tube of 1.3 mm inner diameter acted as the reaction tube and also helped to achieve longer residence times. The results were found to be consistent with the data from literature obtained with conventional equipment on lab scale, while deviations were seen at long reaction times and high catalyst concentrations. A change in the residence time can be achieved by changing the total flow rate.

The merits are typically attributed to having features like small volumes, high area, and small size, low energy consumption present in micro-domain, which propagates the driving forces i.e. diffusional flux per unit volume or unit area, other effects that may play a more significant role on the micro scale include viscosity variation near the solid surface, slip flow at the boundary, and micro polar fluid effects mentioned in [2], [5], [6], and [7]. Reynolds number indicates whether the flow is laminar or turbulent. In micro fluidics, it is often smaller than 30, which means a totally laminar flow. Reaction performance studies by T.Sankarshana et al [3] suggested that Millimetre reactors which are of the order of 1.0-2.0mm internal diameters may be worthwhile in producing bulk quantities, but while losing very high rate of conversions which are supposed to be micro reactors. It has been reported that greater conversions and selectivity are possible in millimetre reactors. The objective is by

choosing a millimetre channel of 1.1mm Internal Diameter and designing a MilliReactor and evaluating its performance.

II. MATERIALS AND METHODS

II.I. MILLIREACTOR - EXPERIMENTAL PROTOTYPE DESIGN



Fig 1: MilliReactor – Prototype Experimental Device

Prototype experimental MilliReactor is a combination of thermal exchanger, Teflon bars supported by tube sheets, where these tube sheets are drilled with holes of 3mm internal diameter. The front end of the device is covered by T-Junction mounted on to spherical dome. T –junction, Spherical dome, Thermal exchanger are made from Boro Silicate glass. The length of total device measures 180 mm.

II.II. EXPERIMENTAL PROCEDURE

To validate the device two types of reactions were performed:

1. *Irreversible Saponification Reaction:* Standard solutions of ethyl acetate (0.05N) and sodium hydroxide (0.05N) are used as reactants. These two reactants were pumped at various combinations of flow rates to the reactor tube. Once individual reactant flowrate is established as per molar ratios, reactions are commenced. Saponification reaction starts at T-junction and continues along the tube length. Reaction time varies with the flow rates of reactants. Hot water circulated over the shell to maintain required temperature. In doing so the factors of reaction time, molar ratios and temperature effects on the reaction rate. The outlet liquid was collected for a predetermined time in a receiver containing known concentration and volume of sulphuric acid (0.05N) which was used to arrest the reaction. Phenolphthalein indicator was added for identification. The mixture appears colour less. The contents of the receiver were titrated against known concentration of sodium hydroxide. At the end the solution turns into pink colour. Conversion of sodium hydroxide is calculated by volume analysis. Experiments were conducted with different flow rates, at different temperatures and the corresponding conversions were determined.

2. *Esterification reaction.* Two precision peristaltic pumps are used to feed each of the reactants, butanol and propionic acid whose ends are connected to a T junction of 2 mm internal diameter, the mixing zone end is connected to high chemical resistive tygon tube of internal diameter 1.1 mm, length 5 m. Reactor channel is arranged in straight sections between two base plates with the support of four supporting Teflon rods. These

base plates have holes of 3 mm internal diameter with triangular pitch. This is enclosed with in cylindrical glass shell which was acts as Thermal exchanger. One end of tygon tube was connected to T-junction outlet and other end was the end of reactor length.

Two reactants i.e., Propionic acid and Butanol were pumped using peristaltic pumps, at T-junction two were brought into contact as the angle between two inlets is 90° making mixing occurs due to collisions and causing micro mixing. The reaction progresses over the length of reactor. Each reactant was pumped using separate Peristaltic pumps. Pump rpm were set manually to obtain required flow rates. These two reactants were fed at same and different flow rates to the MilliReactor. Both flowrates of 1-Butanol and Propionic acid was adjusted as per molar ratio total combined flowrate was measured. Few drops of H_2SO_4 acid catalyst (3ml/100ml of 1-Butanol) is added to reactant. The esterification reaction initiates at T-junction and continues along the MilliReactor length. Hot water is circulated over the tube to maintain required temperature. Reaction times, molar ratios and temperatures will effects the reaction rate. The outlet liquid was collected for a predetermined time in a receiver containing 0.1N concentration and 10 ml volume of sodium bi-carbonate which was used to arrest the reaction. Methyl orange indicator was added to identify the end point. Upon the addition of methyl orange indicator, the mixture colour turns into yellow colour. The contents of the receiver were titrated against 0.35N concentration of hydro chloric acid. Because of titration the solution it will turns into mud red colour, indicating all of excess sodium bicarbonate is consumed. Conversion of propionic acid to 1-butyl propionate was calculated using the volume of hydro chloric acid consumed. Experiments were conducted with different flow rates, different residence times, different molar ratios of reactants at different temperatures and the corresponding conversions were determined.

