



Review

Catalytic synthesis of polyoxymethylene dimethyl ethers (OME): A review



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ABSTRACT

Polyoxymethylene dimethyl ethers (OME) containing 3–5 CH₂O units (OME_{3–5}) are appealing oxygenated fuels, which can be used in diesel engines with only slight fuel system modifications. Their combustion leads to reduced hazardous exhaust gas emissions compared to standard diesel. Due to the absence of C-to-C bonds, they considerably reduce soot formation, allowing in turn significantly higher exhaust gas recirculation (EGR) rates to reduce NO_x emissions. Established liquid-phase OME production processes involve trioxane as a costly intermediate. Moreover, the OME product equilibrium composition follows a Schulz-Flory distribution making selective synthesis of specific chain length cumbersome. Current research efforts focus on simplifying the existing processes by using fewer steps, simpler reactants and less energy. Several catalyst classes were reported to catalyze OME acid synthesis. Little is known about the reaction mechanisms and the elementary steps involved. This review highlights the need for more systematic research on new reactants, efficient catalysts and simpler processes.

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Contents

1. Introduction	408
2. OME properties as synthetic fuel	408
2.1. Physico-chemical properties	409
2.2. Combustion and emission characteristics	409
3. Synthesis routes for the production of OME	410
3.1. Synthesis routes	411
3.1.1. Anhydrous synthesis of OME [B2]	411
3.1.2. Aqueous synthesis of OME [A1, A2, B1, C1]	411
3.1.3. Selective, one-step oxidation of methanol to OME [1,D3]	411
3.2. Side reactions during OME synthesis	412
4. Catalysts	412
4.1. Liquid catalysts	412
4.2. Heterogeneous catalysts	413
4.3. Catalyst for direct gas-phase synthesis of OME	414
5. Reaction mechanisms	415
5.1. Decomposition of formaldehyde sources	415
5.2. Chain growth mechanisms	415
5.3. Simultaneous vs. sequential OME formation	416
5.4. Molecular size distribution	416
5.5. Kinetic models	416
6. Conclusion and outlook	418
Acknowledgements	418
References	418

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1. Introduction

Diesel engines have a higher thermal efficiency than gasoline engines due to their higher pressure and temperature. However, the combustion of diesel fuel lead to hazardous exhaust gas emissions, which contribute to air pollution [1]. These exhaust emissions are classified as carcinogenic to humans by the International Agency for Research on Cancer [2]. In this context, polyoxymethylene dimethyl ethers (OME, also referred to as OMEs, POME or POMDME in the references) have recently received increasing attention, since various studies [3–10] demonstrated that a blend of OME with diesel fuel reduces soot particles formation, unburned hydrocarbons and carbon monoxide emissions during combustion. At the same time, nitrogen oxide emissions (NO_x) remained at a similar level, at which both slight increase [4,9,10] and decrease [8,11] have been reported.

OME, shown in Fig. 1, are oligomers composed of CH_2O units, which are highly stable since their chains are capped with one methyl and one methoxy group. The oxymethylene chain of variable length dictates the molecule properties.

A particularly attractive property of OME is that the blends of diesel fuel and OME with the appropriate chain length can be used in slightly modified diesel engines [4]. Their properties, notably boiling point, cetane number and viscosity, can be controlled via the chain length. Their large scale usage therefore requires no modifications to the fuel distribution infrastructure and only slight adjustment to the injection system. If produced from renewable sources such as biomass, their usage may reduce the global CO_2 emissions compared to fossil fuels in addition to their emission reduction effect [12].

Biofuel usage will become mandatory in many areas of the world such as in the European Union with a ratio of 10% of bio-fuels for transport by 2020 [13]. The current source of biodiesel is mainly first generation biofuels such as fatty acid methyl esters (FAME) biodiesel. However, their usage was shown to increase CO_2 emissions up to 20% compared to oil-based diesel when effects of indirect land use are considered [14]. OME may provide a sustainable alternative to first generation biofuels and part of the fossil fuels.

