



Full Length Article

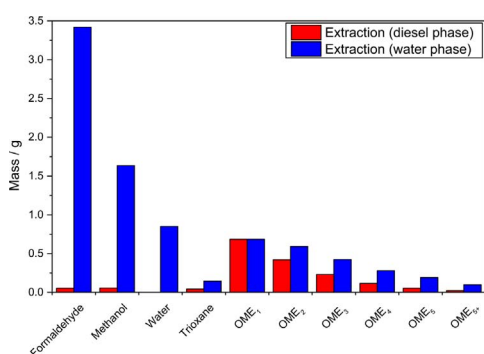
Production of oxymethylene dimethyl ether (OME)-hydrocarbon fuel blends in a one-step synthesis/extraction procedure



Dorian Oestreich, Ludger Lautenschütz, Ulrich Arnold*, Jörg Sauer

Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Oxymethylene dimethyl ethers
Diesel fuels
Emission reduction
Fuel additives
Methanol
Oxygenate fuels

ABSTRACT

Oligomeric oxymethylene dimethyl ethers (OMEs) of the type $\text{CH}_3\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$ are promising diesel fuels with an enormous potential for the reduction of soot and NO_x emissions. Oligomers with $n = 3-5$ are particularly advantageous, since their physicochemical and combustion properties are similar to conventional diesel. OMEs can be produced from methanol and formaldehyde but a series of byproducts, especially hemiformals, glycols, water and minor amounts of cyclic ethers, are also formed. These need to be separated from the product mixtures, which affects efficiency of this synthesis pathway. To isolate the desired OMEs, a one-step synthesis/extraction procedure is described. It implies highly selective extraction of OMEs from aqueous reaction solutions employing hydrocarbons as extraction agents. If fuel-type hydrocarbons are used, the resulting OME-hydrocarbon blends can be directly used in fuel applications. The corresponding oxymethylene diethyl ethers (OMDEEs) have also been investigated. Compared to OMEs, OMDEEs exhibit an increased solubility in nonpolar media but, as a result, solubility of educts and byproducts also increases. OME blends with hydrogenated vegetable oil and diesel have been prepared containing 10% of OMEs. It could be shown that such blends meet current diesel standards to a large extent.

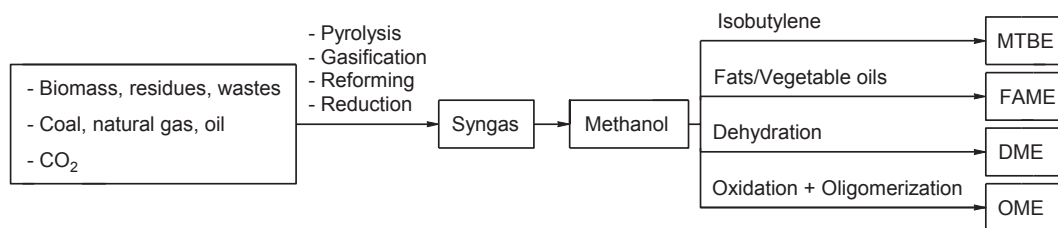
1. Introduction

Several organic ethers exhibit outstanding combustion properties and therefore some of them are widely employed as fuels or fuel

additives. Prominent examples are methyl and ethyl tert-butyl ether (MTBE and ETBE), which are well-established octane boosters for spark ignition engines [1]. Regarding diesel engines, fatty acid methyl esters (FAME) are the main constituents of biodiesel. Furthermore, dimethyl

* Corresponding author.

E-mail address: ulrich.arnold@kit.edu (U. Arnold).



Scheme 1. Synthesis of fuel-related ethers via synthesis gas and methanol.

ether (DME) has been extensively investigated as an alternative diesel fuel [2–4].

In this context, an enormous interest in oligomeric oxymethylene dimethyl ethers (OMEs, $\text{CH}_3\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$, $n = 1-5$) awakened and activities in this research field extremely increased in recent years. OMEs are related to DME ($\text{CH}_3\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$, $n = 0$) and exhibit an enormous potential for the reduction of soot and NO_x emissions. Due to their high oxygen content and the absence of carbon-carbon bonds in the molecular structure, formation of pollutants is suppressed during combustion [5–7]. Thus, strict exhaust emission standards can be met and exhaust gas treatment can be simplified. Properties of OMEs strongly depend on the chain length and OMEs with $n = 3-5$ exhibit physicochemical as well as fuel properties similar to conventional diesel [8,9]. Therefore, no serious changes of the fuel supply infrastructure and engines are necessary. Further advantages are their good miscibility with established fuels, low corrosivity as well as favorable health- and safety-related properties.

Regarding the production of OMEs and other fuel-related ethers, many strategies are based on methanol (Scheme 1). Methanol is produced from synthesis gas, which is usually stemming from fossil resources, especially natural gas. Synthesis gas can also be obtained from renewable resources via different pretreatment technologies, depending on the feedstock type, and subsequent gasification [10]. If renewable feedstocks are employed for OME synthesis, not only soot and NO_x emissions can be reduced but also total CO_2 emissions considering the entire system from feedstocks to combustion.

