

Synthesis of poly(oxymethylene) dimethyl ethers from methylal and trioxane over acidic ion exchange resins: a kinetic study

Raquel Peláez, Pablo Marín, Salvador Ordóñez*

Catalysis, Reactors and Control Research Group (CRC), Dept. of Chemical and Environmental Engineering, University of Oviedo, Oviedo 33006, Spain

Corresponding author: Salvador Ordóñez

Phone: 34-985 103 437, FAX: 34-985 103 434, e-mail: sordonez@uniovi.es

Abstract

Poly(oxymethylene) dimethyl ethers (POMDME) are fuel additives that can reduce the emissions associated with diesel fuels considerably. POMDME have been synthesized from methylal and trioxane, catalyzed by the acidic ion exchange resin Amberlyst 15. A batch autoclave reactor has been used to carry out experiments conducted up to equilibrium conditions. The resulting POMDME distribution is modelled using the Schulz-Flory distribution theory, which confirms a sequential chain growth with insertion of one formaldehyde molecule at each reaction step. The kinetic experiments were carried out in an isothermal continuous fixed-bed reactor. The influence of temperature (45-80°C) and space-time (1.6-3.2 kg h/m³) on trioxane conversion and product selectivity was determined. A kinetic model of the reaction has been proposed and validated with the experimental results. It has been demonstrated that trioxane decomposition to formaldehyde is the kinetically limiting step of the reaction scheme, with an activation energy of 112.2 kJ/mol. POMDME chain propagation reactions are in equilibrium under the conditions studied.

Keywords: polyoxymethylene dimethyl ethers; renewable fuels; platform molecule; fixed-bed reactor; kinetic modelling.

1. Introduction

The reduction of the emissions to the atmosphere from exhaust gases is currently a need for tackling environmental pollution and climate change. The contribution of the transportation sector to air pollution is very important. For this reason, new techniques for treating the exhaust gases, improve combustion or formulate new fuel additives or biofuels are under development.

The use of oxygenated compounds, as fuel additives or to substitute diesel fuels, is an alternative widely studied in recent years [1-3]. Poly(oxymethylene) dimethyl ethers (POMDME) have been proven as one of the most interesting options, with many advantages in comparison to other additives. POMDME are oxygenated compounds formed of a chain of oxymethylene units (CH_2O) with a methyl group and methoxyl group at the ends. There are many studies available in the bibliography about the improvement of combustion in diesel engines associated to these compounds [1, 4-8]. The use of POMDME/diesel blends results in a significant decrease in particulate and NO_x emissions, as well as, CO and hydrocarbons.

From an economic point of view, it must be also taken into consideration that POMDME with the appropriate chain length present physicochemical properties very similar to those of diesel fuels. This is an important advantage to ensure direct use in current engines and infrastructures without further modifications [9]. Based on this, the POMDME with a number of oxymethylene groups between 3 and 5 are preferred as diesel additives [10-12].

The POMDME synthesis requires the reaction, in the presence of acid catalysts [13], between a molecule supplying the methyl terminal group, such as methanol, DME or methylal, and a molecule supplying the methoxyl group, such as formaldehyde, paraformaldehyde or trioxane. These compounds can be obtained from syngas [14, 15]. When syngas is produced biomass or biogas feedstocks, the generated POMDME are a renewable biofuel. In this way, the use of POMDME as fuel additives not only reduces soot emissions, but also the net CO_2 ones [16].

According to previous studies available in the bibliography, POMDME can be synthesized from methanol in a process that involves one or two steps. In the one-step process, POMDME are obtained directly from methanol and formaldehyde in a single reactor using an acid catalyst [17-21]. This reaction generates stoichiometric amounts of water and,

consequently, undesired byproducts like hemiformals and glycols are formed. This leads to lower POMDME yield and makes product separation and purification more complex [22, 23]. The presence of high amount of water in the reaction media also results in an inhibitory effect, due to water adsorption over the cation exchange resins (causing blockage of active centres) [24, 25]. The two-step process can solve all these drawbacks. In a first reaction step, methylal is synthesized from methanol and formaldehyde [26-28]. Then, methylal is separated from water and, in the second reaction step, reacts with additional formaldehyde to generate POMDME [22, 29, 30]. Therefore, the latter reaction proceeds in the absence of water, leading to high catalyst activity and POMDME yield.

The reaction between methylal and formaldehyde has been investigated in recent years [10, 22, 23, 30-32]. Baranowski *et al.* summarizes the results published in the scientific literature [13]. Homogeneous catalysts, such as sulfuric acid or acid ionic liquids, have demonstrated good activity [33, 34]. However, problems associated to their use, e.g. corrosion or difficulty of separation, make solid acid catalysts a preferred alternative. Among them, ion-exchange resins are one of the best choices [10, 23, 30], sharing benefits with homogeneous catalysts and having the reusability of heterogeneous catalysts.

The knowledge of the kinetics of the reaction is essential for the scale-up of the process (e.g. the determination of the optimum operating conditions and the design of the reactor). There have been some previous kinetic studies on POMDME synthesis in the literature, but due to the differences between the proposed models and their underlying assumptions, the reaction is still not clear at all. Some of the published models correspond with the use of methanol as reactant for POMDME production [17, 18, 21]. Regarding the synthesis from methylal, Burger *et al.* [30] studied the kinetic of POMDME synthesis from methylal and trioxane over the acidic ion-exchange resin Amberlyst 36 in a batch reactor. They developed a pseudohomogeneous model and an adsorption-based kinetic model. Zheng *et al.* [35] investigated the kinetics of the reaction between methylal and paraformaldehyde with NKC-9 as catalyst in an autoclave reactor. They proposed a mechanistic model based on a sequential reversible reaction scheme. The accuracy of the model is not clear, especially at transient stage. The study of Wang *et al.* [36] is one of the most recent articles about kinetic modeling of POMDMEs synthesis. They performed a set of batch experiments using methylal and trioxane reactants and a sulfonic acid functionalized ionic liquid, as catalyst. In the

model, different rate constants were considered simultaneously for the reversible reactions of propagation-depolymerization.

In the present work, the synthesis of POMDMEs from methylal and trioxane has been studied with Amberlyst 15 acidic ion-exchange resin. The influence of the main operation parameters, such as, temperature or space velocity, has been evaluated in a continuous fixed-bed reactor. Based on the experimental results, this article proposes and validates a kinetic model, which represents all the reactions involved in POMDME synthesis adequately. This model is one of the first developed in a continuous reactor and, hence, constitutes a key step prior to the scale-up of the process to industrial scale.

2. Material and methods

2.1 Catalyst and chemicals

Methylal (ReagentPlus[®], 99% purity) and 1,3,5-trioxane (Sigma Aldrich, ≥99% purity) were used as raw materials for the reaction. Methanol (VWR, 99% purity) was also used for calibration purposes.

The acidic ion exchange resin Amberlyst 15 (dry, hydrogen form), supplied as spherical pellets (<300 μm diameter) by Sigma Aldrich, was used as catalyst. Its textural properties have been analyzed: surface area (BET, Brunauer-Emmett-Teller) of 80 m²/g, pore volume (BJH, Barrett-Joyner-Halenda) of 0.442 cm³/g and pore average size of 25.9 nm. According to these data, the catalyst is mesoporous. The active sites of the resin consist of sulfonic groups inserted in the styrene-divinylbenzene matrix, corresponding to a strong acidic character. The capacity of Amberlyst 15 is 4.7 mmol H⁺/g_{cat (dry)} (manufacturer-supplied).

