

# Production Process for Diesel Fuel Components Polyoxymethylene Dimethyl Ethers from Methanol and Formaldehyde Solution

Xiangjun Li, Huaiyuan Tian, Wujie Zhang, Dianhua Liu

**Abstract**—Polyoxymethylene dimethyl ethers (PODE<sub>n</sub>) as clean diesel additive can improve the combustion efficiency and quality of diesel fuel and alleviate the problem of atmospheric pollution. Considering synthetic routes, PODE production from methanol and formaldehyde is regarded as the most economical and promising synthetic route. However, methanol used for synthesizing PODE can produce water, which causes the loss of active center of catalyst and hydrolysis of PODE<sub>n</sub> in the production process. Macroporous strong acidic cation exchange resin catalyst was prepared, which has comparative advantages over other common solid acid catalysts in terms of stability and catalytic efficiency for synthesizing PODE. Catalytic reactions were carried out under 353 K, 1 MPa and 3 mL·g<sub>cat</sub><sup>-1</sup>·h<sup>-1</sup> in a fixed bed reactor. Methanol conversion and PODE<sub>3-6</sub> selectivity reached 49.91% and 23.43%, respectively. Catalyst lifetime evaluation showed that resin catalyst retained its catalytic activity for 20 days without significant changes and catalytic activity of completely deactivated resin catalyst can basically return to previous level by simple acid regeneration. The acid exchange capacities of original and deactivated catalyst were 2.5191 and 0.0979 mmol·g<sup>-1</sup>, respectively, while regenerated catalyst reached 2.0430 mmol·g<sup>-1</sup>, indicating that the main reason for resin catalyst deactivation is that Bronsted acid sites of original resin catalyst were temporarily replaced by non-hydrogen ion cations. A separation process consisting of extraction and distillation for PODE<sub>3-6</sub> product was designed for separation of water and unreacted formaldehyde from reactive mixture and purification of PODE<sub>3-6</sub>, respectively. The concentration of PODE<sub>3-6</sub> in final product can reach up to 97%. These results indicate that the scale-up production of PODE<sub>3-6</sub> from methanol and formaldehyde solution is feasible.

**Keywords**—Inactivation, polyoxymethylene dimethyl ethers, separation process, sulfonic cation exchange resin.

## I. INTRODUCTION

MUCH work so far has focused on PODE as ideal clean diesel fuel additive, for PODE can be added into diesel fuel in slightly modified diesel engines [1]. Numerous studies indicated that adding PODE into diesel fuel can improve the combustion efficiency of diesel fuel and reduce nitrogen oxides and exhaust soot particles emissions significantly [2]-[4].

PODE are general terms for a class of substances, and their chemical structures are CH<sub>3</sub>-O-(CH<sub>2</sub>O)-CH<sub>3</sub> with n≥1. PODE are oligomers consisting of varying CH<sub>2</sub>O units as center section group and methyl as end group. Methylal is known as the simplest PODE for only containing one CH<sub>2</sub>O unit, and for

their similar general formula PODE has certain regularity in physicochemical properties as shown in Table I [5].

TABLE I  
PHYSICO-CHEMICAL PROPERTIES OF PODE<sub>n</sub>

PODE	Oxygen Content (%)	Cetane Number	Boiling Point (°C)	Melting Point (°C)	Density (kg/m <sup>3</sup> )
PODE <sub>1</sub>	42.1	29	42	-105.0	860
PODE <sub>2</sub>	45.2	63	105	-69.7	980
PODE <sub>3</sub>	47.0	78	156	-42.5	1030
PODE <sub>4</sub>	48.1	90	202	-9.8	1070
PODE <sub>5</sub>	48.9	100	242	18.3	1110
PODE <sub>6</sub>	49.5	104	280	--	1140

