



Analysis of di-methyl ether production routes: Process performance evaluations at various syngas compositions



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HIGHLIGHTS

- Evaluated dry methane reforming (DMR) and bireforming (BiR) for DME production.
- Modeling and process analyses were conducted across various H₂/CO ratios.
- Methane intensity (tonne_{CH₄}/tonne_{DME}) is governed by the DME mass balance, not by H₂/CO ratio.
- Bireforming showed better overall process performance.
- DMR and BiR save ~22% methane feed uptake on average by utilizing captured CO₂.

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ABSTRACT

This paper investigates direct di-methyl ether (DME) production based on dry methane reforming (DMR-to-DME) and on bireforming (BiR-to-DME). Technically, DMR-to-DME is preferred to BiR-to-DME because the former produces synthesis gas (syngas) with a hydrogen to carbon monoxide molar ratio (H₂/CO) of 1 which is the ideal ratio for DME synthesis. Whereas the latter produces a H₂/CO close to 2 and consequently suffers from two apparent drawbacks: (1) lack of the so-called 'synergy effect' – a feature that enhances DME yield when operating at H₂/CO close to 1, and (2) generation of a high heat capacity by-product (H₂O) which makes DME recovery energy intensive. In this paper, we find that those two disadvantages actually enhance the performance of BiR compared to DMR across a range of performance metrics. Although the presence of water increases the cooling/heating duty and the distillation columns' reboiler duty in the BiR route, more heat released from DME synthesis reactor can be utilized in the reboilers to make BiR techno-economically compatible. To assess the sustainability of DMR and BiR, evaluations are carried out against an existing industrial scale DME production route (auto-thermal-reforming (ATR)). By utilizing the carbon in the CO₂ from an attached post-combustion carbon capture plant, DMR and BiR can save 22.3% methane feed uptake on average compared to the ATR process, which results in the DMR and BiR reducing CO₂ emissions by at least 6.5% on average.

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1. Introduction

Di-methyl ether (CH₃OCH₃) is the simplest ether, with some important properties: non-toxic colorless gas, non-corrosive, non-carcinogenic and environmentally friendly (Kiss and Suszwalak, 2012). DME can be used as a fuel, a building block for important chemicals such as ethylene and propylene and also as a replacement for chlorofluorocarbons in aerosols (EPA, 2012). Research

that looks at using DME as a fuel substitute in diesel-cycle engines has been conducted (Arcoumanis et al., 2008; Zhao et al., 2005; Golovitchev et al., 1999). DME possesses a higher cetane number (Olah et al., 2008) (> 55) in comparison with diesel (40–55), which makes it an excellent alternative fuel for diesel engines with low ignition temperatures (Fleisch et al., 2012). DME is a 'clean' fuel due to its high oxygen content as well as the absence of C–C bonds which helps to reduce NO_x, SO_x and particulate matter (Semelsberger et al., 2006). Due to similar properties of DME with LPG, DME can use the current LPG infrastructure with minimal modification expenditure. In 2011, the worldwide annual production of DME was 5 million tonnes/year, however this is expected to rise to 20 million tonnes/year by 2020 (DME, 2006). Due to the above merits, DME has been integrated into the so-called novel conceptual framework of 'Methanol economy' developed based on

Abbreviations: DME, di-methyl ether; DMR, dry methane reforming; ATR, auto-thermal-reforming; CCU, carbon capture and utilization; BiR, bireforming

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Table 1
Reaction steps for DMR ($H_2/CO=1$) and BiR ($H_2/CO=2$) based DME synthesis (Olah et al., 2009).

Route	Raw feeds					→	Syngas			→	DME+by-product			
	CH ₄	+	CO ₂	+	H ₂ O		H ₂	+	CO		CH ₃ OCH ₃	+	CO ₂	+
DMR	1.5		1.5		0	3		3	1		1		0	
BiR	1.5		0.5		1	4		2	1		0		1	

the idea of carbon capture and utilization (CCU) (Olah et al., 2009). In the CCU framework, dry methane reforming (DMR) and bi-reforming (BiR) are key reactions that produce synthesis gas (or syngas – a mixture of CO and H₂) that can be used for DME synthesis (Table 1).

1.1. DME production routes

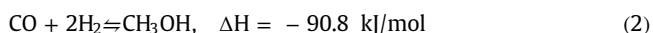
DME can be formed via the catalytic dehydration of methanol (MeOH) on solid acids such as alumina or phosphoric acid modified γ -Al₂O₃ as shown in reaction (1) (Olah et al., 2008).