2.2 Experimental device

A process flowsheet of the experimental device used in the continuous reaction experiments is included in the Supplementary Information, Figure S1. The continuous fixed-bed reactor consisted of a stainless-steel tube with 10.9 mm inner diameter and 600 mm length. The reactor tube was filled with a fixed-bed, according to the following distribution (from the

bottom to the top of the tube): first, a steel wool plug and a small supportive bed made of ground glass (355–710 μm) were introduced to support the catalytic bed; then, the catalyst (0.9 g) was introduced in its commercial form (bed length \approx 20 mm); finally, two beds made of glass were placed on top of the catalytic bed (one made of 355–710 μm particles and another of 1 mm beads). This glass bed placed at the top of the tube is the first bed encountered by the feed and contributes to distribute feed over the cross-section homogeneously. The catalyst swells in the presence of solvents. Hence, in order to prevent plugging, it is recommended to submerge it in methylal before introducing in the reactor.

The reactor was operated at isothermal conditions with reactants and products in the liquid phase. The isothermal behavior was achieved by means of an electric furnace that surrounds the reactor tube. Temperature was measured by three different thermocouples: one thermocouple was placed outside the reactor tube (45 mm above the catalyst bed) and the other two were placed inside (35 mm above the catalyst bed and 5 mm below it). The latter thermocouple was used to control the electric furnace using a feedback controller. The reactor feed was preheated outside the reactor using a heating tape.

The feed consisted of mixtures of methylal and trioxane (also water was added in some tests). Methylal was in excess, acting as reactant and solvent. The liquid feed was introduced by means of a dosing pump (Dostec-AC, ITC Dosing Pumps). At the reactor outlet, two sampling cylinders (denoted as 1 and 2 in the flowsheet of Figure S1), made of Teflon-lined stainless steel, were used to alternatively accumulate the reactor effluent and collect the samples (for this purpose high pressure valves, Autoclave Engineers, are used). Initially, the feed is pumped to the reactor, while operating conditions stabilize and become constant. When the steady state is reached, all the accumulated volume of reactor effluent corresponding to transient conditions is discarded, since only samples taken at steady state are considered valid.

The reactor pressure was maintained at 8.5 bar using a pressure regulator (back-pressure type, GO regulator), placed downstream the sampling cylinder. This pressure is enough to ensure that the reaction takes place in the liquid phase (boiling point of methylal at 8.5 bar: 123.1°C). Nitrogen gas was used to pressurize the sampling cylinders after the liquid samples

were collected, preventing the de-pressurization of the reactor. Nitrogen gas flow was controlled by using a mass flow controller (3 NL/min, Bronkhorst High-Tech instruments).

A batch reactor was also used to carry out discontinuous experiments aimed at determining the equilibrium conditions. A 0.5 L stirred autoclave reactor, equipped with a PID temperature controller (Autoclave Engineers), was used for these experiments. The reactor was loaded with 0.25 L of the reactant solution and 0.4 g of the catalyst. The air was purged with nitrogen gas and the reactions were carried out under 8 bar of nitrogen. The mixture was heated up to reaction temperature and maintained for 30 h, while stirring at 700 rpm. Samples were taken at different reaction times.

2.3 Analytical and characterization techniques

Liquid samples were analyzed by gas chromatography using a Shimadzu GC-2010. The GC is equipped with a 30 m long CP-Sil 8 CB capillary column and a flame ionization detector (FID). The analysis was carried out according to the following temperature program: 33°C for 10 min, then a ramp of 20°C/min up to 240°C where holding 3 min, after that a second ramp of 5 °C/min up to 250°C and hold 5 min, and finally a ramp of 10°C/min up to 270°C, holding 5 min. The error associated to the analysis (based on the standard deviation) was estimated as less than 5%. The identification of the main products was verified with GC-MS (Shimadzu GC/MS QP2010 Plus), using a TRB-5MS capillary column (30 m length).

Commercial standards of methylal, methanol and trioxane were used for peak assignment and calibration. Poly(oxymethylene) dimethyl ethers were quantified using the extended effective carbon number method, based on the calculation of relative response factors using the flame ionization detector [37].

The results of the analysis were used to calculate trioxane conversion (X_{tri}), product selectivity (S_i) and carbon balance (C.B.) according to the following expressions.

$$X_{tri} = 1 - \frac{w_{tri}}{w_{tri\ in}} \quad (1)$$

$$S_i = \frac{M_{tri}}{M_i} \frac{w_i}{(w_{tri\ in} - w_{tri})} \frac{v_{tri}}{v_i} \quad (2)$$

$$C.B = \frac{\sum_i w_i/M_i n_{C_i}}{3 (w_{trio\ in}/M_{tri} + w_{DMM\ in}/M_{DMM})} \quad (3)$$

where w_i and M_i are, respectively, the mass fraction and molar weight of compound i , v_i is the stoichiometric coefficient of compound i and n_{C_i} represents the number of carbon atoms in each compound. The mass fraction is used to calculate conversion and yield, instead of mole fraction, to be more accurate and consider any possible change in density during the reaction.

The carbon balance was over 98% for all the operating conditions.

2.4 Modelling

The continuous fixed-bed reactor is modelled according to the ideal plug flow reactor model. The assumption of plug flow is fulfilled for long beds packed with small particles: bed height/particle diameter > 50 and bed diameter/particle diameter > 10 (in this work 90 and 36, respectively). Thus, the following mass balance equation is used:

$$\frac{dF_i}{d\tau_w} = q \sum_j v_{ij} r_{mj} \quad (4)$$

where F_i is the molar flow of compound i , τ_w is the space time expressed in $\text{kg}_{\text{cat}} \text{h}/\text{m}^3$, q is the volumetric flow rate, v_{ij} is the stoichiometric coefficient of compound i in reaction j and r_{mj} is the rate of reaction j per unit weight of catalyst.

The model is solved using a MATLAB code, responsible of performing all the calculations and solving the set of ordinary differential equations (ode15s). The fitting of the unknown parameters from the model (e.g. parameters of the kinetic equation) is accomplished by the least-square method, using the MATLAB function `lsqnonlin`. The objective function of the least-square based regression consisted of trioxane and POMDME concentrations. The 95% confidence intervals were calculated with MATLAB function `nlparci`, which uses the residuals and jacobian matrix previously calculated by `lsqnonlin`.

3. Results and discussion

3.1 Catalyst stability

The catalyst stability has been evaluated by operating the continuous fixed-bed reactor for several hours at constant conditions: 80°C, 8.5 bar, space-time 2.8 kg h/m³ (liquid flow rate 5 mL/min). The feed consisted of a mixture of 18 mol% of trioxane in methylal. The evolution of trioxane conversion and selectivity to POMDME are shown in **Figure 1**. No noticeable deactivation was detected after more than 10 h of reaction, with a constant trioxane conversion of 73.4%.

Different formaldehyde sources have been proposed for POMDME synthesis from methylal. In general, trioxane and paraformaldehyde are the preferred ones, since they are anhydrous sources of high-purity formaldehyde. This prevents the formation of undesired by-products and catalyst deactivation, due to water [24, 38, 39]. However, it should be taken into account that these sources of formaldehyde are more expensive. The final product of the traditional formaldehyde manufacturing process is an aqueous formaldehyde solution, which requires further purifications to produce paraformaldehyde or trioxane. For this reason, in the present work, the influence of water on the activity and stability of the catalyst has been evaluated.

