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Fluid Dynamics and Transport Phenomena

Modeling and experimental studies of methyl methacrylate polymerization in a tubular reactor☆

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ABSTRACT

In this study, rheological examination of the mixture of a tubular reactor in which methyl methacrylate was polymerized has been studied. The *n* (flow behavior index) value of Power Law Model of mixture contained in the reactor has been determined within the span of 0.3492 to 0.9889 by curve fitting. Employing these numerical data for velocity profile, the reactor has been modeled. Moreover, the functions of the reactor have been compared in the three modes of plug, mixed and laminar flow. The results obtained in this research indicate that the polymethyl methacrylate mixture contained in the reactor is pseudo-plastic. Moreover, as the conversion grows, the velocity profile starts as a parabolic profile and approaches the plug mode; although it never reaches the plug. The other conclusions borne in this study indicate that when the reactor's radius is decreased, the conversion rate grows. However, as decreasing the radius would also reduce the productions rate, this procedure is not economical. Finally, in this modeling, the amount of conversion is equal to 56.47% at the end and according to its laboratory proportion which is 55.88%, it has reached the conclusion that the modeling duly undertaken is applicable and valid.

1. Introduction

Tubular reactors are often used in processes of large scales in chemical industries as they are easy to maintain and have higher rate of converting raw materials in reactors' volume unit in grade n reactions than other reactors of continuous systems [1]. Polymerization reactions are one of the most central reactions occurring in these reactors. In these types of reactions, monomers are inserted into the reactors with a predetermined concentration. After the residence time span, these monomers are emitted as a mixture of polymers and residues of monomers. One of the most important reactions of this type is the polymerization of methyl methacrylate which results in producing Polymethyl methacrylate, one of the most commonly used industrial polymers [2].

In tubular reactors, many measures and values affect the conversion rate. The type of fluid flow and velocity profile of substances in the reactor are one of the most central measures [3,4]. Rheological models can be employed to study the velocity distribution and the behavior of fluids; Power Law Model is one of the most commonly used models. The n value (flow behavior index) is one of the most essential and effective outputs of velocity profile equation of Power Law Model. As this value changes in the laminar flow, the velocity profile is also modified and as a result, the products yielded have different conversion [5].

Many experimental studies of the polymerization of methyl methacrylate and the modeling of tubular reactors have been conducted formerly [3,6–11]. Looking through these studies, it has been indicated that the flow has been usually considered uniform - like plug - in the former set of researches. Or in the other studies, that the Power Law Model has been employed to examine the viscosity, the values n and k have been kept constant. As far as the hypotheses of previous experiments are considered to be the deficiencies of modeling, evaluating and calculating the mixture's velocity profile through rheological models with different values and attaining such a profile within different lengths of a reactor are of high value. Thus, the above-mentioned procedure increases the precision of mass balance calculations and modeling.

In this study, at the outset it has been studied the plug and mixed patterns and their conversion rates. The pattern of fluid flow is then assumed to be the laminar flow. Through rheological examination of the reactor's mixture using a rheometer, the n value of the Power Law Model has been attained at different sections of the selected reactor. Using these numerical data, modeling has been carried out and conversion rate has been calculated. Moreover, the functions of the reactor have been compared in three modes of plug, mixed and laminar flow. As a final point, the precision of the modeling has been evaluated through comparing the conversion rate of the modeling and its laboratorial corresponding quantity.

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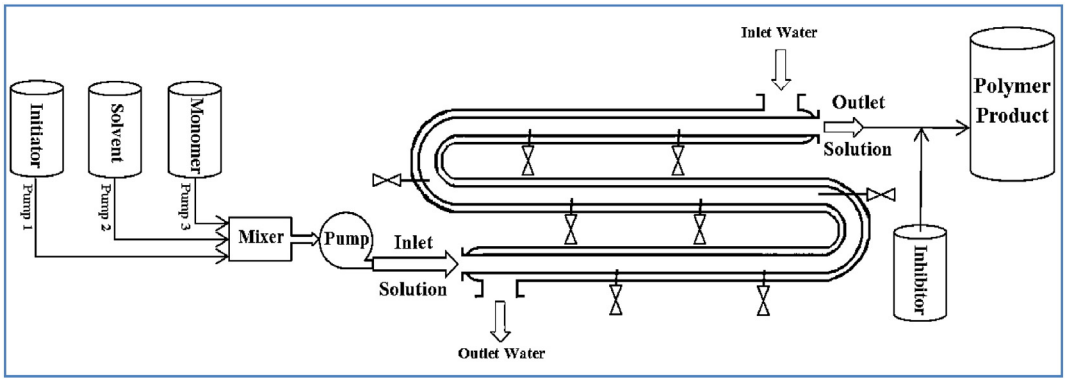

Fig. 1. The pilot-plant tubular reactor.

