

Research progress on synthesis and process technology of polymethoxy dimethyl ether

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Abstract: Polymethoxy dimethyl ethers (PODEn) are the new kind of green and environment-friendly diesel fuel additive, which have excellent performance and great application potential because of their high cetane number, high oxygen content and non-intermiscibility gap between diesels. It can improve the diesel fuel's cetane number and combustibility while reduce the emissions of pollutant. This work provides an overview of the progress of PODEn research in China and abroad, with the focus on the research background and significance, advantages of PODEn, synthesis methods, process and technology. Finally, potential applications of PODEn were analyzed, and it is prospected that they are favorable to be used as diesel blending compounds, solvents or low temperature flow improver for diesel fuel.

1. Introduction

With the rapid development of economy, domestic gasoline and diesel consumption has been rising sharply, but it has also brought serious environmental problems [1]. One of the more notable is the increasingly serious haze problem in recent years, which has caused a great negative impact on the ecological environment and human health [2]. The Institute of Earth Environment of the Chinese Academy of Sciences and the Swiss PSI Institute jointly published a report in the internationally renowned publication "Nature", pointing out that huge primary energy consumption is the main cause of haze weather [3]. The secondary aerosols emitted from the combustion of gasoline, diesel, coal and biomass contribute 30~77% of the PM_{2.5} concentration on average [4]. The continuous increase in total energy consumption and the severe haze weather induced by energy combustion have formed a sharp contradiction, which has become a research hotspot and difficulty that needs to be solved urgently [5].

Gasoline and diesel is an indispensable source of power for urban traffic, production and construction, and transportation, and secondary aerosols emitted by the combustion of gasoline and diesel are one of the most important sources of haze [6]. During the combustion process of diesel, the secondary aerosol emission is significantly greater than that of gasoline, and the contribution to the induction of haze is more prominent. On the premise that energy consumption continues to grow, adding green blending components to gasoline and diesel to achieve clean combustion and reduce secondary aerosol emissions of tail gas has become a feasible solution to alleviate haze weather [7]. Oxygen-containing components such as methanol, dimethyl ether (DME) and polymethoxy dimethyl ether (PODE) as blending components of gasoline and diesel can significantly improve the combustion effect of gasoline and diesel [8]. It reduces the secondary aerosol emissions in gasoline and diesel combustion tail gas by 70%, and is an effective green and environmentally friendly fuel component. At present, gasoline and diesel combustion exhaust pollution is serious, so the development of green diesel has important socio-economic significance.

2. Introduction and advantages of polymethoxy dimethyl ether

Polymethoxy dimethyl ether (PODE_n) is a kind of homologues with the general structure CH₃O(CH₂O)_nCH₃ (n=1~10), with high oxygen content (42%~51%) and ten Hexane number (≥70). Adding an appropriate amount of polymethoxy dimethyl ether to diesel fuel can effectively improve combustion efficiency and reduce CO_x and NO_x emissions in the exhaust without modifying the diesel engine structure [9]. It is a new type of diesel additive component with application prospects. Experiments by the Automotive Research Institute of Tsinghua University have shown that adding 20% PODE₃₋₅ to conventional petrochemical diesel reduces exhaust fumes by more than 70% to 90%, and the highest drop is 97%. This result shows that adding a certain proportion of PODE_n to conventional diesel can increase diesel cetane number, significantly improve diesel combustion efficiency, and reduce secondary aerosol emissions in exhaust gas [10].

Some physical and chemical properties of PODE_n components with different degrees of polymerization are shown in Table 1. It can be seen from Table 1 that PODE₃₋₅ with a degree of polymerization of 3 to 5 has the best physical and chemical properties that match 0# diesel, and is the most ideal diesel blending component under normal conditions. PODE_n products can adjust the distribution of components with different degrees of polymerization according to the application conditions of the product. For example, the relative content of PODE_{2~3} can be increased under cold conditions, and the relative content of PODE_{4~5} can be increased under high temperature conditions.