The experiments co-feeding water have been carried out at the same operating conditions as the previous stability test. Two water feed concentrations were considered, 1 and 10 mol%. Figure 2 shows the results of the experiments. The negative effect of water is very clear: trioxane conversion decreases from 73.4% to 38.5%, when 1 mol% water is used, and to 3.6%, for 10 mol%. This decrease in conversion also affects selectivity, which shifts towards shorter chain POMDME (e.g. selectivity 43.5% to POMDME₂, 51.0% to POMDME₃₋₅ and 5.4% to POMDME_{>5} in the water-free reaction, and 66.6% to POMDME₂, 33.0% to POMDME₃₋₅ and only 0.4% to longer POMDME when there is 1 mol% water in the feed).

Reaction was started with water co-feeding, which was discontinued after 2 h. As shown in Figure 2, after removing water from the feed, trioxane conversion increased very fast to the value corresponding to water-free conditions. Consequently, the effect caused by water is reversible and does not imply permanent deactivation of the catalyst, which recovers its initial activity.

Different studies carried out in batch reactors have shown that the presence of water in the feed leads to reversible side reactions of glycols and hemiformals formation [17, 18, 40]. However, these secondary compounds have not been detected in the present work. In the experiments, carried out in the continuous fixed-bed reactor at low space-time (1.6-3.2 kg h/m³), the main detected products correspond only to poly(oxymethylene) dimethyl ethers. Considering that the sum of selectivity and carbon balance are close to 100%, the formation of these lateral compounds can be ruled out, due to the low space-time used in the reactor. Based on this, at these conditions, any possible thermodynamic effect due to water can be discarded.

According to the observed behavior, the inhibition caused by water is attributed to the competitive adsorption of water on the catalyst surface. At high water concentration, a higher fraction of active centers is blocked with water and, hence, trioxane conversion decreases. Previous studies with this type of catalysts indicated that temperatures of 150-180°C are required to desorb water from the resin completely [41].

To sum up, water constitutes a great limitation towards POMDME polymerization. The presence of only 1 mol% of water means a loss of conversion close to 50%. For this reason, direct synthesis of POMDME from methanol is not a recommended reaction pathway. Water is generated in the first reaction, the synthesis of methylal, which inhibits the further polymerization of methylal to POMDME. A two-stage process with intermediate methylal separation and purification to eliminate water is advised to prevent the inhibition caused by water.

3.2 Reaction kinetics

Once the catalyst stability has been proved, the influence of the main operating parameters (temperature and space-time) on reaction rate has been evaluated. These experiments were carried out in the continuous fixed-bed reactor. As it can be observed in **Figure 3**, trioxane conversion increases, on increasing temperature (45-80°C) and space-time (1.6-3.2 kg h/m³). The influence of temperature is more marked: trioxane conversion is almost twice when temperature increased only 10°C.

Figure 4 represents the relationship between selectivity and conversion. For clarity, the selectivity to the different reaction products have been split into three groups: selectivity to POMDME₂, to POMDME₃₋₅ and to POMDME_{>5}. As previously indicated, POMDME with n=3-5 are better as diesel additives, so it is important to maximize their productivity. POMDME of other chain length and unreacted reagents can be separated and recycled to the reactor. To obtain the plot of Figure 4, all the experiments of Figure 3 have been considered (i.e. for all the temperature and space-time values). The selectivity adds up to 100% for all the reaction conditions studied, which allows us to rule out the presence of other unidentified by-products or free formaldehyde. The first finding is that product distribution (selectivity) only depends on conversion, being independently of the operating conditions required to achieve this conversion. Thus, the same conversion can be achieved by a different combination of temperature and space-time value, resulting in the same selectivity. The plot has been completed with the equilibrium selectivity, determined in the batch reactor when operated at high reaction times (the batch experiments are discussed latter in Section 3.3).

Selectivity to POMDME₂ decreases on increasing conversion, since this compound is the first product of the reaction between methylal and trioxane. The selectivity of the group formed by POMDME₃₋₅ increases with conversion, approaching the equilibrium one. Thus, at 70% conversion, selectivity to POMDME₃₋₅ is 51.4%, which is almost the equilibrium selectivity, 54.4%. The selectivity to POMDME_{>5} is nearly zero below 45% conversion. Then, this selectivity increases very slowly with conversion, approaching the maximum value at the equilibrium, 8.2%. This selectivity behaviour is characteristic of reaction systems in series, suggesting that the formation of POMDME evolves by insertion of oxymethylene groups one

by one (rather than by the insertion of a complete trioxane molecule formed by three oxymethylene groups).

The knowledge of this relationship is of great importance, since it allows selecting the optimal conditions for the process. According to Figure 4, selectivity and yield to POMDME₃₋₅ are maximum for the equilibrium conversion. Thus, a reactor designed for a high conversion close to the equilibrium would require the separation (e.g. using distillation) of the compounds of the reactor effluent into three groups: methylal and POMDME₂ (recycled to the reactor), POMDME₃₋₅ (the final product) and POMDME_{>5}. The compounds of the latter group are not desired in high amounts in the final product, because some of their properties are not compatible with the use as fuel additives [10, 11]. Alternatively, the reactor can be designed for a medium conversion, so that the formation of POMDME_{>5} is maintained below a given threshold. By this way, the separation of the reactor effluent would be less complex (and cheaper), since only methylal and POMDME₂ are separated and recycled to the reactor. For example, for a maximum selectivity to POMDME_{>5} of 2%, trioxane conversion should be 45%, which would lead to 44% selectivity to POMDME₃₋₅.

3.3 Reaction equilibrium

The reactions of POMDME synthesis are reversible. In order to study the extent of the equilibrium, high reaction times, difficult to achieve in continuous reactors, are required. For this reason, additional experiments in a batch autoclave reactor have been carried out with reaction times of 30 h. The feed consisted of 18 mol% trioxane on methylal. Pressure was maintained over 8 bar with nitrogen gas to prevent vaporization of the liquid reaction mixture. Different temperatures were tested in the range 50-90°C.

As an example, **Figure 5a** shows the evolution with time of the concentration for a reaction temperature of 50°C (results at other temperatures are included as Supplementary Information). It can be observed that trioxane is not consumed completely by the end of the reaction. Thus, equilibrium conditions are reached with trioxane conversion of 96.4% and selectivity of 37.3% to POMDME₂, 28.6% to POMDME₃, 16.4% to POMDME₄, 9.4% to

POMDME₅ and 8.2% to longer POMDME ($n>5$). The equilibrium product distribution is depicted in **Figure 5b** in terms of mass fractions (wt.% of trioxane \approx 1%).

Additional tests, carried out in the batch reactor using the acid catalyst (Amberlyst 15) and only trioxane as reactant (i.e. without methylal and using acetone as solvent), confirmed that trioxane decomposition is a reversible reaction. In these tests, first, trioxane decomposed to formaldehyde and, then, this formaldehyde polymerized to paraformaldehyde. At 60°C, 18 mol% trioxane and 1.6 g/L of catalyst, trioxane conversion decreased upon time and, after only 2 h of reaction, a constant value of 22% conversion was achieved. This means that all the reactions related to trioxane and formaldehyde are reversible and equilibrium is reached for a trioxane conversion of only 22%. On the contrary, the equilibrium was reached at trioxane conversion of 96.1% for the case of POMDME synthesis, carried out at the same operating conditions. This suggests that, in the latter reaction, the equilibrium is shifted towards products, while in the polymerization of formaldehyde to paraformaldehyde is shifted towards reactants.

