



Physico-chemical properties and fuel characteristics of oxymethylene dialkyl ethers



Ludger Lautenschütz^a, Dorian Oestreich^a, Philipp Seidenspinner^b, Ulrich Arnold^{a,*}, Eckhard Dinjus^a, Jörg Sauer^a

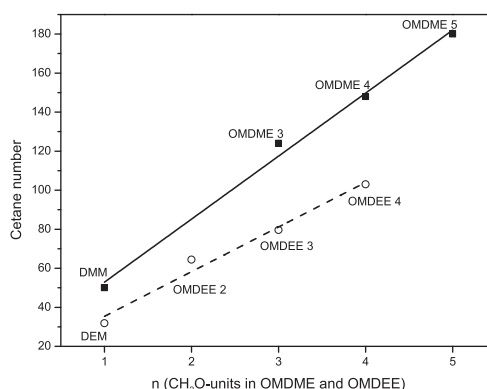
^aKarlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

^bAnalytik-Service Gesellschaft mbH (ASG), Trentiner Ring 30, 86356 Neusäss, Germany

HIGHLIGHTS

- OMDMEs and OMDEEs were synthesized from DMM/DEM and trioxane.
- OMDME 3, 4, 5 and OMDEE 2, 3, 4 were purified by distillation (purity 99.9+%).
- Their physico-chemical properties were compared to *n*-alkanes.
- Fuel characteristics of OMDME 3–5 and OMDEE 2–4 were determined.
- OMDME 3–5 and OMDEE 2–4 exhibit very high cetane numbers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 March 2015

Accepted 19 January 2016

Available online 25 January 2016

Keywords:

Oxymethylene ether
Oxymethylene dimethyl ether
Oxymethylene diethyl ether
Oxygenates
Diesel fuel
Cetane number

ABSTRACT

Oligomeric oxymethylene dimethyl ethers (OMDMEs, $\text{CH}_3\text{O}-(\text{CH}_2\text{O})_n-\text{CH}_3$) are promising diesel fuel additives, which can reduce soot formation as well as NO_x emissions. Due to the poor availability of high purity OMDMEs a comprehensive characterization of diesel standards was not feasible until now. Two types of oxymethylene dialkylethers (OMDMEs and oxymethylene diethyl ethers, OMDEEs) were synthesized, purified and characterized with respect to their physico-chemical and fuel properties. Density, melting point, flash point, auto ignition point as well as lubricity, kinematic viscosity and surface tension of OMDMEs and OMDEEs were measured and compared to the corresponding *n*-alkanes. Fuel requirements such as boiling points, flash points and surface tensions can be fulfilled by OMDMEs and OMDEEs. Furthermore, OMDMEs ($n = 3-5$) and OMDEEs ($n = 2-4$) are, due to their high cetane numbers of 124–180 and 64–103, particularly promising since cetane numbers in this range can lead to improved motor efficiency and smoother fuel combustion. Additionally, the heat of combustion as well as the standard enthalpy of formation and reaction were determined. Apart from somewhat lower heating values, OMDMEs exhibit fuel properties similar to conventional diesel complying the required fuel standards without the need of changing engines or fuel infrastructures.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Even for modern diesel engines, soot formation during the combustion process is still a problem. New emission standards (e.g.

* Corresponding author. Tel.: +49 721 608 23694.

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

Euro VI) define, especially for commercial vehicles, a significant reduction of hydrocarbon (HC), carbon monoxide (CO) and nitrogen oxide (NO_x) emissions as well as a decrease of particulate matter (PM) and threshold for the particle number (PN). To meet these high emission standards, sophisticated exhaust gas aftertreatment is needed on a high level of complexity. Due to technical restrictions this comes along with high costs.

To lower the formation of pollutants during combustion, fuel additives can be blended into diesel. Several studies have shown that additives with high oxygen content and without carbon-carbon bonds lead to a reduction of soot formation and lower other harmful emissions (CO, NO_x, HC, PM and PN) [1–4]. Oligomeric oxymethylene dimethyl ethers (OMDME, CH₃–(OCH₂)_n–OCH₃) are particularly suitable as soot reducing diesel fuel additives due to their favorable physico-chemical properties [5,6]. Because of the predicted high flash points and cetane numbers (CN) [7] as well as the matching boiling points [8], OMDMEs with *n* = 3, 4 and 5 (OMDME 3, OMDME 4 and OMDME 5) are especially preferred as diesel additives. These can be employed with slight engine modifications and nearly no changes in the fuel supply infrastructure. Further studies have shown that OMDMEs also enhance the thermal efficiency and decrease the brake specific fuel consumption by supporting the combustion process with oxygen [2]. Besides the benefit of lower pollutant emissions, OMDMEs can be synthesized on large scale from methanol, which can be obtained from biomass via syngas or CO₂ [9].