Table 1. Some physicochemical properties of PODE_n with different degrees of polymerization [11].

| Sample | Density/kg·L ⁻¹ | Oxygen content % | Cetane number | Boiling point/°C | Melting point/°C | Viscosity /MPa·s |
|-------------------|----------------------------|------------------|---------------|------------------|------------------|------------------|
| 0# Diesel oil | 0.845 | 0 | 49 | 170-390 | 0 | 2.71~2.98 |
| PODE ₁ | 0.853 | 42.1 | 29 | 42.5 | -105 | 0.58 |
| PODE ₂ | 0.960 | 45.3 | 63 | 105.0 | -69.7 | 0.64 |
| PODE ₃ | 1.024 | 47.1 | 78 | 155.9 | -42.5 | 1.05 |
| PODE ₄ | 1.067 | 48.2 | 90 | 201.8 | -9.8 | 1.75 |
| PODE ₅ | 1.100 | 49.0 | 100 | 242.3 | 18.3 | 2.24 |
| PODE ₆ | | 49.6 | 104 | 280.0 | 58 | |

Note: The density, viscosity, etc. in the table and on the table are all measured at 25 °C.

3. Synthesis method and synthesis mechanism of PODE_n

According to the molecular formula of PODE CH₃O(CH₂O)_nCH₃, the raw materials for the synthesis of PODE include compounds that can provide capping (CH₃O- and -CH₃) such as methanol, dimethyl ether, methylal, and those that can provide the degree of polymerization (-CH₂O-) Compounds such as formaldehyde, trioxane, and paraformaldehyde [12]. The synthesis methods can be divided into 3 categories: 1. methanol and formaldehyde, trioxane, paraformaldehyde one or more of the reaction synthesis of PODE; 2. dimethyl ether and formaldehyde, trioxane, paraformaldehyde or one of the Several reactions generate PODE; 3. Methylal reacts with one or more of formaldehyde, trioxane and paraformaldehyde to generate PODE.

Zhao [13] et al. used methylal, paraformaldehyde, and trioxymethylene as raw materials in a tank reactor and used sulfuric acid, sulfonated activated carbon and acid resin as catalysts to study the chain growth mechanism of PODE under the action of different catalysts, and proposed the synthesis The process of PODE consists of 3 steps. The following takes PODE₁ to generate PODE₂ as an example to illustrate the mechanism.

Step 1: Paraformaldehyde or trioxane is decomposed into small molecules of formaldehyde units. Methylal is decomposed into CH₃OCH₂O- and -CH₃ or CH₃O- and -CH₂OCH₃, which is the group formation process.

Step 2: The formaldehyde molecules are bonded to the $\text{CH}_3\text{OCH}_2\text{O}$ -or- CH_2OCH_3 group one by one, which is a chain growth process. In the course of the direction to the right in Figure 1, polymer precursors with higher molecular weight are gradually generated.

Step 3: The intermediate group generated in the second step reacts with a methyl group or a methoxy group to form the target product PODE_n with different polymerization degrees. In the downward reaction process in Figure 1, this process is a group recombination process and also a chain termination process.

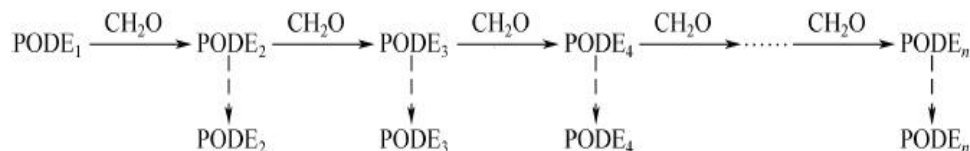


Figure 1. Schematic diagram of stepwise condensation to form PODE_n .

Researchers put PODE_2 and a catalytic amount of sulfuric acid together, and after a period of time, they found that the product contained PODE_n with various degrees of polymerization. This shows that under the experimental conditions, PODE_2 has undergone a process of decomposition and reassembly, which confirms the rationality of the group recombination chain growth model to a certain extent [4]. This result shows that under the experimental conditions, it is impossible to obtain pure PODE_n by refining methods such as rectification and then synthesize PODE_{n+1} . It is worth noting that the above mechanism can indeed explain the decomposition of PODE_2 , but if the reaction is carried out according to the above mechanism, dimethyl ether should be generated in the reaction. The literature does not mention that there is a detection response in the gas chromatography, which may be an intermediate process. Because dimethyl ether is easily volatile and its content is below the detection limit, it may be that the amount produced is very low or no dimethyl ether is produced [14].