3.3.1 Mechanism of chain propagation

Two different routes have been proposed for POMDME synthesis from methylal and trioxane. Some authors have suggested that POMDME growth takes place by direct trioxane insertion. Thus, trioxane breaks into a linear chain, which is inserted directly into a POMDME molecule [30, 31]. The other route involves the decomposition of trioxane into oxymethylene units (i.e. formaldehyde) and the growth of POMDME chains takes place by insertion of these units one by one [36, 42].

Figure 5a shows POMDME distribution obtained as function of reaction time in the previous experiment. POMDME concentrations gradually descend with chain length. Considering the first 7 h of reaction, when equilibrium has not yet been reached, it can be seen that while POMDME with $n=2$ appeared after 20 min of reaction, POMDME with $n=3$ and 4 were not detected until 40 and 60 min, respectively. The sequential appearance of POMDME _{$n+1$} after POMDME _{n} , suggests that polymerization occurs by monomeric formaldehyde insertion. Direct incorporation of trioxane would favor the formation of POMDME _{$n+3$} , with significant

changes in products distribution [36]. Some previous studies reported that POMDME synthesis follow a Schulz-Flory distribution, for the case of using both trioxane [22, 36] and paraformaldehyde, as reactants [35, 43]. Schulz-Flory distribution theory describes the relative ratios of polymers of different length that occur in an ideal step-growth polymerization process. This theory is widely used, for example, in the determination of the hydrocarbon distribution in the synthesis of Fisher-Tropsch.

Zhao *et al.* [43] defined Schulz-Flory distribution as:

$$W_n = C n \alpha^n, \quad \text{with} \quad \alpha = \frac{r_p}{r_p+r_t} \quad (5)$$

where α is the propagation probability factor, calculated from the net rates of chain propagation and termination (r_p and r_t respectively) and W_n is the mass fraction of each component. After integrating and linearizing, the resulting equation is:

$$\ln \frac{W_n}{n} = n \ln \alpha + \ln((\ln \alpha)^2) \quad (6)$$

In the same way, Zheng *et al.* [42] developed a theoretical molecular size distribution model at equilibrium:

$$\ln \frac{w_n}{n + 1.533} = n \ln \frac{\alpha_e}{\alpha_e + 1} + \ln \frac{1}{\alpha_e(2.533 + \alpha_e)} \quad \text{with} \quad \alpha_e = \frac{N_{CH_2O,R}}{N_{DMM,0}} \quad (7)$$

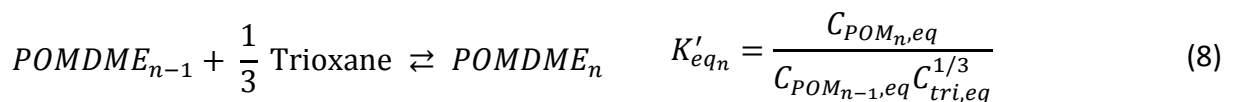
where α_e is a dimensionless factor, calculated from the ratio of reacted amount of formaldehyde to initial amount of methylal.

Both methodologies have been applied to the experiments at equilibrium conditions with good results, as shown **Figure 6** ($R^2 = 0.998$ and 0.994 , for Zhao *et al.* [43] and Zheng *et al.* [42] models, respectively). Both equations were applied also for conditions before reaching equilibrium (50°C, 6 h of reaction), with regression coefficients of $R^2 = 0.999$ and 0.998 in this transient state. Similar results were obtained with the experiments carried out at the other temperatures. These results confirm that the chain is formed step-wise by insertion of oxymethylene units.

The extent of the reaction can be calculated according to the method of Zhao *et al.* [43]. The temperature range studied in this work is narrow, so a relationship between the degree of polymerization and temperature cannot be obtained. An average value of $\alpha=0.32$ was obtained for equilibrium conditions, indicating a low degree of polymerization. This value is in accordance with those previously reported by Zhao *et al.* [43]: $\alpha=0.41$, for the reaction with trioxane and acidic carbon (sulfonated) as catalyst (50°C, 48 h), and $\alpha=0.34$, for the reaction with acid resins from paraformaldehyde (120°C, 2 h). Since POMDME₃₋₅ are preferred as fuel additives, this low degree of polymerization is good to maximize the formation of these POMDME.

3.3.2 Determination of equilibrium constants

In the batch experiments, the concentrations measured at the end of the reaction correspond to equilibrium conditions. These concentrations can be used to determine the equilibrium constants of the reactions. Given the difficulty of quantifying the amount of free formaldehyde in the reaction mixture, the equilibrium constants corresponding to the overall reactions are calculated. These constants are the result of reformulating the reaction equilibrium (eq. 8), considering trioxane as reactant.



The influence of temperature over the equilibrium constants was fitted according to Van't Hoff equation (equation 9):

$$K' = K'_{ref} e^{\frac{\Delta H_R}{R} \left(\frac{1}{T} - \frac{1}{323} \right)} \quad (9)$$

where K'_{ref} is the equilibrium constant at a reference temperature of 50°C and ΔH_R is the reaction enthalpy. The parameters obtained by fitting of the experimental equilibrium concentration are shown in Table 1. The calculated K_2 behaviour, corresponding to POMDME₂ synthesis, differs slightly from the rest, being its reaction enthalpy a little smaller. This is probably caused by the high volatility and concentration of methylal, which could underestimate its concentration in the samples collected from the reactor.

The chain propagation probability can be used to predict the equilibrium constants. Thus, the molar concentration of POMDME_n appearing in eq. (8) can be substituted by the concentrations predicted by the Schulz-Flory distribution expression, eq. (5). After simplification (full derivation included as Supplementary Information S2), this results in the following expression:

$$K'_{eq,n} = \frac{C_{POM_n,eq}}{C_{POM_{n-1},eq} C_{tri,eq}^{1/3}} = \frac{\alpha}{C_{tri,eq}^{1/3}} \frac{n}{(n-1)} \frac{M_{n-1}}{M_n} \quad (10)$$

Where M_n are the molecular weights and α is the propagation probability factor. As explained in section 3.3.1, an average value of $\alpha = 0.32$ was fitted at equilibrium conditions. This value has been used in eq. (10), together with the experimentally determined value of $C_{tri,eq} = 78.7 \text{ mol/m}^3$ at 50°C. The predictions of the equilibrium constants at 50°C are included in Table 1. As shown, there are some deviations, but this methodology is able of predicting the equilibrium constants with an error of $\pm 8\%$.

Some authors simplify the equilibrium model assuming that the absolute values of the equilibrium constants for different chain lengths are identical, based on the ratios between constants K_n ($n \neq 2$) and K_2 close to unity [30, 36]. In this work, the ratios between constants have been calculated with respect to K'_{POM3} to avoid the introduction of any possible error due to K'_{POM2} inaccuracy: $K'_{POM2}/K'_{POM3} = 1.11$, $K'_{POM4}/K'_{POM3} = 0.99$, $K'_{POM5}/K'_{POM3} = 0.95$ and $K'_{POM6}/K'_{POM3} = 0.92$. Although the values obtained for equilibrium constants are very similar, a slight decreasing trend has been detected, which has also been observed in the results of other studies in the literature [30]. The values of reaction enthalpy obtained in this work for the different POMDME are, therefore, close but not equal. It can be detected a linear relationship between the reaction enthalpy and chain length, as depicted in **Figure 7**.

