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Dimethyl ether (DME) as an alternative fuel

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Abstract

With ever growing concerns on environmental pollution, energy security, and future oil supplies, the global community is seeking non-petroleum based alternative fuels, along with more advanced energy technologies (e.g., fuel cells) to increase the efficiency of energy use. The most promising alternative fuel will be the fuel that has the greatest impact on society. The major impact areas include well-to-wheel greenhouse gas emissions, non-petroleum feed stocks, well-to-wheel efficiencies, fuel versatility, infrastructure, availability, economics, and safety. Compared to some of the other leading alternative fuel candidates (i.e., methane, methanol, ethanol, and Fischer–Tropsch fuels), dimethyl ether appears to have the largest potential impact on society, and should be considered as the fuel of choice for eliminating the dependency on petroleum.

DME can be used as a clean high-efficiency compression ignition fuel with reduced NO_x, SO_x, and particulate matter, it can be efficiently reformed to hydrogen at low temperatures, and does not have large issues with toxicity, production, infrastructure, and transportation as do various other fuels. The literature relevant to DME use is reviewed and summarized to demonstrate the viability of DME as an alternative fuel.

Keywords: Dimethyl ether; Steam reforming; Fuel cells; Well-to-wheel; Hydrogen; Diesel substitute; Ethanol; Methane; Methanol; Efficiency; Greenhouse gases; Biomass; Fischer–Tropsch

1. Introduction

At the turn of the 19th century, petroleum was plentiful, and the US built its society around this fuel. Petroleum was the fuel that supplied much of the energy needs of our society and the industrial revolution. It is estimated that the world has peaked in petroleum production, and world petroleum consumption has outpaced new-found reserves. A century later, our generation is faced with reverse engineering a society based on petroleum to a new society based on an alternative fuel that will maintain economic, political, and environmental security for future generations.

In 1997, the US transportation sector consumed 13 million barrels day^{-1} (accounting for 66% of the US petroleum consumption) and is forecasted to reach 21 million barrels day^{-1} by 2025 [1]. As developing countries such as China, India, and Russia increase consumption, the petroleum demand could increase by as much as 75%. In

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Abbreviations: Bio, biomass; CGH2, compressed gaseous hydrogen; CI, compression ignition; CIDI, compression ignition direct injection; CNG, compressed natural gas; CP, central processing plant; DI, direct injection; DME, dimethyl ether; Eq, equivalent; EtOH, ethanol; EU, European Union; FC, fuel cell; FPFC, fuel processor fuel cell; FRFG2, federal phase 2 reformulated gasoline; FT, Fischer–Tropsch; FTD, Fischer–Tropsch diesel; FTN, Fischer–Tropsch naptha; GV, gasoline vehicle; HEV, hybrid electric vehicle; HTD, hydro deoxygenation/hydrothermal upgrading; ICE, internal combustion engine; LH2, liquefied hydrogen; LHV, lower heating value; LNG, liquefied natural gas; LPG, liquefied petroleum gas; M90, 90% methanol–10% water; MeOH, methanol; MTA, automatic transmission; NG, natural gas; Petrol, petroleum; PP, poplar plantation; RFD, reformulated diesel ($S < 10$ ppm); RFG, reformulated gasoline ($S < 10$ ppm); RS, residual straw; RWB, residual woody biomass; S, sulfur; SB, sugar beets; SI, spark ignited; SIDI, spark ignited direct injection; 35VT, compressed hydrogen delivered to a 35 MPa vehicle tank

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China, the vehicle population was 16.56 million in 2000, and is forecasted to reach 65.38 million by 2010.

A means of reducing or eliminating the dependency on petroleum is to use fuels derived from natural gas, biomass, or coal. For this reason, methanol, ethanol, Fischer–Tropsch fuels, biodiesel and biogasoline are being researched as alternative fuels. Whatever fuel is to replace petroleum, it must address the following criteria:

- Availability
  - Are there production facilities? What are their capacities?
  - Is there a pre-existing infrastructure?
  - What natural resource is used as the raw material?
    - fossil fuels (natural gas, coal);
    - renewable (timber, switchgrass, corn, sugar beets, etc.).
- Economics
  - What are the fuel production and fuel distribution costs?
  - What are the costs of constructing new production facilities?
  - What is the cost of the raw material used for fuel production?
  - What are the costs of retrofitting old equipment to process the new fuel (if possible) or to replace them with new technology?
- Acceptability
  - Is the new generation fuel inherently safe in handling and refueling?
  - Are there inherent health risks to humans or animal life?
- Environmental and emissions
  - How does the new generation fuel affect global warming?
  - In the event of a large scale release, how does it affect the environment?
- National security
  - Are the raw material(s) readily available and processed without reliance on foreign materials?
- Technology
  - Are there commercially available or emerging technologies that can process the fuel?
  - Are they more efficient?
- Versatility
  - Is the new generation fuel versatile in application (e.g., can the fuel be used as a residential fuel for heating and cooking, as a transportation fuel, as a power generation fuel, as a fuel that can produce hydrogen-rich fuel-cell feeds)?
  - Can the new generation fuel be manufactured using various feedstocks (e.g., coal, natural gas, and biomass)?