OME are synthesized from methanol, which can be produced via biomass gasification and subsequent syngas conversion. Methanol is a versatile chemical considered for storing renewable energy and a product of CO_2 recycling processes which constitutes the basis of the methanol economy [15]. The different ways methanol is produced and used in the OME synthesis processes are shown in Fig. 2. Several combinations of reactants are available to synthesize OME. Formaldehyde is produced through methanol oxy-dehydrogenation process, which is then used to produce trioxane (TRI) or paraformaldehyde (PF). Dimethoxymethane (OME_1 , also referred to as DMM in the references) is the shortest OME and is synthesized from methanol and formaldehyde by reactive distillation. Current trends highlight the shift of focus towards production processes requiring less steps and simpler reactants such as dimethyl ether (DME), methanol or aqueous formaldehyde.

Researchers have proposed various OME production methods using ion exchange resins as well as ionic liquids as catalysts [16,17]. Considering the undesirable formation of byproducts,

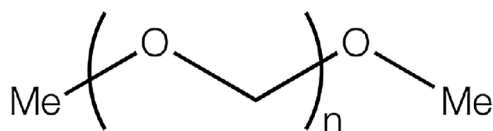


Fig. 1. Structure of polyoxymethylene dimethyl ethers (OME). $\text{OME}_n = \text{H}_3\text{C}(\text{—O—CH}_2)_n\text{—CH}_3$.

energy intensive separation steps are required to obtain concentrated, high-quality OME of the desired chain length. The first efforts to synthesize OME were accomplished as early as 1904, when Descudé prepared OME_2 by reaction of dichlorodimethyl ether and sodium methylate [18]. In the 1920s, Staudinger and Luthy [19] systematically investigated their properties and synthesis. High molecular weight polyoxymethylene ethers are interesting polymer materials, called POM, and in the middle of the 20th century several companies, notably DuPont in the 1960s, invented production processes to obtain thermally stable POM polymers [20]. Boyd determined some physico-chemical properties of OME_{2-5} [21]. As oxygen-containing compounds demonstrated promising combustion and emission properties, interest in OME production started at the beginning of the 21st century. BP corporation [22–29] patented various production methods from several reactant combinations from 1999 to 2003, followed from 2007 to 2011 by BASF [30–33] and others [34,35]. Recently, Chinese academics and industry have been very active in methanol and dimethyl ether synthesis from coal [36]. They have therefore taken the lead, in terms of number of publications or patents, on the development of OME as a solution to use their coal feedstock and alleviate their air pollution problems. Shandong Yuhuang Chemical Co. inaugurated an OME synthesis plant in 2015 based on a fluidized-bed reactor process [37,38]. To the best of our knowledge, it is the only reported OME production facility alongside with pilot plants projects in Germany [4,9,10,39–42]. Recently, interest in Germany in OME production has regained much interest, reflected in these pilot activities and a rapidly increasing number of publications, however, with a focus on carbon-neutral production of OME in contrast to the Chinese focus on coal as primary carbon source.

Even though OME synthesis is relatively easy and involves catalytic steps, the current production routes are either expensive or energetically rather inefficient, leading to uneconomical production or modest CO_2 footprints, respectively. A recent study from Schmitz et al. assessed the production costs of large-scale OME production [43]. The major costs were predicted to be of around 60% for raw material and 20% for energy consumption. Large-scale production of OME requires technically feasible processes and economically viable prospects. Furthermore, more suitable catalysts have to be developed for these processes and more research on the reaction mechanism is necessary. Although much literature is now available on liquid-phase and batch reactor synthesis, research is still required on the scale-up to larger, continuous processes. This paper reviews the literature on OME synthesis with the objective to stimulate new insights into and new ideas for catalytic processes to this fascinating type of fuel molecules. We will begin by briefly discussing the properties of OME as fuel additives. The main synthesis routes will then be delineated and the catalysts used and their performances will be described. Finally, a short discussion of the proposed mechanisms will be provided.

2. OME properties as synthetic fuel

There have been many investigations on the usage of oxygen-containing compounds (oxygenates) as fuels or additives to conventional fuels in spark-ignition engines. They were initially of interest for their high octane numbers as anti-knocking agent to replace tetraethyl lead with oxygenates such as methyl tertiary butyl ethers [44]. Further research on fuels containing a higher weight percentage of oxygen demonstrated their soot reduction properties during combustion in diesel engines [45].

The simplest oxygenates with a higher oxygen weight percentage are dimethyl ether and methanol. The former has a high cetane number, a low autoignition temperature and combusts almost

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