Li [15] et al. used a sulfonated titanium oxide catalyst to replace PODE_1 with PODE_2 and PODE_3 to react with trioxane, and found that the conversion rates of PODE_2 and PODE_3 were very low. The product contains polymethoxy dimethyl ether with different polymerization degrees except for the reactants. The content decreases as the degree of polymerization increases. On the whole, the reaction in this system is restricted by the chemical equilibrium. Researchers believe that the chain growth mechanism is simply a PODE_n molecule combined with a formaldehyde molecule under acid catalysis to generate PODE_{n+1} . Figure 2 is a schematic diagram of the reaction process of PODE_1 condensing with formaldehyde to form PODE_2 under the action of an acid catalyst. The chain growth reaction mechanism is a simple chain growth mechanism model.

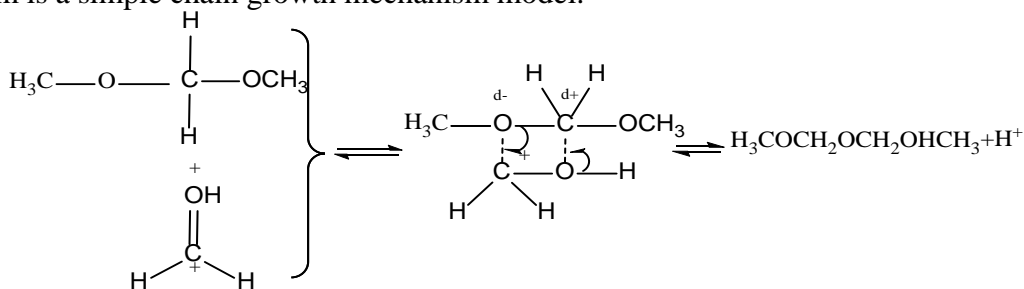


Figure 2. Schematic diagram of the reaction to form PODE_2 from the condensation of PODE_1 .

The above two reaction models are the exploration of the reaction system composed of specific reactants and catalysts. For systems with different raw materials and catalysts, the results of the reaction are quite different. Among them are the influence of the transfer process on the reaction, as well as the thermodynamic limitations and kinetic differences of the reaction itself. Therefore, for the specific reaction system, it should be established to meet the needs and in line with the actual reaction mechanism and kinetic model.

4. Synthesis process technology of PODE_n

The synthesis process of PODE_n can be divided into many types according to the different raw materials and reaction conditions. According to the type of reactor, it can be divided into high pressure reactor type process, fixed bed type process, rectification catalytic process, fluidized bed process, and homogeneous reaction, etc. the characteristics of various processes are as follows:

4.1 High pressure reactor type process

The pressure reactor is a typical innovation of the magnetic transmission device applied to the reaction equipment. It fundamentally solves the problem of shaft seal leakage that cannot be overcome by the previous packing seal and mechanical seal without any leakage or pollution. The most ideal device for chemical reaction, especially for the chemical reaction of flammable, explosive and toxic media, shows its superiority. The high pressure reactor in the PODE_n synthesizer is more used.

Li [16] et al. used sulfonated titanium oxide as a catalyst to synthesize PODE with methylal and trioxane in a 100 mL autoclave. The conversion rate of methylal can reach 58.4%, and the selectivity of PODE can reach 50%. Wu et al. of Lanzhou Institute of Chemical Technology synthesized PODE in a 100 mL autoclave under the reaction conditions of 0.5 MPa and 4200 h⁻¹ space velocity. The methylal conversion rate was 50.61% and the selectivity was 30.65%. Zhao [17] et al. used molecular sieve catalyst and autoclave to synthesize PODE under the following reaction conditions (m(DMM): m(POM)=0.5~4, temperature 80°C~160°C, PODE selectivity as high as 92.87%. Hu [18] et al. used the macroporous strong acid cationic tree HD-8 as a catalyst to synthesize PODE in an autoclave. Under the process conditions of 4% catalyst dosage, 95 °C temperature, 1.0 MPa initial pressure, and 650 r/min stirring speed, the yield of PODE₃₋₈ can reach 39.66%. The Chinese Academy of Sciences Chengdu Organic Chemistry Co., Ltd. uses the GS-0.1 batch high-pressure reactor of Weihai Chemical Machinery Co., Ltd. to synthesize PODE with a selectivity of 90%. The reaction device is shown in Figure 3.

