Reaction Performance in Micro and Milli Tubes

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Abstract—Mixing in micro sized devices enhances the performance of reactions, heat and mass transfer operations. This phenomena is due to the characteristics of small diameter, micro and milli tubes. The mixing of fluids in these small diameter tubes can be assessed by an identification number which is the ratio of hydraulic diameter of the tube to the characteristic length called Kolmogorov length. To demonstrate this, the esterification reaction of propionic acid with alcohol using sulfuric acid as catalyst was performed in the different sized micro and milli tubes of 0.7, 1.0, 2.0 and 3.0 mm diameter. The identification numbers obtained from the hydrodynamics have been compared with the performance of the reaction conversion in these tubes. In this study the number ranged from 4 to 13. For a particular flow rate, the performance as percentage conversion was better in the smaller diameter where the identification number is higher and lower in the larger diameter tube where the identification number is lower. The process reaction need not be restricted to micro tubes but can be extended to milli tubes up to 2mm. This helps bulk production without compromising much on the percentage conversion and facilitates ease of handling and easy fabrication of the micro/milli tubes.

Index terms-- esterification, identification number, micro tubes, propionic acid

I. INTRODUCTION

THE concept of performing unit operations in micro sized devices has gained importance during the last few years. Significant improvements in throughputs have been reported. These micro and milli size units have features like small volumes, high area, small size, low energy consumption. The main feature of these devices is their extremely large surface to volume ratio. The small dimensions in micro devices imply small Reynolds numbers and laminar flow so that mixing occurs by diffusion. Literature cites a number of studies on various aspects of flow, heat and mass transfer and also reactions in these micro tubes. The mass transfer performance data was obtained by monitoring the extraction of succinic acid from n-butanol to aqueous droplet containing sodium hydroxide [1].

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Mono dispersed aqueous droplets with average diameters of 130-550 μm were generated and mass transfer rate obtained was 10-1000 times higher compared to the traditional liquid-liquid systems. Probably the vortex flow pattern within the droplets generated during its formation stage must have enhanced the mass transfer rate greatly. The results of competitive-consecutive reaction of bromination reaction of dimethylphenol experimentally as in [2] showed that the product yield of primary reaction depend on two dimensionless numbers: the mixing-reaction number which is the ratio of the diffusion time to the reaction time in the chemical reactions and the ratio of the secondary reaction to the primary reaction rate. The product yield of primary reaction increased with decreasing mixing reaction number and decreasing reaction rate ratio. Reference [3] gives the performance of the transesterfication of sunflower oil with methanol in a micro tube reactor to form fatty acid methyl esters using potassium hydroxide as catalyst. By this reaction, they observed that the oil conversion was significantly affected by micro tube length, micro tube diameter, the methanol/oil molar ratio and reaction temperature. They examined the relationship between flow pattern and oil conversion. It has been observed [4] that in micro reactors the process development periods can be reduced and the process improvement can also occur. Direct synthesis of hydrogen peroxide from hydrogen and oxygen was investigated [5] using capillary and stacked micro reactors in which the silicone wall of a micro channel had been coated with Pd/C catalyst. Experiments have been conducted in smooth channels of varying cross sections and concluded that Navier–Stokes equations are valid for laminar flow in smooth channels [6]-[8]. It is stated in [9] that Reynolds number is a poor measure of the flow regime in a micro device therefore, they have reported an identification number to identify the different regimes, namely, laminar vortex and engulfment flows. Reference [10] reports a review of literature on single phase liquid friction factors and a data base has been generated to critically evaluate the available experimental data. It has been concluded that conventional Stokes and Poiseuille theories are applicable for single phase liquid flow in micro channels. New experimental data has also been presented and the pressure drop components have been analyzed. The predominant effect of uncertainties in geometry measurement on the experimental uncertainties was also demonstrated. A study on the flow in micro devices was evaluated and classified as slow speed flow by in [11]. Although a variety of reactions have been reportedly studied in micro-systems in the recent years there is still no clear understanding of conditions under which micro-reactors should be preferred. As reported in [12], at times the micro channel reactors will have several problems. During reactions big molecules and sticky substances like

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polymers may block and plug the channel. In addition, the rate of production per unit tube will be too low to realize any large quantity of the product and requires some precision in handling. Scanty information is available in milli tubes as compared to micro sized tubes. Hence, it will be worthwhile to do a comparative study of reaction performance in both micro and milli tubes. In this work, experimental studies were conducted in micro and milli tubes of different sizes, using the esterification reaction of propionic acid with methanol. The identification number obtained from the hydro dynamics within the tubes was compared with the percentage conversion of the reaction.