According to varieties of reactants that provide the methyl group and CH<sub>2</sub>O units, synthetic process of PODE can be roughly classified into three categories: formaldehyde and methanol (or dimethyl ether, methylal), trioxane and methanol (or dimethyl ether, methylal), paraformaldehyde and methanol (or dimethyl ether, methylal) [6]-[9]. Initially, synthesizing PODE mostly used liquid acids as catalysts due to their high catalytic activity and low cost, such as sulfuric acid, formic acid and trifluoromethanesulfonic acid [10]-[12]. But, there will be difficulties in equipment corrosion and product separation. Compared to liquid acid, solid acid catalysts including molecular sieve and metallic oxide are better at weak corrosive, separation, and catalyst recycle [6], [8]. The application of acidic ionic liquids in the synthesis process has certain advantages on high catalytic activity, but high catalyst cost, difficult separation and catalyst loss limit acidic ionic liquids to be applied on large scale production [9]. Cation exchange resin is particularly attractive as catalyst in PODE synthesizing process due to its high quality in acidic activity, exchange capacity and catalytic activity, while there will be much work on improving its mechanical properties and thermal stability [7], [13]-[15].

The production process of PODE<sub>n</sub> from methanol and formaldehyde solution is known as much more economical than the other processes, because in these processes the raw materials such as methylal and trioxane are intermediates and generally require additional process steps [16]. In general, the process of PODE<sub>n</sub> production consisted of a synthesis process in a fixed bed reactor with acidic catalyst and a separation process of distillation. The presence of water in the reaction system will affect the activity of catalyst, and the presence of water and unreacted formaldehyde in the product can adversely affect separation of target product. It should be pointed out that

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the water content in the product will increase during the reaction when the reactants are methanol and formaldehyde solution.

In this work, we prepared a macroporous strong acidic cation exchange resin catalyst for synthesizing PODE<sub>n</sub> from methanol and formaldehyde solution and investigated the effects of reaction conditions. The reason of deactivation for catalyst lifetime was discussed in briefly. The separation process of PODE<sub>3-6</sub> production was also designed.

## II. EXPERIMENTAL SECTION

### A. Catalyst Preparation

Methyl amyl alcohol, styrene, divinylbenzene, butanol, paraffin, fuming sulphuric acid were obtained from commercial sources and used as-received without further purification.

Macroporous strong acidic cation exchange resin catalyst was prepared by following steps. According to proportion, the solution containing deionized water, methyl amyl alcohol, potassium chloride, sodium nitrite was poured into the stainless steel stirred tank. Under stirring, the solution was heated to 353 K, and then organic mixture containing styrene, divinylbenzene, butanol, and paraffin was added into former solution and heated to 368 K for 5 h. The white beads were obtained after washing and drying. The white copolymer beads were added into a corrosion-resistant glass mixer and sulfonated with fuming sulphuric acid for 5 h under stirring at 403 K. Then, the sulfonated macroporous strong acidic cation exchange resin (SMR) catalyst was filtered, washed several times with deionized water until neutralization, and dried under air environment at 373 K for 10 h.

### B. Catalyst Characterization

The physical properties (BET surface area, pore volume, and pore diameter distribution) have been determined by N<sub>2</sub> adsorption-desorption (Micromeritics ASAP 2020 V3.05H). The morphology of the samples was examined using a JSM-6360LV scanning electron microscope (SEM).

### C. Catalytic Reaction and Separation Process

The reaction of PODE<sub>n</sub> synthesis from methanol and formaldehyde solution was carried out in a fixed-bed reactor with SMR catalyst, and the reaction unit was shown in Fig. 1. Raw material was composed of 10 wt.% water and 90 wt.% formaldehyde and methanol, and the ratio of formaldehyde to methanol was 2.0. The prepared raw material was transported at 0.1 mL·min<sup>-1</sup> flow rate to the reactor after preheating. The catalyst loading and reaction temperature were within 0.5 to 2.5 g and 338 to 363 K, respectively. The reaction pressure was conducted at the range of 0.1 to 2.0 MPa. The product was collected after condensation and followed by analyzed by gas chromatography and titrimetric method.

The conversion of reactant was determined by:

$$C_i = \frac{m_{i,in} - m_{i,out}}{m_{i,in}} \times 100\%$$

where  $C_i$  was the conversion of component  $i$ ,  $m_{i,in}$  and  $m_{i,out}$

were the mass fraction of component  $i$  in the reactant and product, respectively.