Ester formed was separated by adding sodium bi-carbonate to the outlet solution to stop the reaction which results in two layers, top layer consists of product & unreacted butanol and bottom layer consists of sodium bi-carbonate solution. Using separating funnel two layers were separated. After separating top layer from bottom layer, concentrated calcium chloride solution was added to the top layer product and agitated well to remove unreacted butanol present in it as concentrated calcium chloride absorbs all butanol. Because of high density differences of concentrated calcium chloride along with absorbed butanol accumulates at the bottom of flask while ester & water, mixture remains as top layer, which was product of reaction. To remove water, anhydrous calcium chloride was added to the solution and agitated. Anhydrous calcium chloride was separated by using filter paper leaving product n-butyl propionate ester.



Fig 2: MilliReactor – Experimental Device with Peristaltic Pumps

III. RESULTS AND DISCUSSION

1. Saponification Reaction: The rate kinetics of saponification reactions was determined at different temperatures and reaction conversions were calculated.

Table1: Saponification Reaction Kinetic Data at temperatures of 35°C, 45°C and 55°C

Ethyl Acetate[mol/L]	NaOH[mol/L]	MFT[mol/L]	K [L/mol.sec] at 35°C	K [L/mol.sec] at 45°C	K [L/mol.sec] at 55°C
0.000065	0.00005	0.000115	0.0003	0.00037	0.00039
0.000075	0.00005	0.000125	0.0009	0.00093	0.00095
0.000097	0.00005	0.000147	0.00122	0.00155	0.00162
0.000115	0.00005	0.000165	0.00174	0.00239	0.00278
0.000145	0.00005	0.000195	0.00289	0.0033	0.00424
0.00016	0.00005	0.00021	0.00392	0.00482	0.005

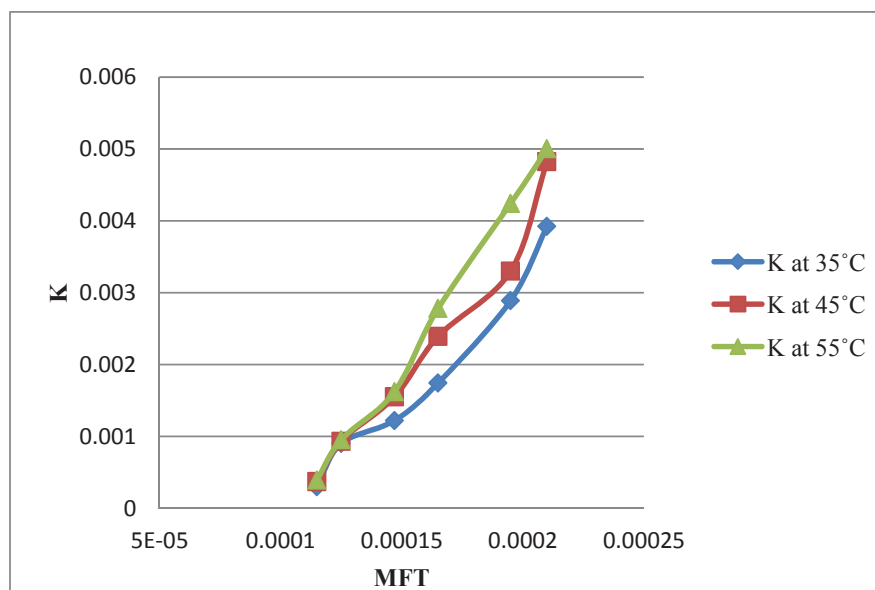


Fig 3: Saponification Reaction kinetics at different temperatures

Table 2: Saponification Reaction Conversion Data at temperatures of 35°C, 45°C and 45°C

Ethyl Acetate[mol/L]	NaOH[mol/L]	MFT [mol/L]	X at 35°C	X at 45°C	X at 55°C
0.000065	0.00005	0.000115	6.67	26.11	40
0.000075	0.00005	0.000125	27.33	35.81	47.33
0.000097	0.00005	0.000147	40	53.33	60
0.000115	0.00005	0.000165	56.67	62.7	72.87
0.000145	0.00005	0.000195	73.33	75.9	80
0.00016	0.00005	0.00021	76.6	79.09	83.33