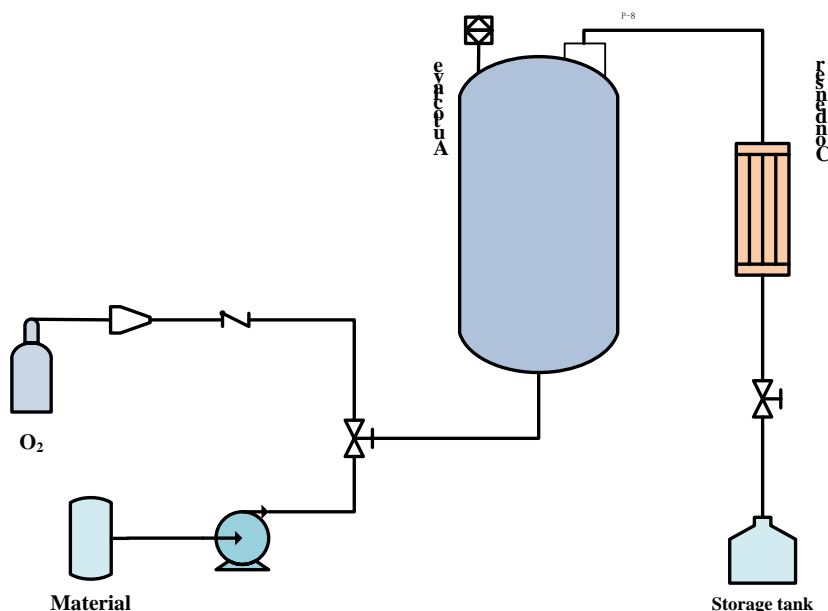


Figure 3. High pressure reactor device diagram.

4.2 Fixed bed process

The fixed-bed reactor is a reactor filled with solid catalysts or solid reactants to realize a multiphase reaction process. The solids are usually granular, with a particle size of about 2~15 mm, and pile up into a bed with a certain height (or thickness). The bed is stationary, and the fluid passes through the bed to react.

Raquel Peláez [19] et al. prepared a MoO_x/Al₂O₃ catalyst and synthesized PODE in a fixed-bed reactor at 0.2 MPa and 140 °C, with a conversion rate of 65%. Liu [20] et al. prepared SnCl₄ modified

macroporous cation exchange resin catalyst, using a fixed bed reactor (as shown in Figure 4), at 70 °C, 1.0 MPa, mass space velocity 1.0 h⁻¹ and the amount of raw materials n(CH₂O): n(CH₄O) =2.5:1 to synthesize PODE under the reaction conditions, the methanol conversion rate is 41.10%, and the target product PODE selectivity is 29.74%. Shi et al. used the modified macroporous cation exchange resin as the catalyst in a fixed bed reactor at a temperature of 40~100 °C, a liquid phase space velocity of 1.32~16.37 h⁻¹, n(CH₂O): n(CH₂OH) =1~4 and the reaction pressure is 0.1~3.0 MPa, using a combination of single factor experiment and orthogonal experiment to systematically study the process conditions of the reaction of formaldehyde and methanol acetal. Under the optimal reaction conditions of 70 °C, n(CH₂O): n(CH₂OH) =3:1, liquid space velocity 1.32 h⁻¹, and reaction pressure 2.0 MPa, the methanol conversion rate is 69.72%, and PODE is selectivity is 62.08%. Liu et al. used methylal and formaldehyde as raw materials, using p-toluenesulfonic acid modified macroporous cationic resin as a catalyst in a fixed-bed reactor, and prepared a diesel fuel additive PODE by continuous feeding. The results showed that under the optimal reaction conditions of reaction temperature of 70 °C, reaction pressure of 1.5 MPa, space velocity of 3 h⁻¹, and raw material ratio of n(CH₂O): n(PODE₁) =4:1, the methylal conversion rate was 60.54 %, the product selectivity is 30.92%.

