The Influence of Viscosity on Micromixing Process for Non-Newtonian Fluids

Dr. Rajab. A. Atibeni, Dr. Kamal M. Sassi, Dr. Mustafa T. Yagub Department of Chemical Engineering - Faculty of Engineering Zawia University

Abstract :

Viscosity of fluids has been considered as one of the most important parameters affecting the mixing process at the molecular scale. The aim of the paper is to investigate the influence of viscosity on micro-mixing of Non-Newtonian fluid by using fast parallel reactions and, different concentrations of HEC. The experiment was carried out in stirred tank of 0.476m diameter agitated by a Rushton turbine. It has been confirmed that precipitation reaction of NaOH and CuSO₄ as one of the two parallel competing reactions, is very efficient for such a study. This was confirmed as by product (X_Q) of parallel reactions varied with the feed time, stirred speed, feed position, viscosity and D_{av}. The experimental results show that; X_Q as a measure of the amount of by-product was increased with increasing HEC concentration and, decreases from position (1) to position (2) from

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position of low to high local energy dissipation rates and, also decreases with increasing agitation speed. And, the experimental results confirmed that, how much the viscosity has a direct influence on the micromixing of Non-Newtonian fluid.

Keywords: micromixing; viscosity; parallel reaction; Rushton turbine.

1-Introduction:

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Studying the influence of viscosity on the mixing at a molecular scale (micromixing) gives an indication of the best way to carry out many industrial applications important processes. in such as polymerization, and competing fast chemical reactions. The variations in viscosity do not influence bluck flow pattern^[1], velocity distributions, turbulent diffusivities, and energy dissipation rates. The fine-scale properties of the turbulence, below the kolmogorov scale, do, however, depend on viscosity. Thus micromixing, but not meso-and macromixing, should be influenced by viscosity changes. Some experimental results confirm the importance of the viscosity for micromixing controlled, competitive- consecutive reactions in semi-batch operation ^[1, 2]. And also several subsequent studies about the influence of viscosity on the product distribution of fast parallel reactions were carried out in stirred tanks ^[1, 3]. In all cases the viscosity has a direct influence on the micromixing and rising viscosity has two simultaneous effects. First, it slows down certain micromixing steps and, therefore, increases the corresponding micromixing times ^[4], the second effect alters the kinetics of the reaction. And also it may be expected in some cases a compensation effect as both micromixing and reaction rates are slowed down by viscosity that means rising viscosity caused increased segregation.

Recently, the influence of feeding location on the micro-mixing performance was studied experimentally using iodide–iodate reaction system ^[5]. The results showed that the feeding location has an important effect on the micro-mixing performance.

In the present work, influence of viscosity on the micromixing has been studied for Non-Newtonian fluid in a stirred tank equipped with Rushton turbine in order to get fast parallel reactions with different concentration of HEC, different feed position, and agitation speed.

2- Parallel competing reactions:

Parallel reactions usually consist of irreversible, second-order reactions of the following type:

$$\begin{array}{c}
 K_1 \\
 A+B \rightarrow P \\
 K_2 \\
 A+C \rightarrow Q
\end{array}$$
(1)
(2)

This reaction is usually instantaneously for example an acid-base neutralization or

Precipitation (k₁ $\approx 10^{7} \frac{3}{m \text{ mol}^{-1} \text{ s}^{-1}}$) with a second a slower one which still fast reaction

 $(k_2 \approx 0.033 \text{ m}^{3} \text{ mol}^{-1} \text{ s}^{-1}) (K_1 \gg K_2)$, e.g. the hydrolysis of an ester. The selectivity of product Q is defined as $X = \frac{Q}{P+Q}$ (3)

In perfectly mixed system, X would be determined by chemical kinetics ^[4] with the production of very little Q. On the other hand, if the reagents are completely segregated ^[6], X is controlled by molecular diffusion; however when there is a partial segregation on molecular scales X depend on chemical factors (reagent concentration, catalysis, etc.) and

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the physical conditions (viscosity of solution, feed location, mixing intensity, etc.)^[6].

Atypical parallel competing reactions is the competition between neutralization and alkaline hydrolysis of ester that was proposed by Bourne and Yu $^{[4,\,6]}$

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$k_2$$

$$NaOH + CH_2ClCOOC_2H_5 \rightarrow CH_2CLCOONa + C_2H_5OH$$
(4)
(5)

This test system has been extensively validated ^[7,8,9].