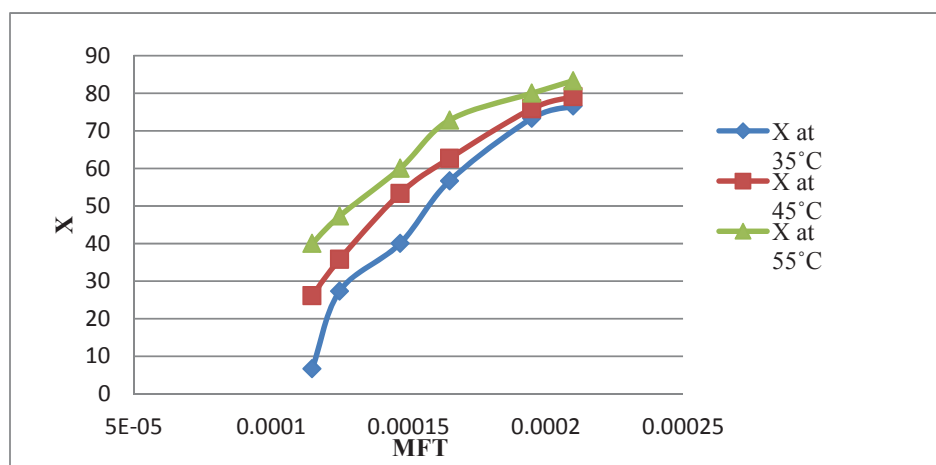


Fig 4: Saponification Reaction conversion at different temperatures.

From the above table one can figure that as temperature increases the rate kinetics of saponification reaction enhances, thereby increasing reaction conversions.

2. Esterification Reaction: The results of esterification reaction runs were listed in Table 3&4. Changing flow rates results in different residence times and the reaction is carried using acid H_2SO_4 catalyst.

Table 3: Esterification Reaction Conversion at 30°C

Propionic acid[ml]	Butanol[ml]	Total Flow Rate[ml/min]	Volume of Product Sample collected[ml]	Residence Time[sec]	$X_{1(30^{\circ}C)}$	$X_{2(30^{\circ}C)}$
0.8	3.1	3.9	3.928	60	96.45	92.29
0.4	2	2.4	3.928	98	96.07	96.07

Table 4: Esterification Reaction Conversion at 40°C

Propionic acid[ml]	Butanol[ml]	Total Flow Rate[ml/min]	Volume of Product Sample collected[ml]	Residence Time[sec]	$X_{1(40^{\circ}C)}$	$X_{2(40^{\circ}C)}$
0.8	3.1	3.9	3.928	60	97.49	95.3
0.4	2	2.4	3.928	98	96.67	90.98

It is clear that though reaction temperature is raised from 30°C to 40°C and catalyst volume raised from 3ml to 6ml based on reactant volume, conversions are dropping, probably due to equilibrium reaching earlier there by commencing backward reaction. It seems that residence time of 60 seconds or earlier residence times are good to obtain maximum conversions in both cases, but the objective is to maximize the production capacity. So, we preferred to carry out esterification reaction at reaction temperature of 45°C and acid catalyst of 3 ml/100ml of reactant volume. Changing flow rates resulted in change in residence times, by which conversions achieved are of magnitudes greater than 99%.

Table 5: Esterification Reaction Conversion at Optimum Temperature of 45°C for 3 ml of catalyst

Propionic acid[ml]	Butanol [ml]	Total Flow Rate[ml/min]	Volume of Product Sample collected[ml]	Residence Time[sec]	$X_{1(45^{\circ}\text{c})}$
1.533	1.66	3.2	3.928	74	99.58
1.533	2.267	3.8	3.928	62	99.5
1.533	2.767	4.3	3.928	55	99.44
1.533	3.267	4.8	3.928	49	99.25
1.533	3.867	5.4	3.928	44	99.19

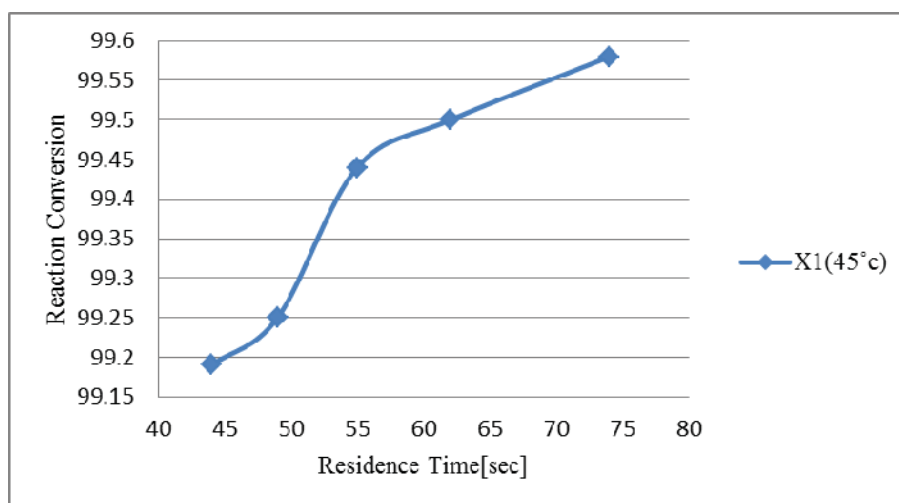


Fig 5: Esterification Reaction Conversion at Optimum Temperature of 45°C for 3 ml of catalyst