2. Experimental

2.1. Materials and equipment

The pilot-plant polymerization reactor is shown in Fig. 1. The reactor tube has an inside diameter of 32 mm and a total length of 5.4 m. The tube is entirely made from 316 stainless steel. The reactor tube is jacketed by water to control the temperature of the reactor. The reactor pressure can be controlled using a pressure control valve. The reactor additionally has eight sampling points that are located along the tubular reactor at lengths 0.6, 1.2, 1.8, 2.4, 3, 3.6, 4.2, and 4.8 m. The following reagents were used in the experiments: MMA (99%, supplied by Lancaster Ltd., UK), xylene (99%, supplied by Fisher Scientific UK), and BPO (97%, supplied by Merck Germany). The MMA was stabilized with hydroquinone as inhibitor. All the materials were used without further purification, which conforms to typical industrial practice.

2.2. Pilot-scale polymerization studies

Operating conditions used in the polymerization experiment is summarized in Table 1. Before being fed to the reactor, BPO/xylene solution and MMA were degassed separately by purging the liquids with Argon for 12 h. Initially, the reactor contained pure xylene at a temperature of 70 °C, thus depicting a typical start-up situation. The reaction was initiated by the continuous flow of MMA, xylene and BPO into the reactor, which was considered as time zero of the polymerization experiment. The flow rate from each pump was set to achieve the desired reactant concentration. For running the experiment, the reaction was conducted over 3 h with the temperature maintained at 70 °C. During the polymerization, aliquots were taken from the eight sample ports along the reactor length every 20 min. Samples were quenched in a solution of cold xylene and inhibitor, and precipitated by adding an excess methanol. Monomer conversion was thus determined by the direct gravimetric method.

Precipitation of the polymer was achieved through the drop-wise addition of the stored polymer mixture to a stirred mixture of 10 times its volume of methanol. The precipitate was filtered (Whatman, Grade 1) and finally dried in a vacuum oven at 100 °C until constant weight. From the weight of the dry polymer the conversion was determined gravimetrically based on the initial concentration of the polymerization mixture. The experimental results for conversion are shown in Table 2.

Table 1
Operation conditions of the reactor

Length of the reactor (L)	5.4 m
Inside radius of the reactor (R)	0.016 m
Input monomer (MMA)	50 cm^3
Input solvent (xylene)	60 cm^3
Monomer feed concentration (C_{m0})	4.15455 $mol/\cdot L^{-1}$
Feed flow rate (Q)	0.402×10^{-6} $m^3 \cdot s^{-1}$
Residence time (t)	180 min
Reaction temperature (T)	70 °C
Pressure (P)	0.1 MPa
Average velocity of mixture ($\overline{u}_z$)	$\overline{u}_z = \frac{L}{t} = \frac{5.4}{10800} = 5 \times 10^{-4}$ $m \cdot s^{-1}$
Water flow rate (Q')	2.19307×10^{-7} $m^3 \cdot s^{-1}$
Water inlet temperature (T')	10 °C

Note: It is assumed that the mixture inside flow the reactor is laminar, steady and axial symmetry.

Table 2
The experimental results of axial conversion in laminar flow

Sample	Residence time/min	Length/m	Conversion/%
0 (inlet)	0	0	0
1	20	0.6	5.89
2	40	1.2	12.92
3	60	1.8	21.49
4	80	2.4	31.11
5	100	3	42.72
6	120	3.6	50.55
7	140	4.2	55.05
8	160	4.8	55.50
9 (outlet)	180	5.4	55.88

2.3. The rheological analysis of the reactor's content mixture

In order to analyze the mixture contained in the reactor, the Physica MCR 301 rheometer is used. This rheometer has two plates which are 25 mm in diameter and parallel to each other. The lower plate - which is fixed - is designed for placing the sample in and the upper plate - which is moveable - for shear stress procedures. The inner temperature of the chamber in the rheometer is kept constant at 70 °C (±0.1 °C) using a compressor. In order to draw the flow curve, a thin layer of the sample is placed on the fixed plate while the moveable plate moves toward the fixed one and is set by 0.8 mm distance from the lower plate. A schematic illustration of the rheometer is presented in Fig. 2.

In this experiment, the flow curve is drawn within an extensive shear rate ranging from 0.1 to 100 s^{-1}. It is worth taking into consideration that no phase transition has occurred in the rheometer and the flow curve measurements have been carried out three times.

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