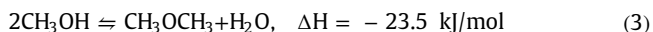
Production of DME is distinctively divided into two routes as shown in Fig. 1. In the indirect DME synthesis route, DME is produced by dehydration of MeOH (reaction (1)) which is produced in a separate reactor, whereas in the direct DME synthesis (the basis for this work), MeOH and DME synthesis happen simultaneously over a bi-functional catalyst (e.g. Cu/ZnO/Al₂O₃ + γ -Al₂O₃) (Chen et al., 2012). This route has been dominant for most of the world DME production (Fleisch et al., 2012). However, the direct DME synthesis route has become a more attractive path for DME production due to several reasons, e.g. the enhancement in DME's yield (Peng et al., 1999); the reduction in the capital and operating costs as only one reactor is needed compared to two in the case of in-direct DME synthesis.

In direct DME synthesis route, the following elemental reactions occur on a bi-functional catalyst simultaneously:

- MeOH synthesis:



- MeOH dehydration:



- Water-gas-shift (WGS) (this reaction requires catalyst that has 'shift' activity):

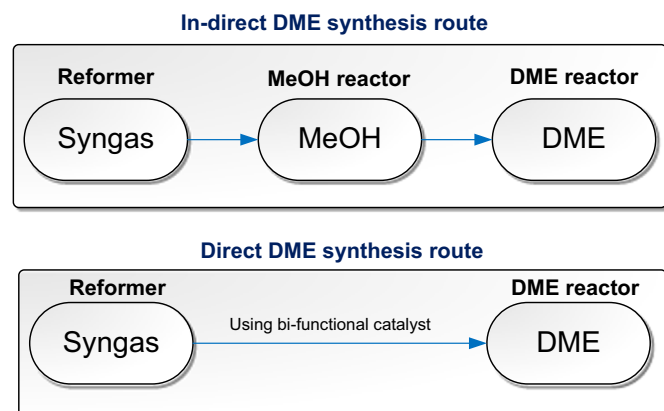
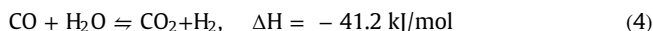
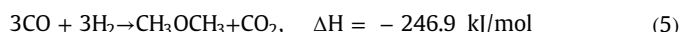
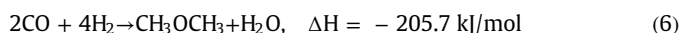


Fig. 1. DME production routes.

It is well-agreed that technically DME can be produced from two routes: either reaction (1) or combination of reactions (2)–(4) which are characterized by the ratio of H₂ and CO in the feed syngas (Jia et al., 2005). For H₂/CO equal to 1, the overall reaction (5) is applied which is a combination of reactions (2)–(4).



whereas for H₂/CO equals to 2, this overall reaction is used (combining reactions (2) and (3)):



Recall the DMR and BiR reactions shown in Table 1, it can be seen that DMR follows reaction (5) whereas BiR follows reaction (6). The deviation point of the two mass balances (reactions (5) and (6)) is the WGS reaction which dictates the associated by-product (H₂O or CO₂). The origin of such deviation is because in the H₂-rich syngas (i.e. syngas used in reaction (6)), the kinetics of WGS reaction are not thermodynamically favorable due to the higher H₂ partial pressure pushes the WGS reaction to the reverse direction. It was observed and experimentally proven that with the removal of water the WGS reaction can bring DME synthesis the so-called 'synergy effect' (Jia et al., 2005; Iliuta et al., 2011) which is an associated feature that helps to enhance DME yield significantly. The role of WGS in DME synthesis is that it consumes water formed during MeOH dehydration to produce H₂ (Jia et al., 2005). As a result, it helps to enhance the yield of DME significantly by breaking the thermodynamic limit of the MeOH dehydration step imposed by the presence of water (Jia et al., 2005). Nevertheless, up-to-date commercial application of DME synthesis have utilized both routes (reactions (5) and (6)) mainly due to the availability of syngas quality (i.e. H₂/CO) (Olah et al., 2009), e.g. for CO-rich syngas derived from coal, reaction (5) is more suitable. Some large scales DME production are summarized in Table 2 which reveals that reaction (5) is a preferred choice over reaction (6) because the former is featured with WGS reaction – the provision of the synergy effect. In addition, most literature studies about DME synthesis are found to be conducted at CO-rich syngas in order to maximize the extent of the synergy effect (Jie and Tiejun, 2003; Clausen et al., 2011; Zhang et al., 2015; Jung et al., 2008; Liu and Larson, 2014; Salkuyeh and Li, 2014). However, this 'synergy effect' might only enhance the performance of DME synthesis and not necessarily of the overall DME production process. Due to the lack of comprehensive evaluation for DME

Table 2
Summary of syngas used in DME synthesis by companies (Takeishi and Akaike, 2010).

Developer	KOGAS	Shizuoka Univ.	JFE	Air products	Haldor Topsoe
H ₂ /CO	1	1	1	0.7	2
Overall DME production reaction	(5)	(5)	(5)	(5)	(6)

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