Fuel 185 (2016) 67–72

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

From methanol to the oxygenated diesel fuel poly(oxymethylene) dimethyl ether: An assessment of the production costs

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ARTICLE INFO

Article history:
Received 9 December 2015
Received in revised form 20 July 2016
Accepted 21 July 2016

Keywords:
Poly(oxymethylene) dimethyl ethers
Diesel fuel components
Methanol economy
Benchmark process chain
Assessment of economy

ABSTRACT

Poly(oxymethylene) dimethyl ethers (OME) are diesel fuel components, which can be produced from methanol, a global future platform chemical. OME reduce the soot formation in diesel engines and their addition to low quality refinery fractions increases the total refinery output. In this work, a benchmark process chain for OME production from methanol is described, which is based on the concepts of Burger et al. (2010). The OME are synthesized from trioxane and methylal, which are produced in intermediate process steps from methanol via the formaldehyde route. In each process step, the process chain uses state-of-the-art reaction- and distillation technology and is therefore scalable to large capacities. The economy of the process chain is assessed by analyzing the influence of the price of methanol and the investment costs, for which crude estimates are given, on the production costs of the OME. It is shown that OME production is competitive with conventional diesel fuel production.

1. Introduction

Poly(oxymethylene) dimethyl ethers (OME) are a group of C1 derived oxygenates which help to improve and enlarge the pool of diesel fuels [1,2]. Their physical property data fit well into those of oil refinery derived diesel fractions, with which they are completely miscible. The blending cetane number of OME is up to 100 and is therefore higher than conventional diesel [3]. Furthermore, OME contain no impurities, which are detrimental for use in combustion engines. OME are also considered as physical solvents for the absorption of carbon dioxide [4] or as safe fuels for small scale fuel cells [5,6].

The chemical structure of OME is $H_3C–O–(CH_2O)_n–CH_3$ with n in the range of 2–8, preferably of 3–5 for use in diesel fractions [1]. Different pseudonyms like DMM or POMDME are also used in the literature. OME were first prepared by Auerbach and Barschall [7] and are widely discussed by Walker in his compendium on formaldehyde [8]. Romano et al. [9] were in 1984 the first to point out the potential of OME as extenders for automotive fuel. Moulton and Naegeli [10] claimed in 1997 a diesel fuel of improved properties which contains OME. Fleisch and Sills [11] proposed in 2004 OME as fuel enhancers. Recently, OME engineering has been intensively studied by several Chinese research institutes [12–21], obviously because of China's strong focus on coal-based synthesis gas chemistry.

OME, as diesel additives, are interesting in many ways [1–3,22–25]:

- Requirements for fuels: They are compatible with diesel fuel without addition of ignition improvers or other expedients. Because of their diesel-like properties, their application does not require major changes in the diesel engine or the fuel injection system.
- Logistics: In-line blending with conventional diesel can be done in the refinery. No special storage and tank infrastructure is needed at the local fuel stations or in the vehicles themselves.
- Emission reduction: By adding several percentages of OME into conventional diesel fuel, soot emissions are strongly reduced.
- Power efficiency of the diesel engine system: There is the potential of overall efficiency increase in combustion and exhaust gas clean up, as for example a particulate filter could be omitted. This is especially of interest in heavy-duty applications.
- Upgrade of low-quality fractions of the refinery into standard diesel fuels: This will increase the total diesel output from the refinery.

The heating value of OME is however lower than that of non-oxidized hydrocarbons like fossil diesel. This is a minor disadvan-

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http://dx.doi.org/10.1016/j.fuel.2016.07.085
0016-2361/

tage if OME do not replace fossil diesel completely, but only upgrade fossil diesel fuel by their admixing.

The US Energy Information Administration states a future global decline in overall liquid fuel consumption, but at the same time a steady increase in diesel fuel consumption up to the year 2040 [26]. On the other hand, the refinery average output of diesel from a barrel of oil is limited to approximately 27% of the oil input [27]. In addition, there is a growing gap between increasing demands for higher fuel quality and a declining crude oil quality [28].

OME are part of the large family of diesel fuel components which could solve these issues. Other members of that family, which do not originate from the classical refinery process, are for example biodiesel, dialkyl ethers, alcohols and Fischer–Tropsch products [29]. In comparison to these, OME have the combined advantages of the above stated application properties and a sound production platform based on the rising methanol economy [30]. Methanol, as the OME precursor molecule, may be of fossil origin or from regenerative resources. It may be produced from conventional natural gas, stranded gas, coal, coke gas or biomass [31], whatever fits best into the regional boundary conditions. Schlögl [32] proposed using carbon dioxide and hydrogen derived from renewable electricity for the production of synthesis gas and methanol. The methanol production technology is available for huge world-scale plants and for local plants of smaller capacity.