II. EXPERIMENTAL

The experimental set up consisted of a reaction tube connected to a T joint of 3 mm I.D and two precision peristaltic pumps to feed each of the reactants, methanol and propionic acid into the reactor tube. The pump outlets were connected to the T-join. Different sized straight sections ranging from micro to milli were used in the study. These two reactants were fed at different flow rate in the reactor tubes. The esterfication reaction occurred in the tube and the outlet liquid was collected for a predetermined time in a receiver containing known concentration and volume of sodium carbonate which was used to arrest the reaction. The contents of the receiver were analyzed for conversion of propionic acid to methyl propionate. It is to be noted that the volume of the milli and micro tube reactors were kept constant at 1.93 cm^3.

Following tube diameters along with their corresponding lengths were used: Diameter (D) in mm and Lengths (L) in cm of the tubes, (0.7, and 500), (1.0, 245), (2.0, 61.2) and (3.0, 27.2). Experiments were conducted with different flow rates in each of the tubes and the corresponding conversions were determined. The flow rate of methanol was varied from 1.3 to 3.0 x 10^{-2} cm^3/s and that of propionic acid from 0.125 to 0.36 x 10^{-2} cm^3/s. The combined flow rates, v_T (Methanol + Propionic acid) in cm^3/s were: 1.46 (1.3 +0.125), 2.42 (2.17 + 0.25) and 3.37 (3.0 + 0.36) x 10^{-2}. Sulfuric acid was used as the catalyst. The catalyst concentration, C_C in methanol was varied from 1.82, 1.15, 0.77 and 0.38 gmol/l. All the reactions were carried out at a temperature of 28°C and at ambient pressure.

III. RESULTS AND DISCUSSION

The results of all the runs are given in the Table 1. For a particular flow rate, the conversion increased with decrease in the diameter and increase in the catalyst concentration. This indicates that the mixing effect is more in lower diameters and this is due to stronger internal circulations present in micro tubes [13] that are characterized by slow flow. The linear fluid velocities are calculated from the volumetric flow rates and the cross sectional area of the tube. These are found to be of the order of 0.207 to 8.76 cm/s. The Reynolds number is less than 100 and falls in the laminar region. That is the coflow reactants retain their laminar flow pattern and mixing occurs only through inter-diffusion.

The pressure drop in the tubes, as reported [11], was calculated using the laminar flow expression

$$\Delta P = \frac{32\, L\, m\, V}{D^2} \qquad (1)$$

It is reported [10] that Re is a poor measure of the flow regime in micro tubes and channels. Instead an Identification number K has been derived which describes the mixing in the tube. K is the ratio of hydraulic diameter D and a characteristic length. This length represents the scale of the created vortices inside the channel and is described as the Kolmogorov length, λ_K. K is expressed as

$$K = \frac{D}{\lambda_K} = \left(\frac{D\,\Delta P\,\rho m}{\mu^3 V}\right)^{1/4} \qquad (2)$$

ΔP = pressure drop in the channel length, ρ = density of the reaction mixture, m = mass flow rare of the fluid μ = viscosity of the liquid and V = volume. K is evaluated from the pressure drop obtained in the micro tubes and is given in the Table along with the percentage conversion. Calculated values are in the range of 4 to 13 and fall under laminar flow and vortex flow regime. From the Table it can be inferred that the percentage conversion is good in small diameter micro tubes where the K value is higher, indicative of flow in the vortex regime and when K is small, the conversion is small. K increases with decrease in residence time which implies decrease in conversion as given in the Table. Figure1 gives the plot of percentage conversion against the residence time for the four tubes. The difference in conversion is large particularly in the case of large diameter tube of 3mm size compared to lower diameters. From this it can be inferred that milli tubes upto 2 mm can also be considered for carrying out the reactions. This helps bulk production without compromising much on the percentage conversion and facilitates ease of handling, less practical difficulties and easy fabrication of the micro/milli tubes.

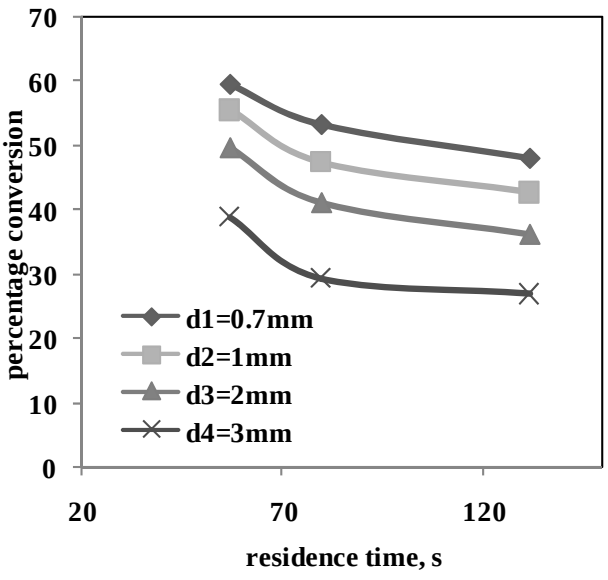

Fig. 1: Effect of tube diameter on percentage conversion

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IV. CONCLUSIONS

The identification number ranged from 4 to 13. For a particular flow rate, the performance as percentage conversion of the esterification of propionic acid with methanol in four different sized micro tubes was found to be better in the smaller diameter tubes where the identification number was higher and lower conversion in the larger diameter tubes, where the identification number was lower.

