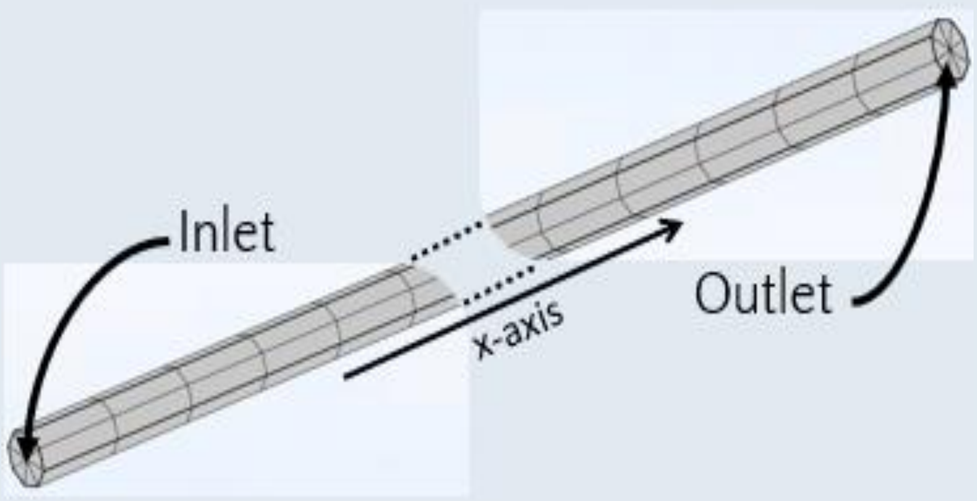
Improved CFD Simulation of Free Radical Polymerization in a Flow Microreactor with additional reaction steps



Simulate free radical polymerization in a flow microreactor to closely mirror real world conditions by implementing variable density, viscosity and new transformation to implement additional reaction steps.

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Abstract

Our research employs Computational Fluid Dynamics (CFD) simulations to understand this complex problem in a flow microreactor. It is a highly coupled problem of heat transfer, mass transfer, momentum transfer and chemical reaction. The numerical model is based on a kinetic scheme that includes eight elementary reaction steps instead of four. Quasi steady-state assumption have been applied to live polymer radical chain length distribution. Transfer to solvent step is considered to obtain improved result. Additional transformation to implement these steps have been proposed and applied to make the mathematical model dimensionless in terms of concentration and normalizing various variables. Results have been obtained for both variable and constant thermophysical properties.

Methodology

Initiator decomposition	$I \xrightarrow{K_d} 2R_0$
Initiation	$R_0 + M \xrightarrow{K_i} R_1$
Propagation	$R_n + M \xrightarrow{K_p} R_{n+1}$
Termination by combination	$R_n + R_m \xrightarrow{K_{tc}} P_{n+m}$
Termination by disproportionation	$R_n + R_m \xrightarrow{K_{td}} P_n + P_m$
Transfer to monomer	$R_n + M \xrightarrow{K_{fm}} R_1 + P_n$
Transfer to solvent	$R_n + S \xrightarrow{K_{fs}} R_1 + P_n$
Transfer to CTA	$R_n + A \xrightarrow{K_{fa}} R_1 + P_n$

FIGURE 1. Kinetic Scheme for Free Radical Polymerization

Based on the kinetic scheme for the free radical polymerization following new transformations were introduced,

For concentration terms,

Initiator, $I' = \frac{I}{I_0}$ Monomer, $M' = \frac{M}{M_0}$ Solvent, $S' = \frac{S}{S_0}$ CTA, $A' = \frac{A}{A_0}$

For kinetic rate coefficients, $K'_d = K_d;\ K'_{pr} = K_{pr}.\sqrt{I_0.M_0};\ K'_t = K_t M_0$

For kinetic rate coefficient ratios,

$$R'_{MM} = R_{MM}.\left(\frac{M_0}{I_0}\right) = R_M.\frac{M'}{M'}.\left(\frac{M_0}{I_0}\right);\ R'_{SM} = R_{SM}.\left(\frac{M_0}{I_0}\right) = R_S.\frac{S'}{M'}.\left(\frac{S_0}{I_0}\right)$$

$$R'_{AM} = R_{AM}.\left(\frac{M_0}{I_0}\right) = R_A.\frac{A'}{M'}.\left(\frac{A_0}{I_0}\right);\quad R'_P = R'_{MM} + R'_{SM} + R'_{AM} = R_P.\left(\frac{M_0}{I_0}\right)$$

Result & Future Work

1. Verify the simulation result for with and without transfer to solvent at higher residence time and constant thermophysical properties
2. Implement variable diffusivity through AK model for gel, cage and glass effect using COMSOL livelink for MATLAB.
3. Run the simulation for different monomers (Butyl Acrylate, Butyl Methacrylate, Styrene) and verify the result with the experimental result of $Iwasaki$[1].

			Without Transfer to Solvent (% relative error)			With Transfer to Solvent (% relative error)		
Residence Time	**Thermophysical Properties**	**f0**	**Conversion (%)**	**MW_n**	**PDI**	**Conversion (%)**	**MW_n**	**PDI**
2.5 min	**Variable**	**1**	16.7% (-21.2%)	9236.13 (-5.8%)	1.99 (8%)	16.7% (-21%)	9055.40 (7.6%)	1.99 (8%)
1.2 min	**Constant**	**1**	8.9% (-30.5%)	9661.54 (3.9%)	1.99 (8.3%)	9.1% (-28.9%)	9460.40 (1.7%)	1.99 (8.3%)
	Variable	**1**	9.1% (-28.9%)	9644.60 (3.7%)	1.99 (8.3%)	9.3% (-27%)	9440.26 (1.5%)	1.99 (8.3%)

REFERENCES

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