Product N-butyl Propionate was separated at conditions of reaction temperature of 45°C, 3ml of acid catalyst. It was compared with Alfa Aesar manufactured N-butyl Propionate by performing UV- Spectroscopy analysis.

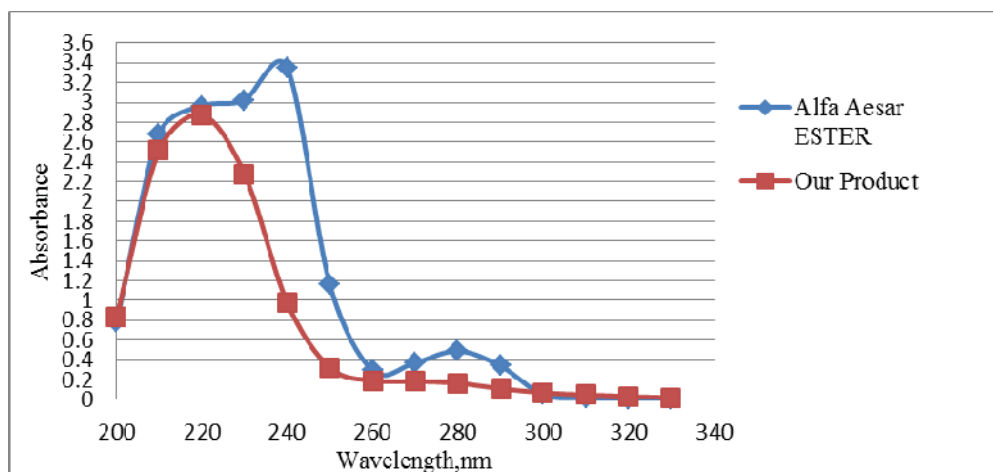


Fig 6: Comparison of Alfa Aesar N-butyl Propionate with product obtained from MilliReactor.

At wavelengths of 200nm, 210nm, 225nm, 265nm, 330nm, are found to be 0.8, 2.65, 3.33, 0.26, and 0.019. While the rest of curve promising that N-butyl Propionate manufactured using MilliReactor is off significantly close to that standard sample.

IV. CONCLUSION

Prototype MilliReactor experimental device performed well for both reversible and irreversible reactions. Its performance was studied by measuring kinetics and conversions. If proper enhancements to existing device are made, its production volumes can be increased. Total investment involved is \$ 2100.00/- which is substantially low when compared to Microreactors, whose cost of operation and initial investment are enormously huge.

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] Prof. Jun-ichi Yoshida, Heejin Kim, Dr. Aiichiro Nagaki. "Green and Sustainable Chemical Synthesis Using Flow Micro reactors". *ChemSusChem*. 2011, 4(3);pp.331-340.
- [5] Stamenković OS1, Veljković VB, Todorović ZB, Lazić ML, Banković-Ilić IB, Skala DU. "Modeling the kinetics of calcium hydroxide catalyzed methanolysis of sunflower oil". *Bioresource Technology*, June 2010, Vol 101, Issue 12, pp. 4423-4430.
- [6] F. Benaskar, A. Ben-Abdelmoumen, N. G. Patil, E. V. Rebrov, J. Meuldijk, L. A. Hulshof, V. Hessel, U. Krtuschil, J. C. Schouten. "Cost Analysis for a Continuously Operated Fine Chemicals Production Plant at 10 Kg/Day Using a Combination of Micro processing and Microwave Heating". *J. Flow Chem*. 2011, Vol2, pp.74-89.
- [7] Jan W. Swarts, Petra Vossenbergh, Marieke H. Meerman, Anja E.M. Janssen, Remko M. Boom. "Comparison of two-phase lipase-catalyzed esterification on micro and bench scale". *Biotechnol Bioeng*. 2008, 99(4), pp.855-61.
- [8] Amol A. Kulkarni, Klaus-Peter Zeyer, Thomas Jacobs, Achim Kienle. "Miniaturized Systems for Homogeneously and Heterogeneously Catalyzed Liquid-Phase Esterification Reaction". *Ind. Eng. Chem. Res*. 2007, 46 (16), pp. 5271-5277.