According to this correlation, the reaction enthalpy decreases slightly on increasing the chain length. Since the reaction enthalpy of POMDME₂ is lower, it is not considered in the correlation with n. The average enthalpy value obtained is 2.5 kJ/mol, with a standard deviation of 0.4 kJ/mol. The values of the reaction enthalpy are similar to those reported in the bibliography for this reaction system. Burger *et al.* [30] considered in their study that equilibrium constants of different chain lengths were the same and estimated an average reaction enthalpy of 2.47 kJ/mol, as obtained in this work.

3.4 Kinetic modelling

POMDME synthesis from methylal and trioxane is a reaction system formed by different steps: first, trioxane decomposes to formaldehyde (FA) in the presence of an acid catalyst and, then, successive polymerization of methylal (DMM) with these formaldehyde units forms long chain POMDME (Schulz-Flory distribution). According to the previous findings (see section 3.3), direct incorporation of trioxane in methylal has been discarded.



Given their low (or even null) concentrations obtained in all the experiments, the formation of POMDME with $n \geq 6$ has not been considered for the kinetic modelling.

Based on this reaction scheme, three different reaction mechanisms and their corresponding kinetic models, denoted as Models A to C, have been proposed, as summarized in Table 2. On the one hand, Model A assumes that all the different steps of the reaction mechanism are kinetically relevant. In the modelling, only tests with trioxane conversion below 40% have been considered. At these conditions far from the equilibrium ones (equilibrium conversion is 96.5%), the influence of the reverse reactions can be considered negligible. Consequently, the reactions of Model A have been treated as irreversible.

On the other hand, Models B and C are obtained from Model A, assuming further simplifications. Free formaldehyde has not been detected in the reactor effluent and given that the sum of the product selectivity is almost 100% in all the experiments, it can be

concluded that its concentration is actually very low. This is in agreement with trioxane decomposition reaction being the rate-limiting step of the reaction scheme, as stated by Model B. Thus, all the formaldehyde produced reacts very fast to POMDME and, hence, its concentration is very low. The POMDME synthesis reactions from formaldehyde are much faster and, hence, can be considered at the equilibrium.

On the contrary, Model C considers the opposite behaviour: POMDME synthesis reactions are the rate-limiting step and trioxane decomposition is assumed to be at equilibrium. This statement is compatible with a low formaldehyde concentration in the reaction media, only if trioxane decomposition is fast and reversible, but with a low equilibrium constant. Thus, the low equilibrium constant means that the reaction is shifted towards reactants and free formaldehyde concentration is low. According to this mechanism, formaldehyde consumed in the synthesis of POMDME would be replaced very fast by the shift of the reversible trioxane decomposition reaction.

Table 2 shows the kinetic equations developed for the proposed models A to C, considering the abovementioned assumptions. The experimental results of the continuous fixed-bed reactor have been used to fit these three kinetic models. The fitting has been done in two steps. First, only trioxane concentration data has been used to fit trioxane decomposition rate equation. A kinetic constant has been fitted for each of the temperatures considered and Arrhenius equation has been used to model the temperature dependence:

$$k = k_{ref} e^{\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{323} \right)} \quad (14)$$

where k_{ref} is the kinetic constant at the reference temperature of 50°C and E_a is the activation energy.

This preliminary fitting has revealed that the best fit of the experimental trioxane concentration data is obtained using a kinetic equation of order 1 (like in Models A and B) rather than order 1/3 (like in Model C).

Using these simple kinetic models, a preliminary estimation of mass and heat transfer limitations has been done. Thiele modulus (ϕ) and effectiveness factor (η) were calculated [44] and revealed the existence of internal mass transfer limitations for reactions above 60°C ($\eta < 85\%$). Consequently, concentration data obtained above 60°C were discarded and the model fitting was repeated. External mass transfer (Mears criterion [45]) or heat transfer

limitations according to Mears criterion for external heat transfer evaluation [45] and an internal heat transfer empirical correlation [46] were ruled out under the conditions studied.

The next step in the fitting is based on all the POMDME concentration data. Trioxane kinetic parameters were introduced in the POMDME concentrations fitting, to obtain POMDME synthesis constants at each temperature. Three sets of parameters at each of the reaction temperatures are obtained. As the variation of the equilibrium constants with the temperature has been found to be very small, and the range of valid data used for the fitting is very narrow, only 10°C (45-55°C), equilibrium constants dependence on temperature cannot be determined, and they are considered independent of the temperature for the next fittings (Model B). Finally, all the kinetic and equilibrium parameters obtained by this way were used as guess solution in a fitting using all the experimental data (different reaction temperature and space times). In Model B, the ratio of the equilibrium constants K_n/K_3 was directly fitted. Thus, the values obtained from the proposed model can be compared with the K'_{POMn}/K'_{POM3} ratios determined from the experimental data of the autoclave reactions, since they are equivalent.

The goodness of the fitting can be assessed by the sum of square errors (SSE), regression coefficients (R^2) and confidence intervals of the fitted parameters. The model with the best fitting is clearly model B, with regression coefficient $R^2=0.99$, sum of square errors $SSE = 2.8 \cdot 10^4 \text{ mol/m}^3$ and narrow confidence intervals. Model A, which considers that all the reactions of similar rate and, hence, kinetically relevant, has a poorer fitting. For this model, different local optimum points were obtained with an unsatisfactory fitting to the experimental data (e.g. $R^2 = 0.98$, $SSE = 3.3 \cdot 10^4 \text{ mol/m}^3$). The confidence intervals of the kinetic constants of the chain propagation reactions (model A) were an order of magnitude greater than the fitted parameters, what suggests that these parameters are not significant. This is in agreement with the statement that trioxane decomposition reaction is the rate-limiting step of the reaction scheme, as stated by Model B. As for the case of Model A, Model C presents excessively wide confidence intervals, ruling out the validity of the model ($R^2 = 0.97$ and $SSE = 4.3 \cdot 10^4 \text{ mol/m}^3$).

The obtained fitting parameters of Model B and the corresponding confidence intervals are shown in Table 3. The Model B predictions are depicted as solid lines in Figure 8 and compared to the experimental data, represented as symbols. A great agreement between

both of them confirms the validity of the model within the range of operating conditions of the experiments. This finding could also explain the Schulz-Flory product distribution, even when reaction system equilibrium is not reached, since POMDME synthesis reactions are in equilibrium during the whole reaction, and trioxane decomposition reaction limits the overall rate. Likewise, the model is capable of accurately predicting results at high temperatures, if the effectiveness factor is used to model the intraparticle mass transfer resistance (Figure S4 of Supplementary Information).

The ratio between the equilibrium constants obtained by the model is similar to that calculated using the experimental data obtained in the batch reactor (section 3.3). The greatest discrepancy corresponds to K_2/K_3 , because the parameter can be affected by inaccuracies in the determination of methylal concentration.

The fitted activation energy of trioxane decomposition reaction was $E_a = 112.2$ kJ/mol. Liu *et al.* identified depolymerization of paraformaldehyde as rate-determining step of the reaction, compared to the fast POMDME synthesis [47]. In the same way, Li *et al.* present trioxane dissociation as a vital step in the reaction system [48]. Nevertheless, most of the studies that study the kinetics of the reaction consider formaldehyde as a starting product, without involving trioxane (or paraformaldehyde) decomposition in the equations system. Wang *et al.*, meanwhile, considered kinetically relevant both the reversible POMDME synthesis reactions and the reversible trioxane decomposition reaction, for which they reported a value of $E_a = 53.2$ kJ/mol, for the forward reaction catalysed by ionic liquids. Burger *et al.* considered trioxane in their modelling, but they proposed a model based on a modified Langmuir-Hinshelwood-Hougen-Watson mechanism where reaction stages are fast and the rate-limiting steps are the sorption processes [30].

