PROCESSES FOR THE PRODUCTION OF OXYGENATE FUELS FROM RENEWABLES

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Abstract

Oxygen-containing compounds of the type $CH_3O-(CH_2O)_n-CH_3$ (n = 0-7) exhibit promising fuel properties like high cetane numbers and soot-free combustion. Thus, dimethyl ether (DME, n = 0) and the corresponding oligomeric oxymethylene ethers (OMEs, n = 1-7) can be favourably employed as diesel substitutes and efficient emission reduction can be realized without costly engine modification and exhaust gas treatment. Furthermore, if such fuels are produced from renewables, e.g. via methanol, they can also contribute to a significant reduction of overall CO_2 emissions. However, commercial production of oligomeric OMEs on a technical scale is not established yet since there is still a lack of efficient processes, which meet economic and ecologic demands. Within this work, recent progress in the direct synthesis of DME from synthesis gas (Synthesis gas-To-DME, STD) is described as well as new strategies for the synthesis of OMEs, preferably from readily available and low-cost substances such as methanol and formaldehyde.

Keywords

Alternative fuels, dimethyl ether, oxymethylene ethers.

Introduction

Several strategies for the production of fuels or fuel additives from renewable resources are known (Dinjus et al., 2009). One can differentiate between oxygen-containing fuels, so-called oxygenate fuels, and oxygen-free fuels, i.e. hydrocarbons. The former offer advantages such as clean combustion with reduced emissions while the latter generally exhibit a higher energy density. In many cases blending of both fuel types is a common procedure to optimize fuel characteristics and to adjust ideal fuel properties for the respective applications.

In this context, short-chain alcohols play a key role, especially methanol. Methanol is produced from synthesis gas and can be further processed to a variety of fuels, e.g. dimethyl ether (DME) or gasoline (Olah et al., 2006). Long-chain hydrocarbons are accessible via conversion of methanol to olefins followed by olefin oligomerization. The required synthesis gas is usually obtained from fossil resources, i.e. natural gas or coal. Synthesis gas can also be obtained via biomass gasification and thus, the corresponding biofuels can be produced enabling a reduction of overall CO_2 emissions.

Regarding oxygenate fuels or fuel additives, methanol is an important raw material for the production of ethers and esters such as methyl *tert*-butyl ether (MTBE) or fatty acid methyl esters (FAME), which are well-established and already employed on large scale. Other methanol-derived fuels like DME or the oligomeric oxymethylene dimethyl ethers $CH_3O-(CH_2O)_n-CH_3$ (OMEs, n = 1-7) are on a comparatively lower stage of development. However, all of them exhibit beneficial combustion properties with an enormous potential for emission reduction and especially OME-3 to OME-5 are in great demand due to their favourable physico-chemical properties (Lumpp et al., 2011). Nevertheless, commercial production of oligomeric OMEs on a technical scale is not established yet, since

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there is still a lack of efficient processes, which meet economic and ecologic demands.

Within this work recent progress in the direct synthesis of DME from synthesis gas (Synthesis gas-To-DME, STD), i.e. without isolation of intermediary formed methanol, is described. Furthermore, different pathways for the synthesis of OMEs are compared and recent results are reported with a focus on chemical reaction engineering.

Synthesis pathways for DME and OME production

Direct synthesis of DME from synthesis gas

Bifunctional catalyst systems for the STD process have been developed (Ahmad et al., 2014). These comprise a component for methanol formation and an acidic component for methanol dehydration. The catalysts were extensively characterized and catalyst testing was carried out employing a fixed-bed reactor. High CO conversion up to 45% (single pass conversion) and maximum DME selectivity were reached.

Currently, the influence of several reaction parameters such as temperature, residence time, pressure, catalyst composition as well as synthesis gas composition and concentration on the catalytic performance is evaluated. Furthermore, the use of CO_2 as feedstock and operational aspects such as catalyst deactivation, passivation and regeneration are studied.

Synthesis pathways for OMEs

With respect to OME production, several strategies have been reported, e.g. reaction of methanol with formaldehyde (pathway 1 in Figure 1), reaction of dimethoxymethane (DMM) with trioxane (pathway 2 in Figure 2) or the reaction of DME with formaldehyde sources like trioxane (pathway 3 in Figure 1). Methanol can be obtained from renewable resources, e.g. via gasification of agricultural residues followed by conversion of the resulting synthesis gas (Figure 2).

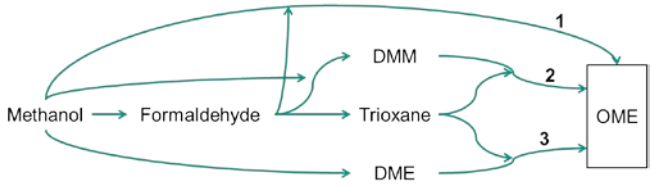

Figure 1. Synthesis pathways for OMEs

OME synthesis via pathway 1 is the most desirable since methanol and formaldehyde can be directly employed without any intermediates. However, water and hemiformals are formed as byproducts, which accumulate in a continuously operating process. Hence, an extraction method was developed to separate OMEs selectively from the aqueous reaction phase (Figure 2).

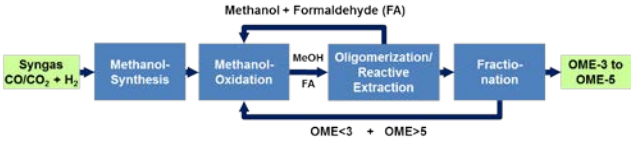

Figure 2. Synthesis of OMEs from synthesis gas via methanol and formaldehyde

Current activities in the field of OME synthesis range from fundamentals, e.g. the development of highly active and stable catalysts, to technical topics, e.g. chemical reaction engineering and scale-up. Furthermore, the synthesized OMEs will be investigated in engine tests to reveal correlations between molecular structures and combustion properties.

Conclusions

Direct synthesis of DME from synthesis gas is on an advanced stage of development and can compete with DME production via methanol dehydration. Regarding OME production remarkable progress was made within the last years. Based on recent results, upscaling is envisaged to improve availability and to enable further testing.

Acknowledgment

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