Fuel 220 (2018) 871–878

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Life cycle analysis (LCA) of low emission methanol and di-methyl ether (DME) derived from natural gas

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ARTICLE INFO

Keywords:
Well to wheel (WTW) emissions
Dimethyl ether (DME)
Methanol
Natural gas reforming

ABSTRACT

This paper presents an analysis of different pathways for synthesising methanol and dimethyl ether (DME) from natural gas. This work seeks to determine the conditions under which methanol and DME might simultaneously have lower lifecycle greenhouse gas emissions and lower price than gasoline and diesel. Lower lifecycle greenhouse gas emissions are found to be possible if the energy used to synthesise these fuels is from low emission sources. Both methanol and DME synthesis should also be economically competitive with these incumbent transport fuels given current clean energy prices, provided that the natural gas price is approximately at current US levels and gasoline and diesel prices are at least 0.6$US/l. This suggests that methanol and DME can be scalable, economic and environmentally preferable alternatives to gasoline and diesel, particularly in the United States.

1. Introduction

Natural gas (NG) is already widely used as a transport fuel [1–3]. It is most commonly stored on-board the vehicle as compressed natural gas (CNG) or liquefied natural gas (LNG). It can also be converted into several other, synthetic fuels. These synthetic fuels include synthetic forms of gasoline and diesel, as well as methanol and dimethyl ether (DME) [4].

Semelsberger et al. [5] specify several criteria for an alternative fuel to be considered as a plausible replacement for petroleum fuels: availability of feedstock; sufficient production facilities and distribution infrastructure; economic competitiveness; low risk; environmental benefits; fuel versatility and a minimum of engine and fuel system modifications needed. According to the Semelsberger criteria [5], these fuels have the following limitations: LNG requires expensive distribution infrastructure and significant vehicle modification; synthesised conventional fuels via Fischer–Tropsch (FT) methods have no economic advantage given current crude oil prices. In addition, synthetic gasoline and diesel require more energy to synthesize than conventional refined fuels from crude oil; methanol leakage can contaminate water reservoirs and can cause corrosion and wear in unmodified engines; DME has lower lubricity and viscosity than diesel fuel, which requires modifications to the fuel injection system and addition of lubricants [6]. Due to lower volumetric mass density and lower energy density (two thirds of that of diesel), fuel chambers need to be almost twice as large, and moderately pressurised [7]. There are also insufficient production facilities to date.

Despite these considerations, methanol could meet Semelsberger's criteria when blended with gasoline, although methanol content in gasoline blends is limited to 10–15% if there are to be no engine modifications. DME could also potentially meet these criteria as a pure component if there were an increase in production capacity.

Of course, an additional, important consideration for any alternative fuel is its lifecycle greenhouse gas emissions relative to the conventional fuel that it displaces. Table 1 shows the lifecycle or well-to-wheel (WTW) emissions of gasoline and diesel in major markets. The WTW emissions are the sum of the well-to-tank (WTT) and tank-to-wheel (TTW) emissions. The WTT emissions are those generated during feedstock extraction, delivery, fuel production and distribution. The TTW emissions are those produced during vehicle use.

An advantage of methanol when blended with gasoline in spark-ignition (SI) engines [10] is a high research octane number (RON) of 120 permitting high compression ratios and higher engine efficiency. Additional superiority is the combination of greater latent heat and wider flammability limits than gasoline results in lower combustion temperature and lower in-cylinder pollutant formation.

DME has several additional advantages as a diesel substitute in a CI engine: a high cetane number (~ 60) and vapour pressure result in shorter ignition delays; the combination of high oxygen content (34.8% w.) and absence of $C-C$ bonds leads to nearly smoke-free combustion,

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https://doi.org/10.1016/j.fuel.2018.02.066
Received 5 September 2017; Received in revised form 8 December 2017; Accepted 8 February 2018

Table 1
lifecycle greenhouse gas emissions of gasoline and diesel across China, the European Union and the United States [2,8,9]

Fuel	WTT GHG ($kgCO_{2e}/GJ$)	TTW GHG ($kgCO_{2e}/GJ$)	WTW GHG ($kgCO_{2e}/GJ$)
Diesel	17–20	74	91–94
Gasoline	14–21	73	87–94

and low emissions of carbon monoxide and unburned hydrocarbons [6]; NO_x emissions are lower when injection timing is optimised [11], and can further be reduced with high exhaust gas recirculation (EGR) rates, which can be achieved due to the absence of the NO_x-soot formation trade-off [6]. Therefore, the diesel particulate filter (DPF) and selective catalytic reduction (SCR) might no longer be required. As these are common components of modern diesel aftertreatment systems, This would reduce production costs and operation complexity [12].

In order to produce methanol and DME, the feedstock is normally first reformed or gasified into a mixture of CO, CO_2 and H_2 called synthesis gas (syngas). Methanol and DME can be synthesized from syngas via two main methods: The first one is the indirect method, which involves synthesis of methanol followed by dehydration to DME, and the second one is the direct method, where syngas is converted to methanol and DME simultaneously in a single, bi-functional catalytic reactor.