3.5 Modelling of the inhibition caused by water

Once the kinetic model that represents the behaviour of the reactor has been validated, the next step consists on the quantification of the inhibition caused by water. As reported in the experiments of section 3.1, water causes a high drop in trioxane conversion, but this effect is completely reversible, when water is removed (Figure 2). For this reason, it has been hypothesized that this inhibition is due to the competitive adsorption of the water molecules

on the catalyst active centres. According to this model, conversion decreases because water blocks part of the active centres and, hence, there is a lower availability for the reaction. Model B can be modified to account for this inhibitory mechanism by the following expression:

$$-r_{tri} = \frac{k_1 C_{tri}}{1 + K_w C_w} \quad (15)$$

Where K_w is the water adsorption constant and C_w is the molar concentration of water.

At steady state (i.e. constant conversion in Figure 2), the concentration of water can be considered uniform throughout the fixed-bed reactor. Consequently, the denominator of eq. (15) is constant and this equation can be easily integrated using the methodology explained in section 2.4. For the present case, the parameters of the kinetic model previously fitted are fixed and only the water adsorption constant is fitted using the water inhibition tests.

It has been found that the proposed inhibitory model provides a good fitting ($R^2=0.996$) of the experimental data (Figure S5 of Supplementary Information). This corroborates the hypothesis of water causing competitive adsorption on the catalyst active centres. A water adsorption constant value of $0.42 \text{ m}^3/\text{mol}$ (at 80°C) has been determined.

Conclusions

Poly(oxymethylene) dimethyl ether synthesis has been studied using methylal and trioxane as reactants. The acid ion exchange resin Amberlyst 15 has demonstrated good activity and stability for the reaction. Experiments carried out in a discontinuous reactor allowed to determine that the reactions are reversible and their equilibrium constants were calculated. In the same way, it has been confirmed that POMDME chain propagation reactions proceed step-wise by insertion of formaldehyde units.

Reaction rate and product distribution have been studied in a continuous fixed-bed reactor operating at different space-time and temperature. It has been concluded that product distribution (i.e. selectivity) only depends of conversion. Based on the experimental results, a kinetic model representing the reactor behavior has been proposed and validated. It has been concluded that trioxane decomposition is the rate-determining step of the reaction

scheme with an activation energy of 112.2 kJ/mol. POMDME chain propagation reactions can be considered in equilibrium.

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Figures

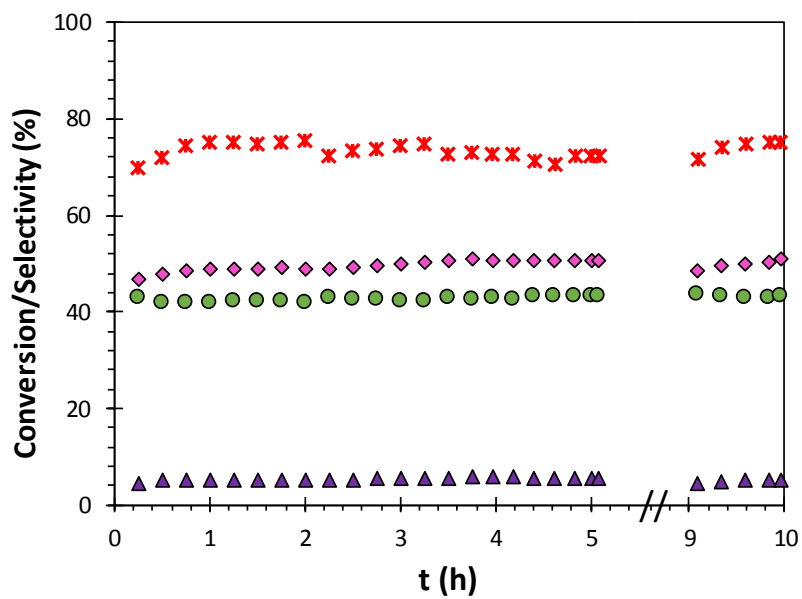


Figure 1. Evolution with time on-stream of trioxane conversion (x) and selectivity to POMDME₂ (●), POMDME₃₋₅ (◆) and POMDME_{>5} (▲). Operating conditions: 80°C, 18.0 mol% trioxane, 8.5 bar and space-time 2.8 kg h/m³.

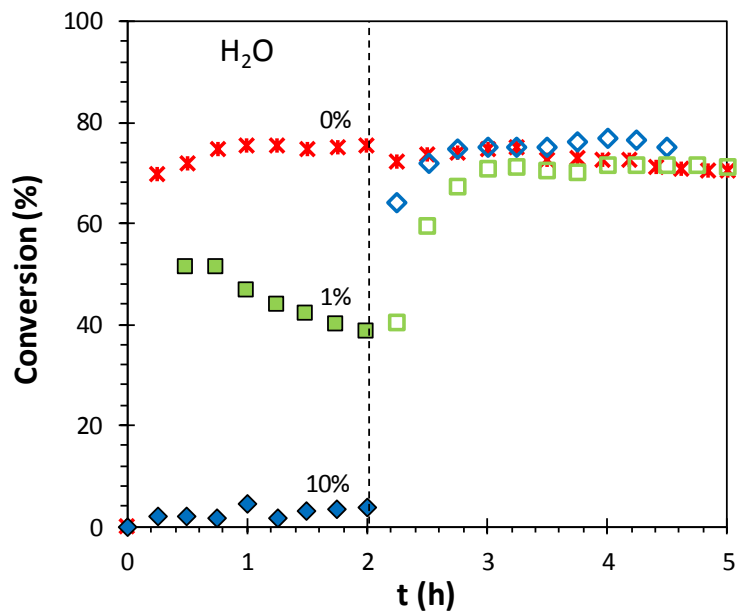


Figure 2. Effect of water co-feeding on trioxane conversion. Water mole fraction: 0% (x), 1% (■) and 10% (◆). Filled symbols: water co-feeding. Empty symbols: water discontinued. Operating conditions: 80°C, 18.0 mol% trioxane, 8.5 bar and space-time 2.8 kg h/m³.

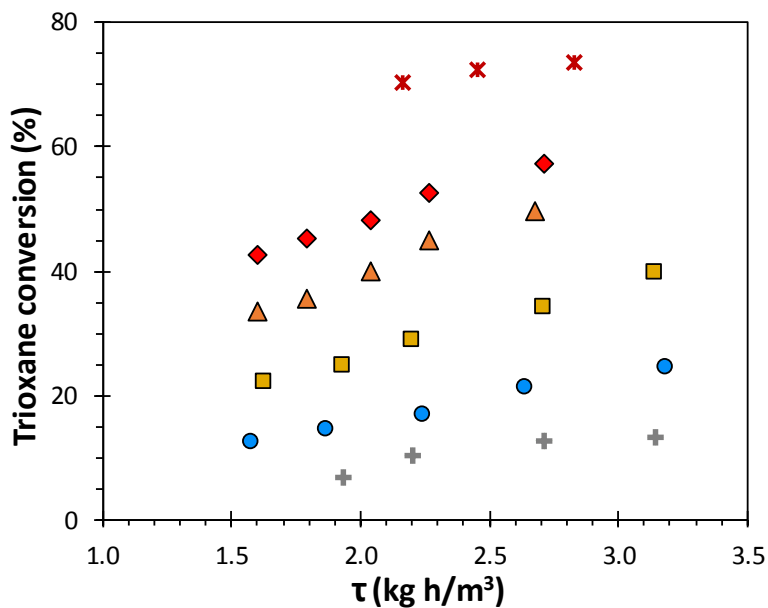


Figure 3. Influence of space-time and temperature on trioxane conversion. Operating conditions: 18 mol% trioxane feed concentration and 8.5 bar. Temperature: 80°C (x), 65°C (♦), 60°C (▲), 55°C (■), 50°C (●) and 45°C (+).