The selectivity of PODE<sub>3-6</sub> was calculated by:

$$S_{PODE_{3-6}} = \frac{N_{PODE_{3-6}}}{N_{PODE_{1-6}}} \times 100\%$$

where  $S_{PODE_{3-6}}$  was the selectivity of PODE<sub>3-6</sub>,  $N_{PODE_{3-6}}$  and  $N_{PODE_{1-6}}$  were the total mole fraction of compounds of PODE<sub>3-6</sub> and PODE<sub>1-6</sub> in product.

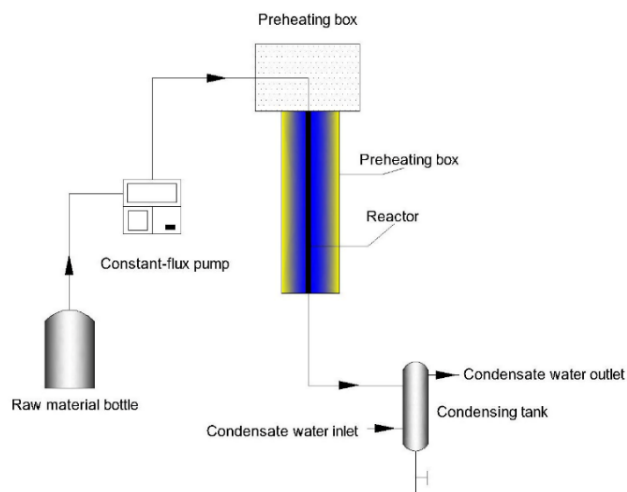


Fig. 1 Reaction unit of PODE synthesis from methanol and formaldehyde solution

Two-step separation process of PODE<sub>n</sub> was designed to produce high purity PODE<sub>3-6</sub>. Extraction separation was applied to separate the water and formaldehyde from PODE<sub>n</sub>, and then the other compounds in the product were separated by rectification. The separation process was shown in Fig. 2. The product from reactor was separated into aqueous phase and organic phase by extraction. The aqueous phase mainly contained unreacted formaldehyde and methanol and generated water. PODE<sub>3-6</sub> was obtained by three-step distillation from organic phase. In the separation process, methylal, methanol and PODE<sub>2</sub> can be used as recirculating reactant and the extractant can be recycled.

### D. Analytical Methods

Organic samples were analyzed using a gas chromatography (GC-2014) equipped with an InertCap WAX capillary column (30 m × 0.32 mm × 0.50 μm) and an FID detector. High purity nitrogen used as carrier gas with constant flow rate at 40 ml min<sup>-1</sup>. The injector and detector temperatures were both maintained at 523.15 K, and the column was heated according to the following program: initial temperature of 318.15 K for 3 min, temperature ramp 20 K min<sup>-1</sup>, and final temperature of 493.15 K for 3 min. The water content of samples was determined by volumetric one-component Karl Fischer titration method. The Karl Fischer standard curve of water should be made every day before sample analysis in order to reduce analysis error. The standard uncertainty for the water content of

an analyzed sample should be kept within 0.0005. Formaldehyde is analyzed using titration by the sodium sulfite method [17].

