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Molecular size distribution in synthesis of polyoxymethylene dimethyl ethers and process optimization using response surface methodology

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HIGHLIGHTS

- Theoretical analysis of $PODE_n$ molecular size distribution (MSD) was performed.
- The MSD model was based on a sequential reaction mechanism.
- The MSD model follows the Schulz–Flory distribution.
- Response surface methodology was used to optimize the MSD.

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ABSTRACT

Polyoxymethylene dimethyl ethers ($PODE_n$, $CH_3O(CH_2O)_nCH_3$, where $n \geqslant 1$) are ideal diesel fuel additives. Among the $PODE_n$ compounds, $PODE_{3-5}$ have the best properties as diesel additives. A theoretical analysis of the molecular size distribution of $PODE_n$ synthesized from dimethoxymethane (DMM) and paraformaldehyde (PF) was performed based on a sequential reaction mechanism. The molecular size distribution model follows the *Schulz–Flory* distribution, and showed a good prediction ability at different reaction temperatures (T) and DMM/CH_2O mole ratios (M), which verified the sequential reaction mechanism during the formation of $PODE_n$. The product distribution was optimized using the molecular size distribution model and response surface methodology (RSM). At optimum operating conditions of $T = 105$ °C and $M = 1.1$, the conversion of formaldehyde X_{CH_2O} has a high value of 92.4%, and the fraction of $PODE_{3-5}$ in the $PODE_n$ mixture is 33.2 wt%, while the fractions of $PODE_{n>5}$ and $PODE_2$ are 9.4 wt% and 24.3 wt%, respectively.

1. Introduction

Polyoxymethylene dimethyl ethers ($PODE_n$, $CH_3O(CH_2O)_nCH_3$, where $n \geqslant 1$) are receiving much attention as ideal diesel fuel additives, which could significantly reduce the smoke and engine exhaust emissions during combustion [1,2]. The production of $PODE_n$ from C1 chemicals, like methanol and formaldehyde, can fully utilize the large surplus of C1 chemicals [3], alleviate the diesel supply crisis, and thus bring enormous economic and environmental benefits.

The studies on the synthesis of $PODE_n$ are very limited in the literature, and most of them are experimental studies on the synthesis reaction [4–8]. Zhao et al. [4] studied the synthesis of $PODE_n$ from methanol and trioxymethylene using molecular sieves as catalysts. In this system, water is produced during the formation of methylal. Because water reacts with formaldehyde and $PODE_n$, the side reactions are notable in this reaction system and make the product purification process very complex [5]. To avoid this problem, Burger et al. [5,6] investigated the synthesis of $PODE_n$ from dimethoxymethane (DMM, namely $PODE_1$) and trioxymethylene, and obtained 23.6 wt% yield of $PODE_{3-4}$. However, trioxymethylene is more expensive as a source of formaldehyde and more prone to form $PODE_{n>5}$ compounds, compared with paraformaldehyde (PF) [8]. In our previous work, we reported the synthesis of $PODE_n$ from dimethoxymethane (DMM) and PF over cation exchange resins [8]. Under optimized conditions, the conversion of formaldehyde was 85.1%, and the fraction of $PODE_{3-5}$ in the product was 36.6 wt%.

In the $PODE_n$ compounds, only the $PODE_{3-5}$ compounds are ideal diesel additives, because $PODE_2$ does not fulfill the security criterion due to its low flash point, and $PODE_{n>5}$ precipitate at low temperatures due to their high melting points [2,6]. Therefore, the $PODE_2$ and $PODE_{n>5}$ compounds need to be separated and

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Nomenclature

$N_{CH_2O,e}$	equilibrium amount of formaldehyde (mol)	$N_{CH_2O,R}$	the amount of reacted formaldehyde
k_p	reaction rate constants of the forward reactions (s^{-1})	M	DMM/CH_2O molar ratio
k_d	reaction rate constants of the reverse reactions (s^{-1})	X_{CH_2O}	equilibrium conversion of formaldehyde
$N_{1,e}$	equilibrium amount of DMM (mol)	a_e	dimensionless factor
$N_{n,e}$	equilibrium amount of $PODE_n$ (mol)	n	polymerization degree of $PODE_n$
$N_{1,0}$	initial amount of DMM (mol)	w_n	mass fraction of $PODE_n$

recycled to the reactor in an industrial process [6]. The overmuch production of $PODE_2$ or $PODE_{n>5}$ would significantly increase the energy cost. When recycled into the reactor, a portion of $PODE_{n>5}$ reacts with formaldehyde and forms larger $PODE_n$ compounds, leading to a complicated separation and recycling process. Therefore, it is of great importance to study the molecular size distribution of $PODE_n$ and optimize the process conditions to improve the molecular size distribution.