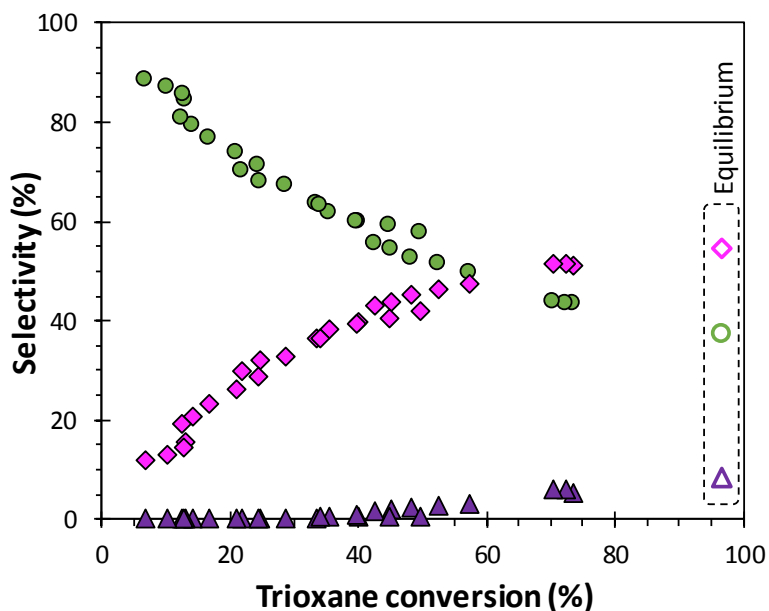
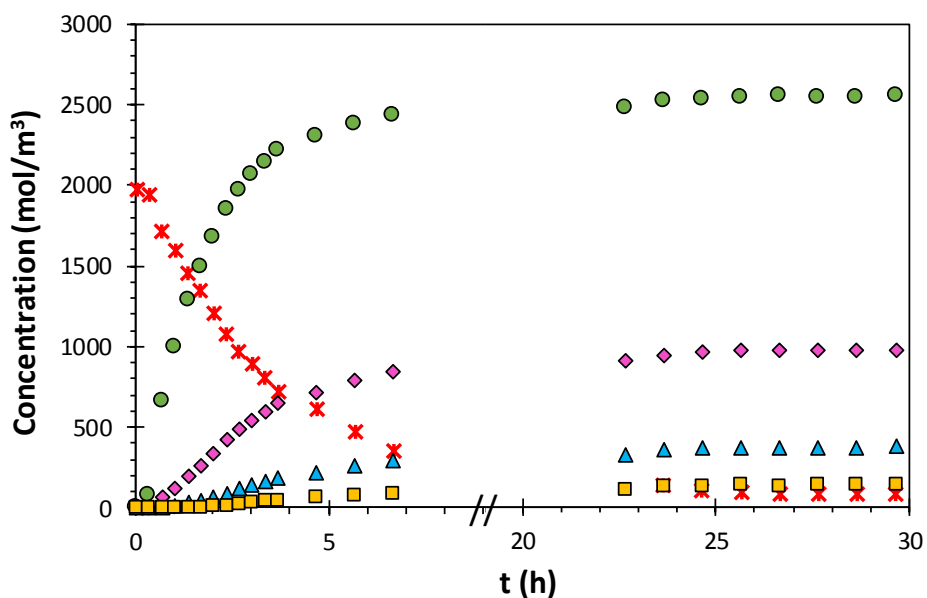
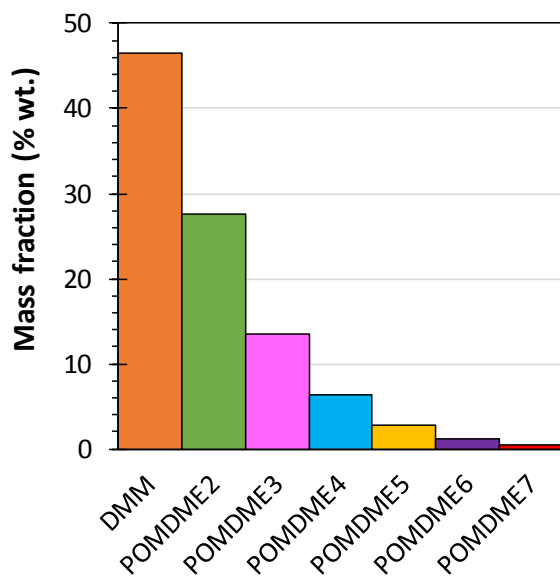


Figure 4. Relationship between selectivity and conversion. Selectivity is grouped as follows: POMDME₂ (●), POMDME₃₋₅ (♦) and POMDME₅₊ (▲). Filled symbols: Fixed-bed reactor experiments (temperature range 45-80°C and space-time 1.6-3.2 kg h/m³). Empty symbols: equilibrium conditions obtained in batch reactor experiments.



a)



b)

Figure 5. Discontinuous reaction experiments: a) Evolution of concentration with time and b) POMDME equilibrium distribution. Compounds: trioxane (⌘), POMDME₂ (●), POMDME₃ (◆), POMDME₄ (▲) and POMDME₅ (■). Operating conditions: 50°C, 18 mol% trioxane feed concentration, 8.5 bar and 1.6 g_{cat}/L.

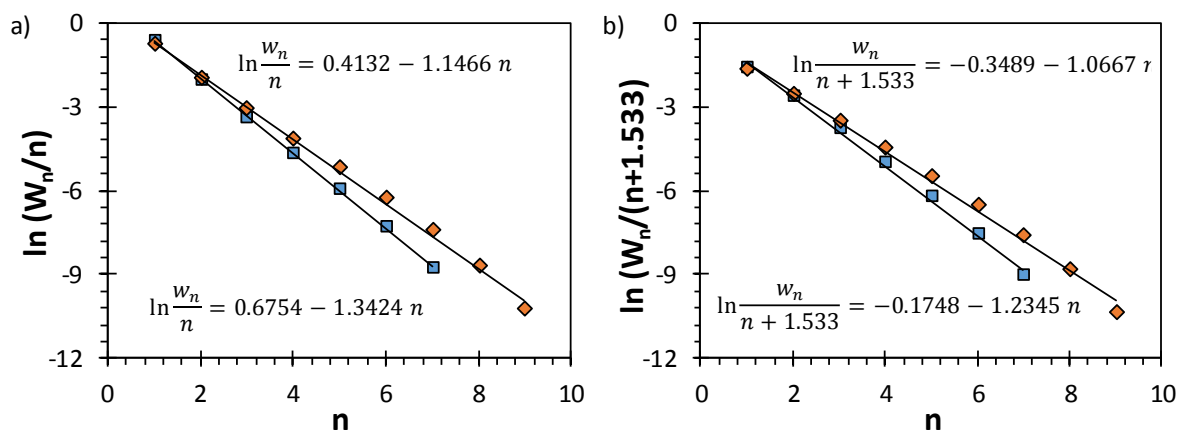


Figure 6. Schulz-Flory distribution evaluation, according to (a) Zhao *et al.* [43] and (b) Zheng *et al.* [42] methods, in discontinuous reaction experiments. Operating conditions: 50°C, 18 mol% trioxane feed concentration, 8.5 bar and 1.6 g_{cat}/L, in transient state: 6 h of reaction (■), and in equilibrium conditions (◆).