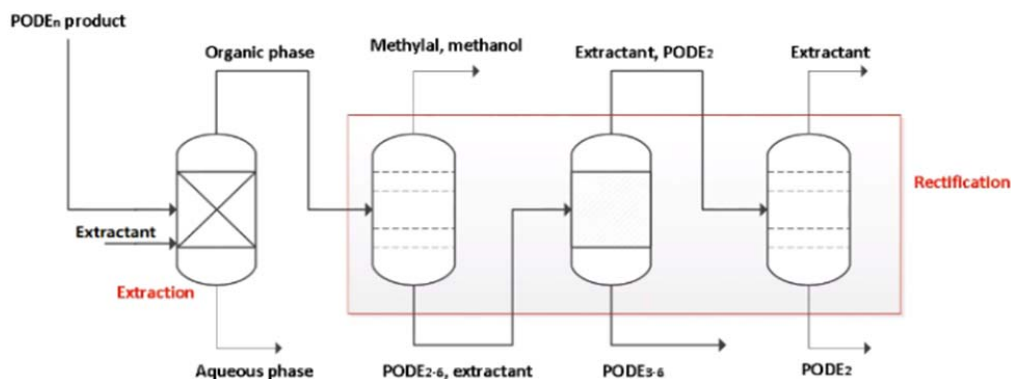


Fig. 2 Two-step separation process of PODE<sub>3-6</sub> production

### III. RESULTS AND DISCUSSION

#### A. Catalyst Characterization Result

Nitrogen adsorption isotherms for the synthesized resin catalyst were measured, and the physical properties of the resin catalyst were listed in Table I. As can be seen in Table I, the average pore diameter of catalyst was 33.67 nm, which indicates that the prepared resin catalyst had macroporous structure. SEM was carried out to have a direct insight into the structure of the resin catalyst. Fig. 3 shows that the surface of resin catalyst had a certain flake structure, which was irregular and porous.

TABLE II  
PHYSICAL PROPERTY OF RESIN CATALYST

Catalyst	BET surface area (m <sup>2</sup> /g)	Average pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)
SMD	76.73	33.67	0.22

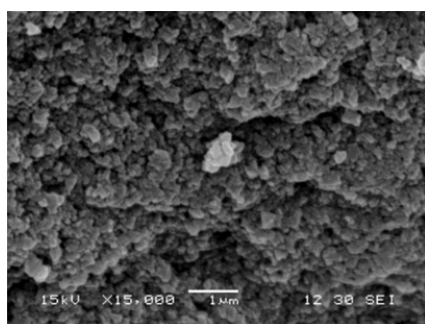


Fig. 3 SEM image of resin catalyst

#### B. Independent Effects of Operating Variables

The PODE<sub>n</sub> synthesis reaction was carried out in a fixed-bed reactor at a raw material flow rate of 0.1 mL·min<sup>-1</sup>. The raw material was composed of 10 wt.% water and 90 wt.% formaldehyde and methanol, and the mole ratio of formaldehyde to methanol was 2.0. The variables affecting reaction such as temperature (338-363 K), catalyst loading (0.5-2.5 g) and pressure (0.1-2.0 MPa) were studied to get higher results under optimal reaction conditions.

The conversion of methanol and selectivity of PODE<sub>3-6</sub> are

strongly influenced by the reaction temperature. The impact of reaction temperature (range of 338-363 K) on the PODE<sub>n</sub> synthesis reaction was investigated under 1 MPa with 2.0 g catalyst dosage. The results were shown in Fig. 4. The optimal temperature was found to be 353 K. The methanol conversion and PODE<sub>3-6</sub> selectivity were increased accompanied by the temperature increased to 353 K. Decrease in methanol conversion and PODE<sub>3-6</sub> selectivity was observed when the reaction temperature exceeds 353 K. Since propagating reaction of PODE<sub>n</sub> is an exothermic reaction, it is not conducive to generate PODE<sub>3-6</sub> from methanol and formaldehyde with temperature increases. But, from the point of view of reaction kinetics reaction rate, the reaction rate increases are accompanied by temperature increases. The optimal yield of PODE<sub>3-6</sub> was obtained at 353 K.

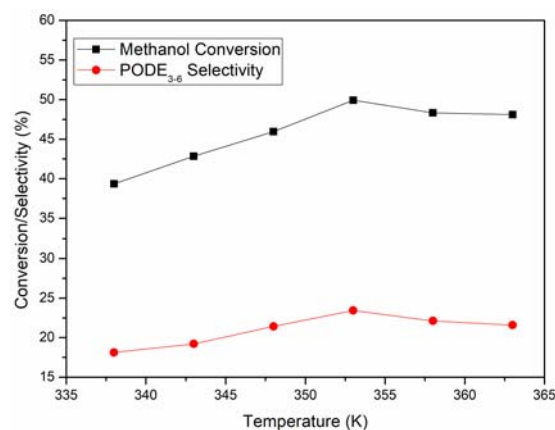


Fig. 4 Effect of reaction temperature on PODE<sub>n</sub> synthesis from methanol and formaldehyde