But in the present work, the neutralization reaction of equation (4) replaced by Precipitation equation (6) $^{[10]}$.

$$\frac{1}{2}$$
Cu²⁺ + OH⁻ $\xrightarrow{k_1} \frac{1}{2}$ Cu(OH)₂

(6)

The precipitation of cupric hydroxide is preferred since it is believed to be less complex, as well as strong coloration of cupric ions in water makes the simple colorimetric analysis possible ^[10]

3. Experimental details : 3.1. Reactions:

NaOH+0.5CuSO₄
$$\rightarrow$$
0.5Cu(OH) ₂↓+0.5Na₂SO₄ (7)
^{K2}
NaOH+CH₂ClCOOC₂H₅ \rightarrow CH₂ClCOONa+C₂H₅OH (8)

The selectivity is defined in term of the undesired product (Q) by equation (9),

$$X = \frac{Q}{P + Q} \tag{9}$$

In the present work, as in all the micromixing studies referred to in this study, a low value of the selectivity X corresponds to the most rapid mixing at fine scale, and the greatest yield of the usually desired product.

3.2-Stirred tank reactor :

Experiments have been carried out in a fully baffled tank with internal diameter and liquid height of to (0.476m), and the tank was equipped with six-bladed Rushton turbine whose diameter and off bottom clearance are (0.19m), (0.159m) respectively, and the turbine speed N varied from 45 to 225 r.p.m for 0% and 0.1% HEC and from 180 to 420 r.p.m for 0.5% HEC.

Two feed location, (1) (0.1m), below the liquid free surface and, (2) (0.159m) from the bottom of the tank which is located in to the impeller discharge flow.



Stirred Tank

Rushton Turbine

Fig. (1) Details of the tank and additional points

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3.3-Viscous solution :

Hydroxy ethyl cellulose (HEC) was chosen here among a number of possible additives ^[1], which has been successfully employed to raise the viscosity. It is superior to CMC. It has no influence on the rate constants. Also chemical analysis and the viscosity are less sensitive to pH than when CMC is employed ^[2, 11]. It exhibits Non-Newtonian behaviors. Figure (2) shows (0.5wt%) solution of HEC.



Fig (2) shear stress vs. shear rate of HEC solution (0.5wt% HEC and 298 k)

3.4-Precipitation of cupric Hydroxide (Reaction Mechanism)

When hydroxyl ions are in excess compared with copper (II) ions, the following reaction takes place:

 $Cu (OH)_2 \rightarrow CuO + H_2O \tag{10}$

On the other hand, when the hydroxyl ion concentration is insufficient, Cu^{2+} Complexes with OH⁻¹⁸.

$$2Cu^{2+} + 2OH \rightarrow [Cu_2(OH)_2]^{2+}$$
 (11)

And the following reaction occurs.

 $[\operatorname{Cu}_2(\operatorname{OH})_2]^{2^+} + \operatorname{SO}_4^{2^-} \to [\operatorname{Cu}_2(\operatorname{OH})_2] \operatorname{SO}_4 \downarrow$ (12)

3.5- Measurements of Copper Ion Concentration

It is well known that, cupric ions have strong coloration in water which makes it possible to measure their concentration by a simple spectrophotometric method. In this work, the concentration of cupric ions in solution was determined from the absorption at 800nm. At this wave length, the absorbance of cupric ions has a maximum value while the absorbance of all the other present species is zero.

Furthermore to measure copper ion concentration, a calibration curve is needed ^[12], and the linear dependence of the absorbance on cupric ion concentration in CuSO4 viscous solution is shown in Figure (3), the calibration curve of copper ion concentration can be accurately measured.



Fig (3) Calibration curve (wavelength 800 nm)

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Fig (4) Calibration curve for the viscosity

3.6 - Measurements of viscosity

To measure the viscosity of Non-Newtonian fluid, a calibration curve is required ^[11], and from the relation between the viscosity and, shear rates as shown in Figure (4), the viscosity can be accurately measured.

(13)

 $\gamma = K_s N$ K_s . Metzner constant = 11.5 for DT-6 γ - shear rate (1/s). N- speed (r.p.s).

3.7- Blank test

A certain amount of copper will be left in the solution after the reaction being completed. This amount can be determined by means of (blank reaction runs), which are performed exactly as the usual runs, except that only the precipitation reaction is involved ^[12]. A sample of the reacted mixture was first centrifuged at 5000r.p.m for 20min in order to remove the

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precipitate. The residual copper concentration in the solution was then determined spectrophotometrically. The amount of copper precipitated as: (C_{12}, C_{12})

 $(Cu_2\,(OH)\,So_2)_{\,4}\,$ can be calculated by the following equation:

$$B_2 = B_0 - B_1 - B_S$$

(14)

Where B_2 is the amount of copper precipitated as $(Cu_2(OH)_2)So_4$, (mol); B_0 is the total copper in the feed, (mol); B_1 is the copper precipitated as $Cu(OH)_2$, (mol); and Bs the copper left in the final solution, (mol). B_1 and Bs can be obtained from Equation (15) and (16) respectively:

$$B_1 = A_0/2$$
 (15)
 $B_s = C_s * V_T$ (16)

Where Cs is the copper ion concentration in the final solution, (mol); V_T is the volume of the final solution (L).