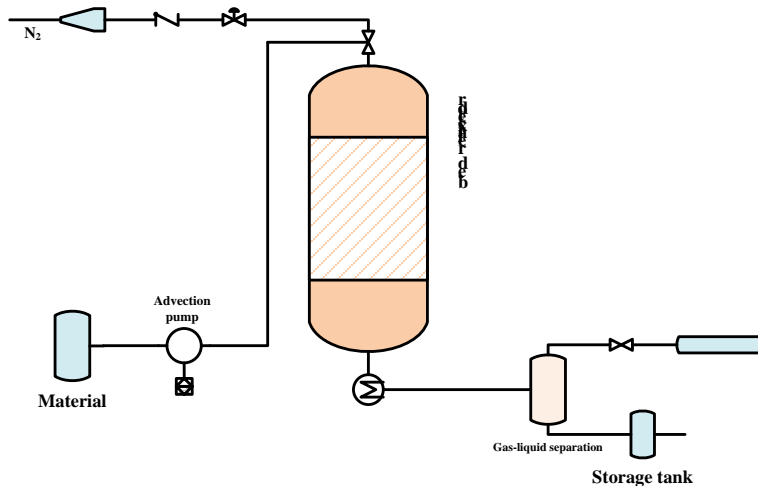


Figure 4. Fixed bed reactor installation diagram.

4.3 Other process

The two synthesis processes described above are the most common, and there are other processes for the synthesis of PODE_n such as: distillation catalytic process, fluidized bed process, homogeneous reaction process, batch process, etc.

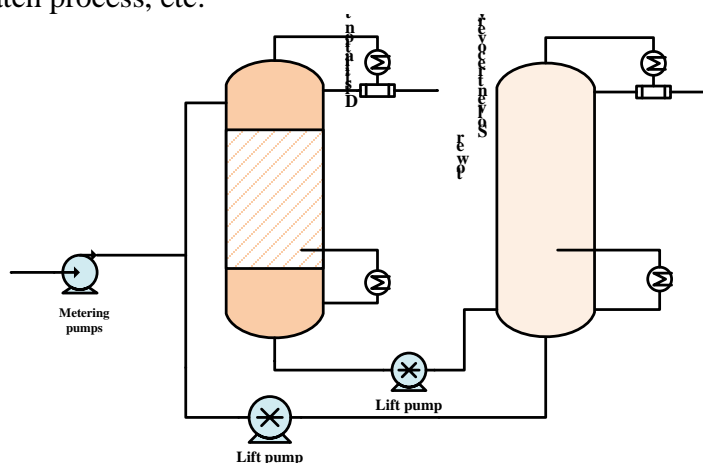


Figure 5. Reactive distillation and extraction compound process flow chart.

Jakob [21] et al. prepared PODE_n with ion exchange resin catalyst in a stirred batch reactor, and transformed it under 0.51 MPa, temperature 50 °C, m(DMM):m(POM)=2~3.5 reaction conditions, the

rate reached 95%. From time to time, using zinc chloride as a catalyst, PODE_n was successfully synthesized under certain reaction conditions in a homogeneous reactor. Gu et al. combined reactive distillation and extraction to prepare PODE_n (as shown in Figure 5), with a yield of over 85%, simple process, and high purity.

5. Conclusions

In summary, polymethoxy dimethyl ether is a promising green and environmentally friendly fuel additive. The focus of research on synthesis of PODE is not only the development of high-activity and high-selectivity solid acid catalysts and the selection of suitable raw materials, but also the key to the reaction process technology. The improvement of catalysts, process routes and reactors can effectively reduce the cost of PODE products. As people's requirements for environmental protection and living environment are getting higher and higher, as well as the continuous improvement and progress of production technologies such as PODE high-pressure reactor technology and fixed bed technology, PODE will have a broad market prospect in the future.

Acknowledgments

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