The impact of catalyst dosage (range of 0.5-2.5 g) on the reaction under 1.0 MPa at 348 K was shown in Fig. 5. To achieve an optimal methanol conversion and PODE<sub>3-6</sub> selectivity, 2.0 g catalyst loading was used. An increase of catalyst loading resulted in both increases in the methanol conversion and PODE<sub>3-6</sub> selectivity. The possible reason is that the reaction residence time of raw material is too small to reach

the reaction equilibrium. Therefore, the reaction reached equilibrium with 2.0 g catalyst dosage, and the reaction results remained constant when the catalyst loading exceeded 2.0 g.

The influence of pressure (range of 0.1-2.0 MPa) on the reaction was conducted at temperature of 348 K with catalyst loading of 2.0 g. The results were shown in Fig. 6. Methanol conversion and  $\text{PODE}_{3-6}$  selectivity both increased slightly with the increase of reaction pressure, and then became constant when the pressure was higher than 1.0 MPa. This may be due to the fact that almost all the substances in the reaction system are liquid at 353 K, and the change of pressure has little effect on the liquid reaction.

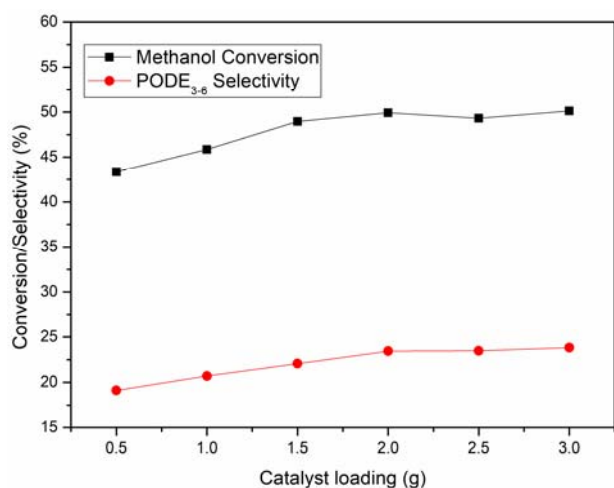


Fig. 5 Effect of catalyst loading on  $\text{PODE}_n$  synthesis from methanol and formaldehyde

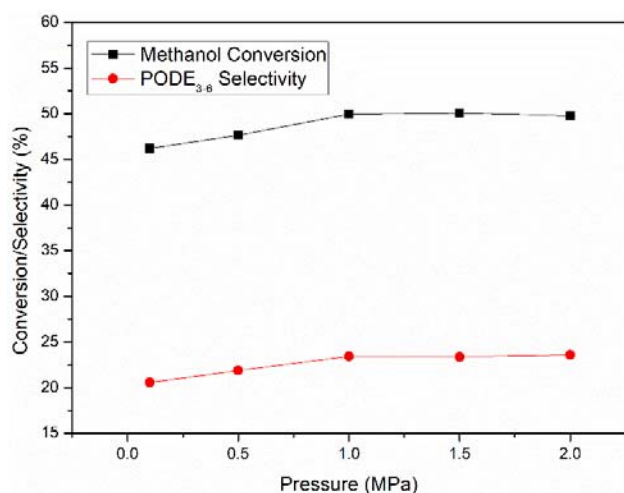


Fig. 6 Effect of reaction pressure on  $\text{PODE}_n$  synthesis from methanol and formaldehyde

### C. Catalyst Stability

The lifetime evaluation experiment with SMD catalyst was carried out over 480 hours under optimal conditions. The tendency of methanol conversion and  $\text{PODE}_{3-6}$  selectivity with reaction time was shown in Fig. 7. It was shown that methanol conversion and  $\text{PODE}_{3-6}$  selectivity both remained constant in 500 hours, which indicated that no obvious deactivation of the