Up to now, the progress towards the application of methanol-based OME in the diesel industry was hampered by the lack of a consistent analysis of the routes leading from methanol to OME. We discuss different routes and describe a benchmark process chain, which is scalable to refinery capacities. The economy of this process chain is evaluated. This analysis creates a basis for further studies on the production technology and the market integration.

2. Discussion of routes

Fig. 1 shows two promising routes for large-scale OME production from methanol. A formaldehyde plant is required in every route, as formaldehyde is the monomer unit of OME. Burger et al. [1,33–35] examined Route 1, in which the OME are synthesized in a non-aqueous environment from trioxane, a cyclic trimer of formaldehyde, and methylal. Methylal could be seen as OME of chain length $n = 1$. Both educts are produced in intermediate process steps from formaldehyde and methanol [36,37]. Route 1 gives the highest yield of OME in the OME synthesis step.

OME may also be produced from aqueous formaldehyde solution and methanol as educts (Route 2 in Fig. 1) [38–41]. The presence of water decreases the yield of OME and complicates the downstream processing, but the production of the intermediates trioxane and methylal is not necessary [39]. In contrast to Route 1, the process technology for Route 2 is presently not sufficiently clear to enable an assessment. This applies also for OME production from dimethyl ether (formally OME of chain length $n = 0$) and either trioxane [42] or formaldehyde [43,44] as second educt. We therefore adopt Route 1 as benchmark process chain. All stages in that chain are well described in the literature and feasible.

3. Benchmark process chain

An overall scheme of Route 1 as benchmark process chain is given in Fig. 2. The technologies of the four different process steps for OME production from methanol (formaldehyde-, trioxane-, methylal-, and OME plant) are described in the following.

3.1. Technology of process steps

3.1.1. Formaldehyde

The process chain starts with well-established formaldehyde production from methanol (reactions (1) and (2)).

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O \quad (1)$$

$$CH_3OH \rightarrow CH_2O + H_2 \quad (2)$$

In this process step, competing reactions reduce the selectivity of methanol towards formaldehyde. The main competing reaction is the consecutive total oxidation of formaldehyde to carbon dioxide (reaction (3)) [45].

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \quad (3)$$

Two main technologies are used. In the metal oxide catalytic process, methanol is partially oxidized in an excess of oxygen. In the silver catalyst process, methanol is partially oxidized and dehydrogenated in a stoichiometric deficiency of oxygen. The technologies are described and benchmarked in the literature [46,47]. For the purposes of the present study, both technologies are similar. For the economic assessment, we use formaldehyde production costs based on the silver catalyst process.

The gaseous reactor effluent is quenched in an excess of water in absorption towers. The product is an aqueous formaldehyde solution. The mass fraction of formaldehyde in the solution is typically between 0.37 g/g and 0.50 g/g.

3.1.2. Trioxane

From aqueous formaldehyde solution, trioxane is obtained using sulfuric acid as homogeneous catalyst (reaction (4)) [36,47].

$$3CH_2O \rightleftharpoons (CH_2O)_3 \quad (4)$$

The conventional trioxane process uses besides distillation, also extraction with chlorinated solvents for the work up of the reactor effluent [36,47]. This leads to a complex process. Furthermore the use of chlorinated solvents is undesired. These issues are circumvented by a new trioxane process, which is based on a series of patent applications since 2005 [48–51]. The production process is distillation-based and scalable to large capacities. The technology was simulated and verified in pilot plant runs [48–50]. It is used here as benchmark technology. As several unit operations are saved, the new trioxane process is cheaper than the conventional process. Furthermore, trioxane usually satisfies strict purity requirements ('polymer-grade') for producing poly(oxymethylene) plastics [47]. This is not necessary for the production of OME, which further decreases the production costs.

3.1.3. Methylal

Methylal is produced from formaldehyde and methanol according to reaction (5).

$$2CH_3OH + CH_2O \rightleftharpoons CH_3O-CH_2O-CH_3 + H_2O \quad (5)$$

Several methylal processes are described in the literature. A reaction-distillation process is preferred here, in which aqueous formaldehyde solution and methanol react to methylal in the presence of an acidic heterogeneous catalyst [37,52]. Subsequent downstream processing of the reactor effluent is based on a pressure-swing distillation [37,52]. The coupled product water is removed at this point of the process chain.

3.1.4. OME

Trioxane and methylal are reacted into OME in the presence of an acidic heterogeneous catalyst according to reaction (6).