Kinetics Modeling of Free-Radical Polymerization on Spinning Disk Reactor

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Abstract—**Spinning disk reactor (SDR) technology reportedly achieves significant enhancements in free radical polymerization rates. The effect on those rates has been attributed to the unique hydrodynamic environment experienced by the reacting polymer films. The rotating surface of SDR promotes extension of the polymer chains, which prevents the propagating chains from terminating through bimolecular reactions. In this work, a numerical simulation is applied to investigate how reduced rates of termination would affect time conversion behavior of free radical initiated styrene polymerization. Comparisons have been made between model predictions and SDR experimental results. The closeness of predicted and experimental results indicates strong evidence that the hydrodynamic regime created on the surface of a SDR can lead to reduced rates of bimolecular termination.**

Index Terms—**Polystyrene polymerization, spinning disk reactor, termination rate constant**

I. INTRODUCTION

The spinning disk reactor (SDR) technology proposes an alternative approach through a step change in manufacturing several operations, most notably with respect to the ability to cope with very fast chemical reactions such as polymerization, crystallization, and competing fast chemical reactions. The technology creates highly sheared thin liquid films which feature superior heat/mass transfer properties. The short diffusion and conduction path length achievable by the very thin films creates the basis for the very high transport rates within the film.

SDR technology has been successfully used for a range of procedures including free-radical and cationic polymerization processes [3] and organic catalytic reactions [7].

The improved product quality including high selectivity and narrow crystal size/molecular weight distributions observed in these processes, are directly influenced by the micromixing intensity in the process liquid. However, so far no comprehensive study of micromixing in SDR thin films has been performed. Here, we study the hydrodynamic conditions for which the SDR film gives the best micromixing efficiency and evaluate its micromixing performance in comparison to other reactor systems. It is assumed that the centrifugal forces and divergent nature of the reacting film on the spinning disc provide conditions which minimize the termination of the macro radicals,

resulting in great increments in the polymerization rate. The experimental data in this study are derived from a previous research carried out by Moghbeli and collaborators [5]. Experimentally, the bulk free-radical polymerization of styrene was carried out on a disc surface at 70°C with 2, 2-azobi- sisobutyronitrile (AIBN) as the initiator.

II. MODEL FORMULATION

Production, consumption, and diffusion in the mass balance equation don't have important role in the total equation due to constant total mass. Therefore mass fraction can be shown as following equation:

TABLE I: KINETICS CONSTANT FOR POLYSTYRENE WITH AIBN AS AN INITIATOR [6].

$K_{P_0}\left(\dfrac{L}{mole.\min}\right)$	$6.128\times10^8\ \exp\left(-\dfrac{7068}{RT}\right)$
$K_{t_0}\left(\dfrac{L}{mole.\min}\right)$	$7.55\times10^{10}\ \exp\left(-\dfrac{1677}{RT}\right)$
$K_d\ \ (\min^{-1})$	$12\times10^{16}\ \exp\left(-\dfrac{30714.02}{RT}\right)$
$R\left(\dfrac{Cal}{mole.K}\right)$	1.987

$$\left[(\rho U_r A)_r - (\rho U_r A)_{r+dr}\right] + \left[(\rho U_z S)_z - (\rho U_z S)_{z+dz}\right] + \left[(\rho U_\theta A)_\theta - (\rho U_\theta A)_{\theta+d\theta}\right] = acc. \tag{1}$$

With extension of Taylor series, the Equation 1 changes to following equation:

$$-\frac{\partial(\rho U_r A)_r}{\partial r}dr - \frac{\partial(\rho U_z S)_z}{\partial z}dz - \frac{\partial(\rho U_\theta W)_\theta}{\partial \theta}d\theta = \frac{\partial(\rho rd\theta dz dr)}{\partial t} = \frac{\partial m}{\partial t} \tag{2}$$

If we suppose to ρ is constant the above equation will be converted to:

$$\frac{U_r}{r} + \frac{\partial U_r}{\partial r} + \frac{1}{r}\frac{\partial U_\theta}{\partial \theta} + \frac{\partial U_z}{\partial z} = 0 \tag{3}$$

The continuity equation of mole fraction in cylindrical coordinates is formulated as:

$$\frac{\partial C_i}{\partial t} + (U_r\frac{\partial C_i}{\partial r} + U_\theta\frac{1}{r}\frac{\partial C_i}{\partial \theta} + U_z\frac{\partial C_i}{\partial z}) = D_{iM}\left[\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial C_i}{\partial r}) + \frac{1}{r^2}\frac{\partial^2 C_i}{\partial \theta^2} + \frac{\partial^2 C_i}{\partial z^2}\right] + \Re \tag{4}$$

Equation 4 can be simplified with some assumptions such

as no potential difference in z axis, and angular symmetry which explained briefly in previous literatures [8]. Therefore, with substituting Newtonian residence time and radial velocity model, the mass balance model changes to following equation:

$$\frac{\partial C_i}{\partial r} + C_i r^{\frac{1}{3}} \left[\frac{-K_p \sqrt{\frac{2fK_d[I]_0}{K_t} \cdot e^{-k_d \frac{t}{2}}}}{\left(\frac{\omega^2 \phi^2}{12\pi^2 \upsilon}\right)^{\frac{1}{3}}} \right] = 0 \qquad (5)$$

If:

$$r = r_i \rightarrow C_i = C_{input} \qquad (6)$$

Then:

$$A = K_p \left(\frac{2K_d f}{K_t}\right)^{\frac{1}{2}} [I]_0^{\frac{1}{2}}$$

$$B = \left(\frac{\omega^2 \phi^2}{12\pi^2 \upsilon}\right)^{-\frac{1}{3}} \qquad (7)$$