SMD catalyst occurred. Surprisingly, the activity of catalyst decreased significantly after over 550 hours. The acid exchange capacities of original and deactivated catalyst were 2.5191 and 0.0979  $\text{mmol}\cdot\text{g}^{-1}$ , respectively. We qualitatively measured the content of iron in the deactivation catalyst and found that the content of iron was greatly increased after a long period of work. In order to determine the cause of catalyst deactivation, regeneration SMD catalyst was obtained by ion exchange between deactivation catalyst and 10 wt.% sulfuric acid solution. The acid exchange capacity of regenerated catalyst reached 2.0430  $\text{mmol}\cdot\text{g}^{-1}$ , which indicated that the main reason for resin catalyst deactivation is that Brønsted acid sites of original resin catalyst were temporarily replaced by non-hydrogen ion cations came from raw materials [18]. Fig. 8 shows that the activity of regenerated SMD catalyst remained the same level as the original catalyst in 500 hours, which indicated that the SMD catalyst deactivation was reversible.

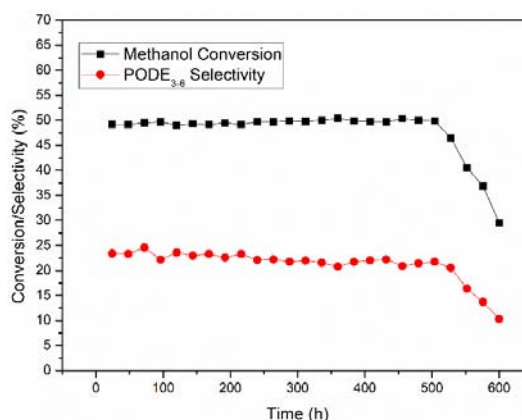


Fig. 7 Effect of reaction time on activity of SMD catalyst

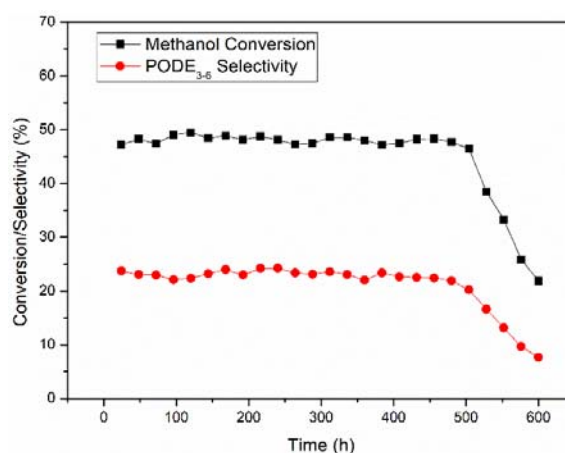


Fig. 8 Effect of reaction time on activity of regenerated SMD catalyst

### D. Separation Process of $\text{PODE}_{3-6}$ Production

The difficulty of  $\text{PODE}_{3-6}$  separation process lies in how to separate water and formaldehyde from other substances in the product and to prevent  $\text{PODE}_n$  from depolymerization at high temperature. In this work, the extraction process was carried out at 298 K under atmospheric pressure and toluene was used

as extractant with a product-to-extractant mass ratio of 1:1.5. The extraction result was shown in Table III. As can be seen in Table VI, the majority of formaldehyde and water were present in the aqueous phase, which are advantageous for subsequent rectification and prevent the depolymerization of PODE and polymerization for formaldehyde during rectification.

The light components of methanol and methylal in the organic phase were separated by atmospheric distillation at 383 K of bottom temperature. The results were listed in Table IV. The mass content of methanol and methylal in the overhead fraction were 38.73% and 60.31%, respectively. And only a small amount of methanol and methylal in the tower bottoms, while most of PODE<sub>2-6</sub> and toluene were existed in the bottom of tower.