$$\mathbf{f} = \mathbf{B}_2 / \mathbf{B}_0 \tag{17}$$

Where f is the factor of copper ion lost due to side reactions. In the present work, (f) is different for different (HEC) Concentration (0%, 0.1%, 0.5%), f =0.2, 0.26, 0.29 respectively and the absorbance of the solution at the end of the blank experiment is Abs_b , and the absorbance before and after the introduction of NaOH in a normal experiment are Abs_1 and Abs_2 respectively. In this case, the selectivity X in equation (9) can be simply expressed as;

$$X = \frac{Q}{P+Q} = \frac{Abs_2 - Abs_b}{Abs_1(1-f) - Abs_b}$$
(18)

4-Experimental Results and Discussion:4.1- Influence of injection time:

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This parameter is known to be as critical: If the injection time is too short in relation to the reaction time and the micromixing time, the value of X_Q becomes a function of the feeding rate due to mesomixing ^[12,13,14] that

means X_Q increase with decreasing injection time and, X_Q decrease with increasing injection time until becomes stable in this case the critical time (t_c) in the present work for (0.5%HEC) and, agitation speed (3 r.p.s) is 2500s and, Figure (5) showed micromixing control of X_Q at sufficiently long feed time.



Fig (5) Influence of injection time on XQ for 0.5% HEC at position (2) and N= (3 r.p.s)

4.2- Effect of turbine speed and Feed position:

Figure (6) shows X_Q decreases with increasing turbine speed and, there for, with increasing mean specific energy dissipation rate as expected $^{[14,15]}$.In this work Figure (6) compares X_Q for different speeds, feed position and, (0%, 0.1%, 0.5%) HEC concentration. Thus, for each speed, X_Q decreases in going from position (1) to position (2), i.e. from position of low to high local energy dissipation rates, position (2) in the impeller discharge; this feed position has very good micromixing. Figure (6) shows that X_Q different for different speeds and feed positions. The same observation for different HEC concentration is noticed.



Fig (6) Influence of turbine speed and feed position on XQ, $t_f = 3480s$

4.3-Effect of HEC Concentration:

Figure (7) shows X_Q values for different stirrer speed, different HEC concentrations (0%, 0.1%, 0.5%) respectively, at the feed position (2). The higher concentration of HEC, the higher value of X_Q , that means, micromixing becomes less efficient when viscosity increases, and also if we looking to the kinetics of the two reactions it would be observed that, when the viscosity increase the precipitation reaction decreases and, the rate of the second reaction increased. Therefore, fewer products are produced and, high by product when the viscosity increased. I.e. X_Q = (0.011, 0.14, 0.23), at (0%, 0.1%, 0.5%) HEC concentrations for the same feed position and the same speed (3r.p.s).

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Fig (7) influence of HEC concentration on X_Q at position (2), and (t_f=3480s)

4.4-Variation of XQ with D_{av} at Different HEC concentration:

Figure (8) shows that Da_{av} increases with increasing viscosity i.e. Da = (0.27, 0.6, 2.86) for (0%, 0.1%, 0.5%) HEC respectively and also at high value of Da_{av} , X_Q was tending to wards. As Da_{av} increases X_Q first increases up to a maximum value then failing to wards. At high Da_{av} , all reactions become instantaneous relative with mixing.



Fig (8) XQ vs. Damkohler number (Da_{av})

Conclusion:

Influence of the viscosity on the micromixing of Non-Newtonian fluid has been studied using Rushton turbine at different speed, different feed positions and, different HEC concentrations (0%, 0.1%, 0.5%) respectively. The experimental results show X_Q decreases with increasing feed time then it becomes constant that means micromixing is a controlling mechanism. Also for feed position (1) and (2) at the same speed, the value of X_Q is much lower at the feed position (2). These findings show clearly the advantage of the feeding at the impeller discharge flow and also for different viscosities. Also, the results confirmed that the viscosity has a significant influence on the micromixing particularly for Non-Newtonian fluid at 0.1%, and 0.5% HEC concentrations.

Nomenclature:

 of NaOH in a normal experiment Abs₂ the absorbance after the introduction of NaOH in a normal experiment Abs_b the absorbance of the solution at the end of the blank experiment B₀ the total copper in the feed, mole
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end of the blank experimentB₀ the total copper in the feed, mole
\mathbf{B}_{0} the total copper in the feed, mole
\mathbf{B}_1 the copper precipitated as Cu(OH)2,
Mole
B ₂ the amount of copper precipitated as
$[Cu_2(OH)_2]SO_4$, mole
$\mathbf{B}_{\mathbf{s}}$ the copper left in the final solution,
mole
C_s the copper ion concentration in the
Final solution, M

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f	the defined factor in equation (18)
	(f=0.2, 0.26, 0.29 in this work)
k	reaction rate constant
P, Q	reaction products
$\mathbf{V}_{\mathbf{T}}$	the volume of the final solution, m^3
Dav	Damkohler number
t _f	feed time, s
t _c	Critical time (s)
Ks	Metzner constant = (11.5) , for Rushton turbine
γ	Shear rate (1/s)

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