In spite of all the benefits mentioned above, a highly optimized and efficient production of OMEs is still a major challenge. Thus, availability is restricted at present and sufficient quantities of OMEs for intense testing can only be purchased from a few Chinese suppliers. However, capacities of Chinese plants are currently exceeding 40,000 tons per year and activities in the field of OMEs are rapidly developing there [11]. Production of OMEs can be carried out employing different educts like methanol, DME, dimethoxymethane (OME_1) and formaldehyde sources like formalin, *p*-formaldehyde, or trioxane. Different homogeneous and heterogeneous acidic catalysts such as sulfuric acid, zeolites, ion exchange resins, metal-oxides or heteropoly acids are typically used [12–15]. A distinction can be drawn between OME synthesis in aqueous reaction systems (e.g. reaction of methanol with formalin or *p*-formaldehyde) and synthesis in anhydrous systems (e.g. reaction of dimethoxymethane with trioxane). In aqueous systems significant amounts of water, hemiformals and glycols are formed as by-products [16–19]. In contrast, formation of such byproducts is largely suppressed in anhydrous systems [20–23]. However, the use of aqueous systems, especially the reaction of methanol with formaldehyde, is highly desired since low-cost educts can be employed.

All reactions, in aqueous as well as anhydrous media, are limited by chemical equilibrium and can be hardly directed by variation of parameters like temperature, pressure or catalyst [17,19,20,23]. The desired OMEs have to be separated from the reaction mixtures and residual educts as well as byproducts have to be recycled and refed into the process for further conversion. Typically, several distillation steps are employed, even in the most advanced processes, which affect the overall process efficiency [24–28]. Thus, alternative separation technologies are crucial for further improvements and realization of a

highly optimized production process. Moulton et al. described reactions of methanol with *p*-formaldehyde without catalyst [29]. In that case, comparatively high temperatures (150–240 °C), high pressures (20–69 bar) and long reaction times (4–7 h) were needed. After reaction, product mixtures were extracted with diesel fuel but compositions of the resulting blends were not reported.

Within this work, a convenient one-step procedure for the production of OME-hydrocarbon blends is proposed. Selective extraction of OMEs from aqueous reaction solutions is described employing hydrocarbons such as *n*-dodecane, diesel and hydrogenated vegetable oil (HVO) as extraction agents. The corresponding oxymethylene diethyl ethers (OMDEEs) have also been synthesized and investigated. Furthermore, fuel parameters of the resulting ether-hydrocarbon blends have been determined.

2. Material and methods

2.1. Materials

Methanol, *p*-formaldehyde, *n*-dodecane, THF and 1-butanol were obtained from Merck while nitrobenzene was obtained from Sigma-Aldrich. Conventional diesel according to DIN EN 590 was employed as well as synthetic diesel from Haltermann (batch: CJ0903T053, product: 30007684). Hydrogenated vegetable oil (HVO) was purchased from Neste Oil (product: NExBTL 395/14). The ion exchange resin Amberlyst® 36 was obtained from Dow/Rohm and Haas [30]. The resin was dried under vacuum (3 mbar) for 24 h at 100 °C and stored under argon before use.

2.2. Synthesis of OMEs and OME-hydrocarbon blends

The synthesis of OMEs was carried out in a stainless steel (1.4571) batch autoclave with a volume of 180 ml. Pressure and temperature have been measured using an analog pressure gauge with an accuracy of 0.05 bar and a NiCr-Ni thermocouple with an accuracy of 1 °C. A valve on the bottom of the reactor was used for taking liquid phase samples during the reaction. The valve was purged with the product before sampling. Samples were taken with a syringe, filtrated with a polytetrafluoroethylene filter (0.2 µm pore width) and quenched with THF.

Synthesis of OMEs was carried out at 80 °C employing 60 g (2.00 mol) *p*-formaldehyde, 40 g (1.25 mol) methanol and 1 g Amberlyst® 36 as catalyst. Reactions were carried out similar to procedures described in literature [17–19,31]. The acidic ion exchange resin Amberlyst® 36 was chosen as catalyst, since it proved to be highly active in previous studies. To obtain a homogeneous phase before reaction, *p*-formaldehyde and methanol were mixed for two days at a temperature of 80 °C. Then, the catalyst was added to start the reaction. Reactions started immediately and the course of reactions was monitored by gas chromatography (GC). The reaction time to reach more than 99% of maximum equilibrium conversion is about 30 min. To ensure maximum yield of all products, reaction time was set to 24 h. Oxymethylene diethyl ethers (OMDEEs) were synthesized by reacting 60.0 g (2.00 mol) *p*-formaldehyde with 57.4 g (1.25 mol) ethanol in the presence of 0.6 g Amberlyst® 36. Reactions were carried out for 24 h at

Download English Version:

<https://daneshyari.com/en/article/6632316>

Download Persian Version:

<https://daneshyari.com/article/6632316>

[Daneshyari.com](https://daneshyari.com)