A key advantage of the direct method is that by consuming the methanol formed in situ, an over-equilibrium yield can be achieved. However, as the methanol synthesis industry has already achieved some level of maturity, an indirect DME plant can be economically preferable as a part of a larger methanol plant. Several companies, such as Haldor Topsoe, Lurgi, TEC and MGC offer licensed processes of DME production with methanol as an intermediate. The indirect method also enables flexibility between methanol and DME production, and is the primary method for DME production today [6,13].

Fleisch et al. [14] investigated the economics of NG and coal derived methanol and DME, but did not detail the technical aspects. Trippe et al. [15] and Ohno et al. [16] conducted an analysis of pathways to DME which are not yet commercially available. Other studies investigated the life cycle of DME, but only some aspects of the WTW GHG emissions [2,17] or aspects of the financial viability of DME [18] separately. More comprehensive economic studies of methanol production are available for Trinidad and Tobago [19] and Nigeria [20]. Since methanol represents the majority of the cost of DME production, these studies are also relevant to DME plants.

This work therefore analyses the conditions under which NG-derived DME and methanol are both economically viable and of lower lifecycle GHG compared to their conventional counterparts. This is achieved by life cycle analysis (LCA) of the technical and financial performance of DME and methanol synthesis pathways. First, the technical performance of different pathways for NG to methanol and DME are investigated. This enables estimation of the WTW GHG emissions. These results are then used as inputs for modelling of the levelized cost of fuel (LCOF, \$/GJ).

2. Chemistry of methanol and DME synthesis

An indirect DME plant is composed of four main parts: a reformer, a synthesis reactor, a dehydration unit, and a separation unit [6]. The reformer converts NG to syngas. The synthesis reactor reacts syngas to produce methanol. The dehydration unit converts the methanol to DME, and the DME is purified to fuel grade by distillation and removal of water and methanol in the separation unit. The dehydration plant is the main addition to a standard methanol plant.

2.1. The reforming process

NG reforming and syngas compression accounts for about 60% of the capital cost of NG conversion plant [13] and a large share of the energy consumption. The choice of the reforming technology can also greatly affect the total cost of production. The two main commercially available reforming techniques are steam methane reforming (SMR) and auto-thermal reforming (ATR), with the reforming technique and its operating conditions constraining the syngas composition.

The syngas molar component ratio M is defined as:

$$M = \frac{X_{H_2} - X_{CO_2}}{X_{CO} + X_{CO_2}}, \tag{1}$$

where X_n is the molar concentration of component n. An M of 2 is generally favourable for methanol synthesis.

The SMR consists of the steam methane reforming reaction and the water gas shift reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_R = 206 \quad \text{KJ/mol} \tag{2}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_R = -41.2 \quad \text{KJ/mol} \tag{3}$$

Reforming typically takes place in a nickel based catalytic tubular reactor at 700–1000 °C and 10–45 bar [21]. As the reaction is highly endothermic, it is favoured by high temperatures, though temperatures over 1000 °C typically result in lower catalyst lifespan and more expensive construction materials [22]. The catalyst-filled tubes absorb heat from a surrounding furnace, which is most commonly provided by the combustion of NG but could be provided by any energy source, including renewable and nuclear energies. As shown in Eq. (2), the forward reaction produces more moles so is favoured by lower pressures. However, lower pressures mean more energy required for compression downstream and a larger, more expensive reformer. Lower steam-to-carbon ratios are also economically beneficial, though reforming at high temperatures and low S/C ratio may cause the formation of soot [23]. While SMR accounts for the majority of the methanol produced worldwide [24], a drawback of the SMR process is an excess of hydrogen for downstream gas-to-liquid (GTL) applications [23,25,26].

In ATR, oxygen is supplied via a top mounted burner to the mixed NG and steam feed, coupling lean combustion with the steam reforming reactions of Eqs. 2 and 3:

$$CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \qquad \Delta H_R = -35.6 \ \text{KJ/mol} \tag{4}$$

ATR produces syngas with an M of 1.5–1.8 and an excess of carbon dioxide, which must be removed before entering the methanol synthesis reactor. The heat for the reforming reaction is supplied by the lean combustion, making ATR technology the most heat effective reforming technology [13]. Oxygen-blown reformers are also usually preferred over air-blown reformers, as the expense of an air separation unit is outweighed by the savings in smaller reflux streams, reactors and column sizes [27].

The most economic method of air separation at large scale is usually cryogenic [24]. In medium size plants, ATRs are more attractive when used in combination with heat exchanger based reformers.

Using a combination of these two reforming technologies in series or in parallel can also offer benefits such as reduced heat requirements and adjustable M. Instead of supplying the heat by burning fuel, the steam reformer gains heat through exchange with the hot stream leaving the ATR [28]. This type of two step reforming layout was first used in Norway [13], and a very large, 5000 t/day methanol plant was commissioned in Saudi Arabia in 2008.

2.2. Methanol synthesis

Methanol is usually synthesized via a high pressure, equilibrium