Therefore:

$$C_i = C_{input} \exp$$
$$\left[\frac{2A}{K_d} \left[\exp(-\frac{3Bk_d}{8}(r_0^{\frac{4}{3}} - r_{in}^{\frac{4}{3}})) - 1 \right] \right] \qquad (8)$$

The conversion equation can be shown as

$$\ln \frac{C_i}{C_{input}} = \ln(1-x) \qquad (9)$$

And the final conversion equation should be as

$$x = 1 - Exp\left[\left[-2K_P \sqrt{\frac{2f[I]_s}{K_t K_d}} \right] \left[1 - Exp\left((-0.5K_d)\left(\frac{81\pi^2 \mu}{16\omega^2 \phi^2 \rho}\right)^{\frac{1}{3}} \left(r_o^{\frac{4}{3}} - r_i^{\frac{4}{3}}\right) \right) \right] \right] \qquad (10)$$

Equation 10 provides the estimation of operational condition and rotational speed in Newtonian fluid which is in agreement with leveson et al., [6]. Table I shows the kinetics parameters which presented by Arrhenius equation.

III. RESULTS AND DISCUSSIONS

The modeling of polymerization in spinning disk in this study has been divided into hydrodynamics and mass sections. This is because of increase in viscosity in one side and use of bulk polymerization in the other side which results into gel effect. The gel effect must be taken into account for free radical polymerization reactions with high conversions, where the termination reaction becomes controlled by diffusion, and the effective constant for termination decreases considerably with the increase of the monomer conversion. Experimental results obtained in a

spinning disc reactor for styrene polymerization can be seen in Fig. 1 in terms of conversion [5]. In Fig. 2 and Fig. 3, the experimental data were employed in mechanistic model previously proposed [4, 8] for estimation of model parameters. MATLAB Software package was used for both modeling and parameters estimations. As the reaction time on a SDR is very short the steady state assumption cannot be applied. SDR model employed in this study accommodate this fact. Fig. 2 is an important result in hydrodynamic section. The graph shows the downward trend in residence time due to rotational disc speed. This a normal behavior due to higher centrifugal force caused by disc speed increase. The other result is related to concentration. In other words, more concentrated fluid resulted to higher viscosity.
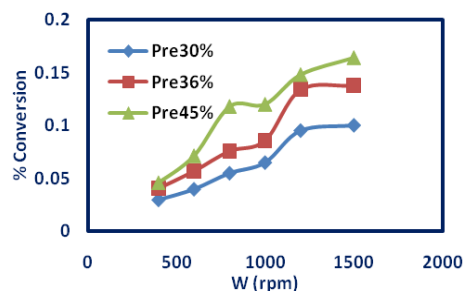

Fig. 1. Rotational disc speed influence conversion of styrene polymerization [5].

Fig. 3 shows a definite decrease in kinetic constants obtained from predicted model which agree with experimental data [5]. Data obtained experimentally were used to estimate rate constants that will prompt in high increase of conversion over short residence time. This is attributable to higher rate constants k_t for bulk polymerization in the SDR as indicated by values estimated in modeling studies (Fig. 3). As can be seen in the Fig, an increase in prepolymer concentration bring to sharp decrease in kinetics constant with 3 to 4 order for termination constant k_t which is in agreement with leveson work [6]. It should be mentioned that Hamielec predicted decrease trend in k_t previously [1], [2].
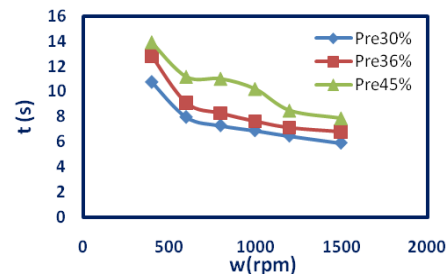

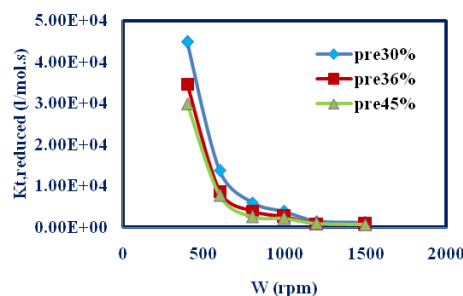Fig. 2. The effect of rotational disc speed on residence time

Fig. 3. The influence of rotational disc speed on kinetics constant (kt)

IV. NOMENCLATURE

ν $\left(m^2/s\right)$ kinematic viscosity

$V_r (m/s)$ Velocity in the radial direction

$V_\theta (m/s)$ Velocity in the tangential

$V_z (m/s)$ Velocity in the axial direction

μ $(pa.s)$ Viscosity

ρ $\left(kg/m^3\right)$ Density

ω (rad/s) Rotational speed

r (m) radial

$\phi \left(m^3/s\right)$ Flowrate

t (s) Time

m (kg) Mass of fluid

t_{res} (s) Residence time

$\Re$ $\left(mole.m^{-3}s^{-1}\right)$ Rate

K_p $\left(m^3/mole.s\right)$ The kinetic rate constant of propagation

K_d $\left(s^{-1}\right)$ The kinetic rate constant of initiator dissociation

K_t $\left(m^3/mole.s\right)$ rate constant of termination

$[I]$ $\left(mole/m^3\right)$ Initiator concentration

χ Changing conversion

R $\left(Cal/mole.K\right)$ Univesal gas constant

C $\left(mole/m^3\right)$ Concentration

o,i outlet,inlet

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