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Dimethyl ether: A review of technologies and production challenges

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ABSTRACT

Dimethyl ether (DME) is a well-known propellant and coolant, an alternative clean fuel for diesel engines which simultaneously is capable of achieving high performance and low emission of CO, NO_x and particulates in its combustion. It can be produced from a variety of feed-stocks such as natural gas, coal or biomass; and also can be processed into valuable co-products such as hydrogen as a sustainable future energy. This review, which also can be counted as an extensive, pioneer review paper on this topic, presents recent developments in synthesis methods of dimethyl ether as an alternative energy while focuses on conventional processes and innovative technologies in reactor design and employed catalysts. In this context, synthesis methods are classified according to their use of raw material type as direct and indirect methods as well as other routes, since different methods need their own operating condition. Also, the available data for the selectivity to DME and its yield as a function of H_2/CO and CO_2 content of the feed is discussed.

Contents

Abbreviations: AF-SPMR, axial-flow spherical packed-bed membrane reactor; ATR, autothermal reforming; CapEx, capital expenditure; CD, catalytic distillation; CDR, carbon dioxide reforming; CFC, chlorofluorocarbon; CPO, catalytic partial oxidation; CZA, CuO–ZnO–Al_2O_3; DME, dimethyl ether; DWC, dividing-wall column; GHSV, gas hourly space velocity; HC, hydrocarbon; H-SOD, hydroxy-sodalite; LHSV, liquid hourly space velocity; LPG, liquefied petroleum gas; MTG, methanol to gasoline; MTH, methanol to hydrocarbons; MTO, methanol to olefins; MWCNT, multi-walled carbon nanotube; OpEx, operating expense; PEFC, polymer electrolyte fuel cell; POX, partial oxidation; RD, reactive distillation; R-DWC, reactive dividing-wall column; SR, steam reforming; STD, syngas to DME; WGS, water gas shift.

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1. Introduction

The inordinate use of oil-based fuels for transportation purposes is one of the major reasons of the rapid depletion of petroleum which causes major environmental problems. These issues have necessitated the development of clean non-petroleum based alternative transportation fuels. In recent years, the application of dimethyl ether (DME) as a potential diesel substitute used in compression ignition engines has attracted considerable attention [1,2]. DME is a volatile substance which forms a liquid phase when pressurized above 0.5 MPa; therefore, it is commonly handled and stored as liquid (see the physical property of DME in Table 1). Burning with a visible blue flame and with similar properties as propane and butane, DME may hence be used as liquefied petroleum gas (LPG) for heating and home cooking [3]. For many reasons, DME is known to be a clean fuel: (1) Unlike other homologous ethers, it has a safe storage and handling as it does not form explosive peroxides [4]. (2) Since DME only has C—H and C—O bond, but no C—C bond, and since it contains about 35% oxygen, its combustion products such as carbon monoxide and unburned hydrocarbon emissions are less than those of natural gas. (3) Owing to its high cetane number, DME is considered to be an excellent alternative to the present transportation fuel with no emission of particulate matter and toxic gases such as NO_x at burning [1,2,4,5]. (4) Moreover, it has a similar vapor pressure to that of LPG, and hence can be used in the existing infrastructures for transportation and storage [6]. Thus, the significant future perspective of DME can be counted as an alternative energy.

Furthermore, DME is widely recommended as environmentally friendly aerosol and green refrigerant since it has zero ozone depletion potential and lower global warming potentials compared with traditional chlorofluorocarbons (CFCs, Freon) and R-134a (HFC-134a) [7]. In addition, DME can be used as pesticide, polishing agent, and anti-rust agent. It can also be considered as an attractive material for producing alkyl-aromatics, a suitable source for the hydrogen used in fuel cells, as well as a key intermediate for producing dimethyl sulfate, methyl acetate, light olefins, and so many other important chemicals [8–10].

DME can be produced from a variety of feed-stock including natural gas, crude oil, residual oil, coal and waste products [11]. Among potentially interesting raw materials, natural gas appears to be the most promising one due to its wide availability and the fact that producing DME from natural gas allows production costs to be independent of the swings in the oil price [12].

Table 1
Properties of DME.

Properties	
Molecular formula	C_2H_6O
Molar mass	46.07 g mol^{-1}
Appearance	Colorless gas
Odor	Typical
Density	1.97 g cm^{-3}
Melting point	−141 °C, 132 K, −222 °F
Boiling point	−24 °C, 249 K, −11 °F
Solubility in water	71 g dm^{-3} (at 20 °C)
log P	0.022
Vapor pressure	>100 kPa

1.1. Scope of the current review

Extensive works have been undertaken to improve DME synthesis methods and the employed catalysts, but the DME subject is still suffering from the lack of a critical review. The underlying goal of this paper is to present an extensive review considering the valuable works accomplished over the years 1965–2013 on dimethyl ether synthesis. The trend of related publications on DME over the years 1996–2013 is shown in Fig. 1. As obvious, the number of published papers rises gradually and has a peak within the year of 2011. It is concluded from Fig. 2 that these publications are drastically concentrated on catalyst and then on reactor technology. Thus, taking these results into account, this paper focuses on production methods and a discussion on their wide variety of reactors and catalyst configurations while also investigating effective parameters including water removal, H_2/CO ratio, CO_2 content of the feed, temperature, pressure, and space velocity.

2. Synthesis methods

As shown in Fig. 3 and mentioned before, DME can be produced in two distinct ways: the first called the indirect route uses the produced methanol to promote its dehydration; the second way which is arguably more efficient is known as the direct route, in which DME is produced in a single stage using bi-functional catalysts. The technology of this single step method belongs to companies such as Haldor Topsoe, JFE Holdings, Korea Gas Corporation, Air Products, and NKK [13,14]. Moreover, Toyo, MGC, Lurgi and Udhe have their own indirect processes for DME production [13].

One of the main steps in DME synthesis is the production of syngas, which is a mixture of hydrogen and carbon monoxide and has