TABLE III  
COMPONENTS OF STREAMS IN EXTRACTION PROCESS

Component	Feed (wt.%)	Organic phase (wt.%)	Aqueous phase (wt.%)
Methanol	15.47	2.37	14.15
Methylal	8.23	3.48	2.90
PODE <sub>2</sub>	5.78	2.49	1.94
PODE <sub>3</sub>	3.88	1.54	1.58
PODE <sub>4</sub>	1.86	0.81	0.61
PODE <sub>5</sub>	1.04	0.45	0.35
PODE <sub>6</sub>	0.55	0.23	0.20
Toluene	0	83.36	11.26
Formaldehyde	47.17	3.95	49.99
Water	16.02	1.32	17.02

TABLE IV  
COMPONENTS OF STREAMS IN ATMOSPHERIC DISTILLATION

Component	Feed (wt.%)	Overhead fraction (wt.%)	Tower bottoms (wt.%)
Methanol	2.37	38.73	0.78
Methylal	3.48	60.31	0.05
PODE <sub>2</sub>	2.49	0.18	2.43
PODE <sub>3</sub>	1.54	0.12	1.59
PODE <sub>4</sub>	0.81	0.08	0.76
PODE <sub>5</sub>	0.45	0.05	0.42
PODE <sub>6</sub>	0.23	0.03	0.24
Toluene	83.36	0.16	87.78
Formaldehyde	3.95	0.13	4.76
Water	1.32	0.21	1.19

PODE<sub>2</sub> and toluene in the stream should be removed to obtain high purity target product PODE<sub>3-6</sub>. Vacuum distillation was carried out at a bottom temperature of 373 K under a vacuum degree of 0.04 MPa. The experimental results of vacuum distillation were shown in Table V. It can be seen that the mass content of PODE<sub>3-6</sub> in the tower bottoms reached over 97%, while overhead fraction hardly contained PODE<sub>3-6</sub>. Since the boiling point of toluene and PODE<sub>2</sub> is close, and the mass content of PODE<sub>2</sub> in the overhead fraction differed greatly from that of toluene, PODE<sub>2</sub> is not suitable to be separated from toluene by distillation. Therefore, the overhead fraction can be recycled as extractant until the mass content of PODE<sub>2</sub> reaches a certain value, and then separated by distillation.

TABLE V  
COMPONENTS OF STREAMS IN VACUUM DISTILLATION

Component	Feed (wt.%)	Overhead fraction (wt.%)	Tower bottoms (wt.%)
Methanol	0.78	0.82	0.00
Methylal	0.05	0.16	0.00
PODE <sub>2</sub>	2.43	3.51	0.24
PODE <sub>3</sub>	1.59	0.08	51.80
PODE <sub>4</sub>	0.76	0.06	25.10
PODE <sub>5</sub>	0.42	0.03	14.16
PODE <sub>6</sub>	0.24	0.01	6.17
Toluene	87.78	89.19	2.19
Formaldehyde	4.76	4.92	0.23
Water	1.19	1.22	0.11

#### IV. CONCLUSION

A macroporous strong acidic cation exchange resin catalyst was prepared and employed in synthesizing PODE<sub>n</sub> from methanol and formaldehyde solution. The effect of reaction temperature, catalyst loading and reaction pressure on PODE<sub>n</sub> synthesis from methanol and formaldehyde were investigated, and optimal methanol conversion and PODE<sub>3-6</sub> selectivity were obtained at the reaction temperature of 353 K, catalyst loading of 2.0 g, and reaction pressure of 1.0 MPa. Methanol conversion and PODE<sub>3-6</sub> selectivity reached 49.91% and 23.43%, respectively. Catalyst lifetime evaluation shows that the resin catalyst retained its catalytic activity over 500 hours without significant changes, and catalytic activity of completely deactivated resin catalyst can reach original level by simple acid regeneration. The main reason for resin catalyst deactivation was that the Brønsted acid sites of original resin catalyst were temporarily replaced by non-hydrogen ion cations came from raw materials. A separation process consists of extraction and distillation was designed for the separation of water and unreacted formaldehyde from reactive mixture and the purification of PODE<sub>3-6</sub>, respectively. The mass content of PODE<sub>3-6</sub> in the final product reached over 97%. The findings in this study have demonstrated that it is feasible to produce high purity PODE<sub>3-6</sub> from methanol and formaldehyde solution.

#### ACKNOWLEDGMENT

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