Oligomeric OMDMEs and the corresponding polymers (polyoxymethylene, POM) are stable acetals, which were first synthesized by Descude [10] from methanol and formaldehyde in 1904 and studied in detail by Staudinger et al. in the 1920s [11,12]. Due to the fact that formaldehyde is a highly reactive aldehyde, which is prone to polymerize spontaneously, various acidic catalysts can be used for the etherification of the end groups under mild reaction conditions [13,14]. Unwanted hemiformals are always formed as byproducts, decreasing the yields of OMDMEs significantly. In 1948, Gresham and Brooks [15] reported a new synthesis method for OMDMEs using dimethoxymethane (DMM), instead of methanol, and formaldehyde sources such as monomeric formaldehyde, *para*-formaldehyde or trioxane. Similar to the previous synthesis from methanol, the oligomerization reaction of DMM can be performed under mild conditions using acidic catalysts (Scheme 1). Due to the absence of methanol and water, the formation of unwanted hemiformals is inhibited and OMDMEs can be obtained with high yields and selectivities in a continuous process [16,17].

Although there is an extensive interest in OMDMEs with *n* = 3, 4 and 5 as diesel additives, fundamental and comprehensive studies on the pure components have not been carried out so far because of their poor availability. To fulfill diesel standards, fuel characteristics such as cold filter plugging point (CFPP), autoignition point, flash point, CN as well as lubricity, kinematic viscosity and surface

tension must be met. In this work, OMDMEs were synthesized, separated, purified by fractional distillation and examined with respect to their fuel properties. Additionally, the analogous oxymethylene diethyl ethers (OMDEE) were also synthesized (Scheme 1), separated, fractionally distilled and characterized. Due to the fact that OMDME and OMDEE are linear compounds similar to *n*-alkanes, a comprehensive comparison between these three substance classes has been carried out.

2. Experimental section

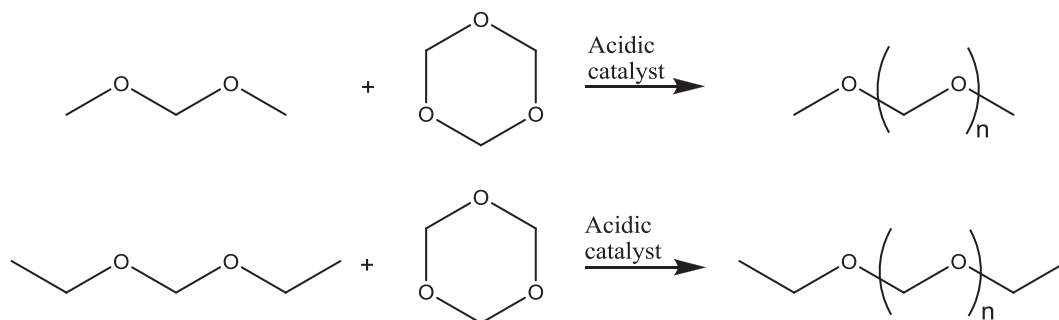
2.1. Materials and synthesis

The reagents DMM (ReagentPlus, 99.9% GC-Area), diethoxymethane (DEM, 99.9% GC-Area) and trioxane (99.98% GC-Area) were purchased from Sigma Aldrich and dried with CaH₂ (Sigma Aldrich) to minimize the formation of hemiformals, formaldehyde and methanol as byproducts. As acidic catalyst, the ion exchanger Amberlyst36 supplied by Rohm&Haas was used. The catalyst was dried at 100 °C under reduced pressure before use. To avoid the formation of waxes consisting of higher oligomers the molar DMM/trioxane-ratio as well as the DEM/trioxane-ratio have been set to 3:1, which means a molar ratio of alkylal/formaldehyde of 1. Due to the high rate of the oligomerization reaction, low catalyst loadings of 1 wt% with respect to trioxane were used. In the absence of water, the OMDME and OMDEE synthesis can be carried out under mild conditions at 40 °C without overpressure. After reaching reaction equilibrium within 2 h, the heterogeneous catalyst was removed by filtration and the product mixture was repeatedly distilled until the purity of the components was above 99.9% with respect to GC-Area. The amount of OMDME 3–5 and OMDEE 2–4 in the equilibrium mixture was approximately 30 and 50 wt%, respectively.

2.2. OMDME and OMDEE characterization

Purity of the products was determined by gas chromatography (GC-FID), ¹H NMR- and FTIR-spectroscopy. Refractometry was also employed.

GC-FID measurements were carried out using a Hewlett Packard 6890 Series gas chromatograph with a DB-5 column from Restek. ¹H NMR spectra were recorded on a Bruker Avance 250 spectrometer (250.1 MHz). The measurements were carried out employing CDCl₃ as solvent. Chemical shifts were determined by reference to residual solvent peaks. The evaluation was done with the software MestRec. FTIR spectra were recorded on a Varian 660-IR FTIR spectrometer in the range from 300 to 3500 cm⁻¹. The refractive indices were measured using an Abbe, Atago 1T type refractometer coupled to a thermostated bath at 20 °C.



Scheme 1. OMDME and OMDEE formation from DMM/DEM and trioxane.

Download English Version:

<https://daneshyari.com/en/article/205232>

Download Persian Version:

<https://daneshyari.com/article/205232>

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