REFERENCES

[1]. H.H.Xu, J.Tan, S.W.Li G.S.Luo, "Enhancement of mass transfer performance of liquid-liquid system by droplet flow in micro channels," Chemical Engineering Journal 141242-249, 2008.

[2]. Tomofumi Shiraishi ,Takeyuki Kondo,Tsutomu Kawamura and Manashi Oda, "Experimental Verification of an Evaluation Method of Chemical Reactions by Dimensionless Numbers in Microchannels," Journal of chemical engineering of Japan 41,980-987, 2008.

[3]. Guoqing Guan, Katusuki Kusakabe, Kimiko Moriyama, and Nozomi Sakurai, "Transesterification of Sunflower Oil with Methanol in a Micro reactor," Ind. Eng. Chem.1357-1363, 2009.

[4]. Otto Worz, Klaus-Peter jackel, Thomas Richter, and Andrej Wolf, "Microreactors-A New Efficient Tool for Reactor Development, Chem.Eng.Technol," 2, 2001.

[5]. Maehara,S., M.Tundo and K.Kusakobe, Catalytic Synthesis of Hydrogen Peroxide in Micro reactors," Chem. Eng. Res.& Design 86, 4, 410-415, 2008.

[6]. J.Judy, D. Maynes and B. W. Webb, "Characterization of frictional pressure drop for liquid flows through microchannels," International Journal of Heat and Mass Transfer, 45, 3477-3489, 2002.

[7]. H.Y.Wu, P.Cheng," Friction factors in smooth trapezoidal silicon microchannels with different aspect ratios," International Journal of Heat and Mass Transfer, 46, 2519-2525 ,2003.

[8]. D. Liu and S.V. Garimella, "Investigation of liquid flow in microchannels," Journal of Thermophysics and heat transfer, 18, 1, 65-72, 2004.

[9]. Michael Engler, Norbert Kockmann, Thomas Kiefer, Peter Woias, "Numerical and experimental investigations on liquid mixing in static micro mixers," Chemical Engineering Journal, 101, 315-322, 2004.

[10]. Mark E. Steinke, Satish G. Kandlikar, "Single phase liquid friction factors in microchannels", International Journal of Thermal Sciences, 45, 1073-1083, 2006.

[11]. Bruce A. Finlayson, Pawal W. Drapala, "Microcomponent Flow characterization" Micro Instrumentation for High Throughput Experimentation and Process Intensification – a tool for PAT, Chapter 8,2007," Wiley-VCH Verlag GmbH and Co., KGaA, Weinheim.

[12]. Takafumi,H, Keisuke,N, Taichi,M, Kazuya,T and O.Naoto, "Lquid-Liquidlow of Millichannel with a Dynamic Mixer," Chemical Engineering and Processing, 50, 1-8, 2011.

[13]. Siva Kumar Reddy, Cherlo, Srinath Kariveti, S. Pushpavanam, "Experimental and numerical investigations of two phase (liquid-liquid) flow behavior in rectangular Microchannels," Industrial Engineering Chemistry Research, 49, 893-899, 2010.

Table1: Performance of reaction with K

v_T x 10^2, cm^3 / s	t, s	C_C, gmol/l	D, mm							
			0.7		1.0		2.0		3.0	
			K	% X	K	% X	K	% X	K	% X
1.46	131.8	1.82	8.77	59.7	7.33	55.5	5.18	49.8	4.31	38.8
		1.15		49.0		46.3		42.0		36.5
		0.77		44.4		41.9		38.7		34.7
		0.38		41.0		39.3		35.4		32.5
2.42	79.6	1.82	10.7	53.3	8.92	47.5	6.31	41.1	5.24	29.3
		1.15		42.7		38.8		34.5		28.4
		0.77		37.6		34.7		31.5		27.2
		0.38		34.2		31.7		28.8		25.7
3.37	57.1	1.82	12.4	48.1	10.4	42.7	7.33	36.2	6.09	26.8
		1.15		38.3		34.3		30.3		25.4
		0.77		34.3		30.9		27.3		24.1
		0.38		30.9		28.4		25.4		22.6

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