The molecular size distribution is most studied in polymer chemistry. Knowledge of molecular size distribution is significant not only for inferring the properties of polymers [9], but also for a better understanding of the reaction mechanism [10]. The Schulz–Flory (SF) distribution [11–13] and Poisson distribution [14–16] are the most widely used theoretical molecular size distributions. Generally, the SF distribution is based on the precondition of constant probability of chain growth [17]. In addition to its wide applications in conventional processes like polycondensation and free radical addition polymerization processes, the SF distribution is also used in Fischer–Tropsch synthesis [18–20] and carbon nano-tube (CNT) preparation [21]. The other theoretical molecular size distribution, namely Poisson distribution, is considered to be a fundamental distribution for the conventional living polymerization [10,22]. The living polymerization refers to a polymerization of organic molecules when termination is avoided but the true equilibrium is not reached [23]. Zhao et al. [24] found that the product distribution follows the SF distribution during the synthesis of $PODE_n$, but did not derive the molecular size distribution model based on reaction mechanism.

The response surface methodology (RSM) is a collection of statistical and mathematic techniques, and has been widely used to develop, improve and optimize a process [25–30]. The use of RSM highly enhances the experiment and optimization efficiency. Based on the designed experimental data, the RSM gave a functional relationship between the response and the independent variables.

In this work, a theoretical analysis of the molecular size distribution of $PODE_n$ synthesized from DMM and PF was performed based on a sequential reaction mechanism. During the process optimization in synthesis of $PODE_n$, both the molecualr size distribution and conversion of formaldehyde should be considered. The optimization of the molecualr size distribution and conversion of formaldehyde was carried out using RSM. To the best of our knowledge, this is the first report on theoretical analysis of the molecular size distribution of $PODE_n$ and optimization of the molecular size distribution by RSM.

2. Materials and methods

2.1. Materials

DMM (analytic reagent grade, AR) was purchased from Alfa Aesar-Johnson Matthey. PF (analytic reagent grade, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. The NKC-9 cation exchange resins were dry resins of H^+ type provided by Tianjin Bohong Resin Technology Co., Ltd.

2.2. Synthesis of $PODE_n$

The reaction experiments were carried out in a 0.5-L stirred autoclave operated in batch. For each experiment, the mixture of PF and DMM was first loaded in the reactor. To obtain the equilibrium concentration data, the reaction proceeded until the concentrations became unchanged with time on stream.

The composition of the $PODE_n$ mixture was quantitatively analyzed by gas chromatography–mass spectrometry (GC–MS). The product sample (0.5 mL) was diluted with 5 mL of undecane. 1.0 μL of the solution was injected into a Shimadzu 2010 plus GC equipped with an MXT-5 column (5% diphenyl/95% dimethyl polysiloxane, 30 m × 0.25 mm × 0.1 μm) and a flame ionization detector (FID). The column temperature program comprised two stages: the initial temperature was set at 40 °C for 5 min, which was then ramped to 320 °C at 20 °C/min and held for 10 min. Nitrogen was used as carrier gas. An Agilent G2579A MS was used to identify the species with different residence times in the GC column.

Because no gas or solid byproducts were formed, the carbon balance was good, with error within ±5%. The overall selectivity to $PODE_{n>1}$ was over 98% at the experimental conditions in this work. In the following theoretical analysis, the equilibrium conversion of formaldehyde (X_{CH_2O}) refers to the mass fraction of formaldehyde converted when the system reached equilibrium, and was calculated by:

$$X_{CH_2O} = \frac{N_{CH_2O,feed} - N_{CH_2O,product}}{N_{CH_2O,feed}} \quad (1)$$

where the amount of formaldehyde (mol) in the feedstock ($N_{CH_2O,feed}$) and in the equilibrium system ($N_{CH_2O,product}$) were determined by the method provide by ASTM D2194-02 (2012).

To evaluate the product distribution, a product distribution index (*PDI*) is defined as follows:

$$PDI = w_{3-5} - \theta_1 w_{n>5} - \theta_2 w_2 \quad (2)$$

where θ_1 and θ_2 are the relative coefficients of $PODE_{n>5}$ and $PODE_2$, respectively. A larger *PDI* means a compromise result of a higher yield of target product $PODE_{3-5}$ and lower yields of the by-products $PODE_{n>5}$ and $PODE_2$. Considering that $PODE_{n>5}$ is more undesirable than $PODE_2$ as discussed in Section 1, θ_1 is set to be larger than θ_2. The values θ_1 and θ_2 can be adjusted according to the process demand. Herein, θ_1 and θ_2 were set as 0.9 and 0.3, respectively.

2.3. Process optimization using RSM

To optimize the process of $PODE_n$ synthesis, both the molecular size distribution (reflected by *PDI*) and the conversion X_{CH_2O} should be considered. In this reaction system, *PDI* and X_{CH_2O} are determined by the reaction temperature (T) and DMM/CH_2O molar ratio (M). While the effect of the reaction time on *PDI* and X_{CH_2O} will be investigated in future work on kinetics.