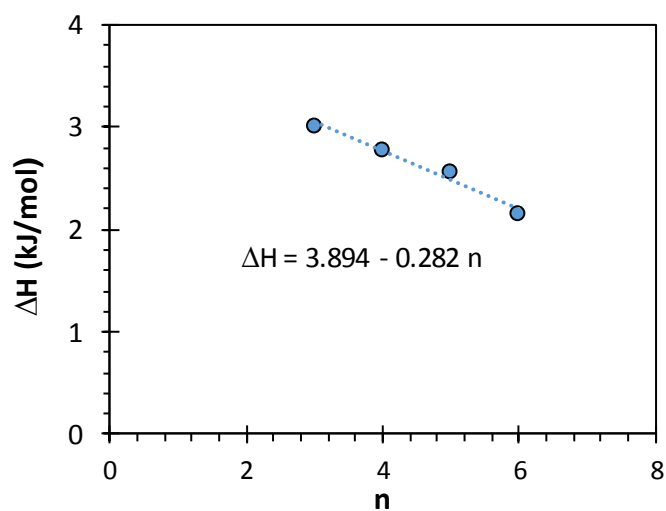
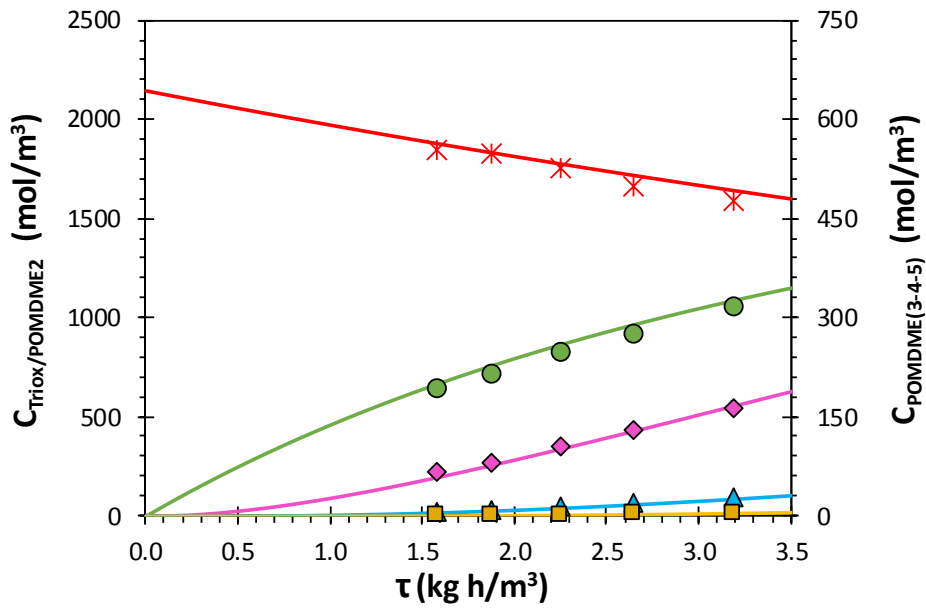


Figure 7. Relationship between reaction enthalpy and chain length of POMDME.

a)



b)

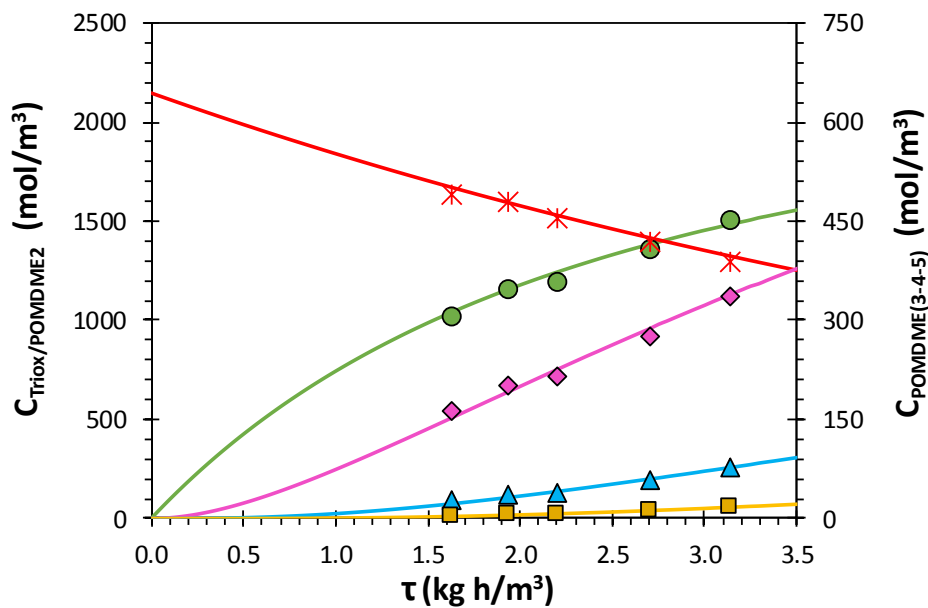


Figure 8. Model fitting for concentration of trioxane (ж), POMDME₂ (●), POMDME₃ (◆), POMDME₄ (▲) and POMDME₅ (■). Operating conditions: 18% mol of trioxane in the feed, 8.5 bar. Temperature: (a) 50°C and (b) 55°C. Symbols: experimental data, lines: model fitting.

Tables

Table 1. Equilibrium constants and Van't Hoff equation parameters.

Compound	K' at 50°C (m ³ /mol) ^{1/3}	ΔH_R (kJ/mol)	R ²	K' at 50°C * (m ³ /mol) ^{1/3}
POM2	0.100	2.1	0.99	0.107
POM3	0.090	3.0	0.96	0.087
POM4	0.089	2.8	0.98	0.082
POM5	0.085	2.6	0.98	0.079
POM6	0.082	2.2	0.94	0.078

* predicted using Schulz Flory distribution with $\alpha = 0.32$

Table 2. Proposed kinetic models for POMDME synthesis from methylal and trioxane.

Model	Kinetic equations
A	$-r_{tri} = k_1 C_{tri}$ $r_{POM_n} = k_n C_{FA} C_{POM_{n-1}}$
B	$-r_{tri} = k_1 C_{tri}$ $C_{POM_n} = K_{eq,n} C_{FA} C_{POM_{n-1}}$
C	$r_{POM_n} = k_n K_{eq,tri} C_{tri}^{1/3} C_{POM_{n-1}}$

Table 3. Fitting parameters of the proposed kinetic model (Model B).

Model parameters	Fitted value
$k_{1, 50^\circ\text{C}} \times 10^5$ (m ³ /kg _{cat} s)	2.26 ± 0.05
E_a (kJ/mol)	112.2 ± 4.1
K_2/K_3	0.85 ± 0.01
K_4/K_3	1.01 ± 0.01
K_5/K_3	0.94 ± 0.01