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Poly(oxymethylene) dimethyl ethers as components of tailored diesel fuel: Properties, synthesis and purification concepts

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ABSTRACT

Poly(oxymethylene) dimethyl ethers (POMDMEs) open a new route for tailoring diesel fuels. POMDMEs belong to the group of oxygenates which reduce soot formation in the combustion when added to diesel fuels. They can be produced on a large scale based on gas-to-liquid technology. The present work first gives an overview of oxygenates as components of diesel fuels and process technology for their production. Then properties and chemistry of POMDMEs are discussed in detail. A particularly favorable route for their large scale production in which they are formed from methylal and trioxane is proposed and a feasible concept for this process is presented together with data on the reaction equilibrium that was taken in a batch reactor.

1. Introduction

It is well known that diesel engines have, due to their high thermal efficiency, revolutionized transportation. Environmental and linked regulatory issues have driven the development of low emission diesel engines. Still, even in modern high performance diesel engines, the formation of soot during the combustion remains a problem. Oxygenated compounds (molecules which contain oxygen in their structure) such as methanol or dimethyl ether (DME), are known to reduce soot formation during the combustion, when added to diesel fuels [1].

Especially DME is often discussed as a fuel additive to reduce soot (e.g., see [2,3]). However, there are some disadvantages for its use. Adding DME to diesel fuel increases the vapor pressure, lowers the viscosity [3] and may result in reduced solubility at lower temperatures [3,4]. To counteract a possible vapor lock due to the higher vapor pressure the engine's fuel supply system has to be modified. The lower viscosity leads to a change in the injection behaviour, which results in a further modification in the injection system [5,6].

Ren et al. [7] and Natarajan et al. [8] come to the finding, that the reduction of particulate matter correlates with the oxygen content and not with the chemical nature of the oxygen-containing species. Therefore, other oxygenates with a lower vapor pressure and higher viscosity are more attractive as diesel fuel additives. Poly(oxymethylene) dimethyl ethers (POMDMEs) with the general structure $CH_3–O–(CH_2–O)_n–CH_3$ have also the potential to reduce soot during the combustion while their larger structure leads to lower vapor pressures and higher viscosity compared to DME. The POMDME with $n = 1$ is dimethoxymethane (DMM), also called methylal, which is also discussed as diesel fuel additive [9,10]. Experiments have shown that using blends of DMM and diesel fuel still requires engine modifications [10]. However, POMDME $n = 2$–5 can be blended to diesel fuel and used without changing the engine's infrastructure [2,11].

2. Properties of POMDMEs

POMDMEs have the ability to reduce soot during the combustion in diesel engines. The presence of activated methylene groups next bound to oxygen atoms ($–O–CH_2–$) in the chemical structure of the POMDMEs leads to the formation of hydroperoxides in an early stage of the combustion. These hydroperoxides decompose into OH-radicals which subsequently degrade soot precursors by oxidative processes [1]. Due to their physical properties POMDMEs can overcome the disadvantages of DME or DMM related to blending fuels. In Table 1, some physical properties of POMDMEs are given and compared to DME, methylal, trioxane and conventional diesel. Trioxane was added, because this oxygenate is used as an intermediate in the POMDME production process in this work.

Higher viscosities and higher boiling points allow the usage of POMDMEs in diesel blends without changing the fuel supply system. Because of the poor solubility of DME in diesel fuel blends

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Table 1
Physical properties of conventional diesel fuel (CDF), dimethyl ether (DME), trioxane (TRI) methylal (DMM) and poly(oxymethylene) dimethyl ethers (POMDMEs) with n CH_2O segments at normal pressure [2,8,10,22–24].

	CDF	DME	TRI	DMM	POMDME		
					$n = 2$	$n = 3$	$n = 4$
Melting point (°C)	–	−141	64	−105	−70	−43	−10
Boiling point (°C)	170–390	−25	115	42	105	156	201
Viscosity (25 °C) (mPa s)	2.71	–	–	0.58	0.64	1.05	1.75
Density liquid (25 °C) (kg/L)	0.83	–	–	0.860	0.960	1.024	1.067
Cetane number	55	55	–	29	63	70	90
Oxygen content (wt%)	–	34.7	53.3	42.1	45.3	47.1	48.2

and the high vapor pressure of DME, diesel/DME blends are not stable at normal pressure. DME and DME/diesel blends must be stored under pressure [5,3]. Additionally DME and diesel fuel show a miscibility gap at temperatures below 0 °C [3]. There is no miscibility gap between POMDMEs and diesel fuel and because of the low vapor pressures of POMDMEs no pressurized tank or fuel system is needed. The cetane number of POMDME $n = 3–5$ is in the range between 70 and 100, which is higher than the values of about 55 for conventional diesel fuel and DME. POMDMEs are therefore very attractive as additives for fuels used in compression ignition engines, such as diesel engines. Natarajan et al. [8] screened different oxygenates with the criteria flash point and oxygen content. A higher flash point than conventional diesel fuel, which is a security criterion, is reached by the POMDMEs with $n > 3$. DME, DMM and trioxane fail in this criterion [8]. The oxygen content of the POMDME is in the range between 42 and 53 wt%. Together with their higher density compared to DME and DMM, the volume which has to be blended into diesel fuel to reach a certain oxygen content, is small. The optimal POMDME chain length n to blend into diesel fuel is $n = 3$, 4. POMDME $n = 2$ shows a low flash point. Longer POMDMEs show the risk of precipitate at low temperatures. This may clog filters or other parts of the fuel system. Furthermore, there are no reports on degradation of seals or other polymer components of the fuel system by POMDMEs. Table 2 shows a comparison of calorific data of POMDMEs and other oxygenates compared to diesel fuel. The high oxygen content of POMDMEs results in lower heating values compared to diesel fuel.

The production costs of POMDMEs are higher than the production costs of DME, DMM and other oxygenates, which results from a higher finishing grade. But especially for DME further costs accrue related to the usage as fuel or fuel component. In addition to engine and fuel system modification costs there are higher costs for storage, transportation and safety of liquified DME under pressure, which are a great hurdle when the fuel is introduced into the market. In the near future, regarding the bottleneck of diesel fuel in Europe and dwindling oil reserves, the POMDME production costs may well become acceptable especially when optimized technology for the production is available.

3. POMDME process chain

Conversion of low molecular weight alkanes such as methane to synthetic fuels and other chemicals has gained increasing attention in the last years. The reasons for this are diminishing petroleum oil reserves and vast quantities of methane in oil wells or natural gas reserves. There are two major groups of routes for this conversion: on the one hand direct oxidative routes, which lead to higher molecular weight alkanes or alkenes by activating the carbon-to-carbon bond, and on the other hand indirect routes, which generate synthesis gas as an intermediate and allow the production of oxygenates.

Table 2
Diesel fuel vs. oxygenates – gross calorific value (GCV) and net calorific value (NCV) at 25 °C.

	Diesel fuel	Methanol	DME	POMDME[a]
GCV (MJ/kg)	45.4	22.7	33.9	21.0
NCV (MJ/kg)	42.6	19.9	31.0	18.0

[a] Mixture of POMDME $n = 3$ 0.5 g/g and $n = 4$ 0.5 g/g.

In the latter, methanol can be obtained in a steam reforming process [12]. DME can be obtained in a low cost dehydration step from methanol [13] or, more favorably in a direct process which combines both steps [14].

POMDMEs can be obtained from methanol in a process chain which is illustrated in Fig. 1. In this chain the intermediates are methylal and trioxane [15]. In a first process step formaldehyde is obtained by dehydrogenation of methanol [16]. The trioxane process consists of the trimerisation of formaldehyde which is usually catalyzed by H_2SO_4 and a work up of the reactor outlet, for example by a pressure-swing distillation sequence [17]. The preferred production method for methylal from formaldehyde and methanol is a heterogeneously catalyzed reactive distillation [18]. Subsequently both formaldehyde based products trioxane and methylal are converted to POMDMEs. The chemistry of this step is explained in more detail in the next section.

Also other routes for the POMDME synthesis are feasible. DME can be used instead of methylal to react with trioxane over an acidic catalyst to POMDMEs [19]. Another possibility is to integrate the methylal process and the POMDME process [20]. In a first step methanol and formaldehyde react to methylal. In a second step over the same acidic catalyst formaldehyde is added to methylal to form POMDMEs. During the formation of methylal, water is produced which is the drawback of this integrated process. Water reacts with formaldehyde to methylene glycol and poly(oxymethylene) glycols, which reduce the selectivity of POMDMEs and are difficult to remove.

4. POMDME chemistry

In the present section the chemistry of the formation of POMDMEs from methylal and trioxane is considered in more detail. The POMDME with n CH_2O segments is labeled as POMDME n in the

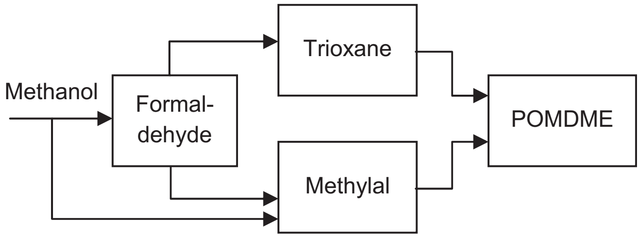

Fig. 1. Block flow diagram of the POMDME process chain.