This report details dimethyl ether as an alternative fuel that could potentially replace petroleum-based fuels. Dimethyl ether is compared to the leading alternative fuel candidates; namely, hydrogen, methane, methanol, ethanol, biofuels, and Fischer–Tropsch fuels. As a benchmark, comparison is also made to conventional diesel and gasoline. A list of acronyms and abbreviations used in the text appear under 'Abbreviations'.

2. Properties of fuels

2.1. Physical and thermo-physical properties

Dimethyl ether is the simplest ether, with a chemical formula of CH_3OCH_3. The physical properties of dimethyl ether are similar to those of liquefied petroleum gases (i.e., propane and butane). Dimethyl ether burns with a visible blue flame and is non-peroxide forming in the pure state or in aerosol formulations.

Unlike methane, dimethyl ether does not require an odorant because it has a sweet ether-like odor. The physical properties of dimethyl ether compared to the other fuels are detailed in Table 1. Values for conventional gasoline and

Table 1
Comparison of dimethyl ether's physical and thermo-physical properties to commonly used fuels

	Methane	Methanol	Dimethyl ether	Ethanol	Gasoline	Diesel
Formula	CH_4	CH_3OH	CH_3OCH_3	CH_3CH_2OH	C_7H_{16}	$C_{14}H_{30}$
Molecular weight (g mol^{-1})	16.04	32.04	46.07	46.07	100.2	198.4
Density (g cm^{-3})	0.00072[a]	0.792	0.661[b]	0.785	0.737	0.856
Normal boiling point[c] (°C)	−162	64	−24.9	78	38–204	125–400
LHV[d] (kJ cm^{-3})	0.0346[a]	15.82	18.92	21.09	32.05	35.66
LHV (kJ g^{-1})	47.79	19.99	28.62	26.87	43.47	41.66
Exergy[e] (MJ L^{-1})	0.037	17.8	20.63	23.1	32.84	33.32
Exergy[e] (MJ kg^{-1})	51.76	22.36	30.75	29.4	47.46	46.94
Carbon Content[d] (wt.%)	74	37.5	52.2	52.2	85.5	87
Sulfur content[d] (ppm[f])	∼7–25	0	0	0	∼200	∼250

[a] Values per cm^3 of vapor at standard temperature and pressure.
[b] Density at $P = 1$ atm and $T = -25$ °C.
[c] Data reproduced from reference [2].
[d] Data reproduced from reference [1].
[e] Data reproduced from reference [3].
[f] Mass basis.

Table 2
Global warming potentials

	Time horizon		
	20 years	100 years	500 years
DME[a]	1.2	0.3	0.1
CO_2[b]	1	1	1
CH_4[b]	56	21	6.5
N_2O[b]	280	310	170

[a] Data reproduced from reference [4].
[b] Data reproduced from reference [1].

diesel are shown in the table; similar values can be expected for biogasoline and biodiesel.

2.2. Environmental and health impacts

Volatile organic compounds (VOCs) can be environmentally hazardous; and are often carcinogenic and mutagenic. Many of the VOCs are ozone-depleting; consequently their industrial emissions have been restricted by the 1990 Clean Air Act amendments.

Dimethyl ether is a volatile organic compound, but is non-carcinogenic, non-teratogenic, non-mutagenic, and non-toxic. The lifetimes and global warming potential for dimethyl ether have been modeled by Good et al. [4,5]. Their results indicate a troposhperic lifetime of dimethyl ether to be 5.1 days—with global warming potentials of 1.2 (20-year time horizon), 0.3 (100-year time horizon), and 0.1 (500-year time horizon). Based on their results, Good et al. conclude that dimethyl ether is environmentally benign. For comparison, Table 2 lists the global warming potentials of carbon dioxide, methane, and dinitrogen oxide.

3. DME production and economics

3.1. DME production

Traditionally, dimethyl ether has been produced in a two step process (a.k.a. the conventional route) where syngas (typically generated from the steam reforming of methane) is first converted to methanol—followed by methanol dehydration to dimethyl ether.

- Methanol synthesis:

$$CO + 2H_2 \rightleftharpoons CH_3OH, \quad \Delta H^\circ_{rxn} = -90.3\,kJ\,mol^{-1}$$

- Methanol dehydration:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O, \quad \Delta H^\circ_{rxn} = 23.4\,kJ\,mol^{-1}$$

- Water–gas shift:

$$H_2O + CO \rightleftharpoons H_2 + CO_2, \quad \Delta H^\circ_{rxn} = 40.9\,kJ\,mol^{-1}$$

- Net reaction:

$$3H_2 + 3CO \rightleftharpoons CH_3OCH_3 + CO_2, \quad \Delta H^\circ_{rxn} = 258.6\,kJ\,mol^{-1}$$

Natural gas is not the only resource that can be used to generate syngas; coal and biomass can also be used. Hence, dimethyl ether production is not limited to one feedstock.

New processes are being commercialized to produce dimethyl ether in a single step via autothermal reactors [6–8], and slurry phase reactors [9]. Fundamental research on dimethyl ether synthesis is ongoing [10–25].

3.2. Economics

Price forecasting is a strong function of plant capacity and raw material costs. NKK Corporation, based on their DME slurry phase manufacturing scheme, forecasted the cost of DME as a function of natural gas price, plant scale, and transportation distance [9,26]. At a natural gas price of US\$ 1.42 GJ^{-1} (US\$ 1.50 per MMBTU) and a transportation distance of 6000 km (~3700 miles), the price of DME is estimated to be US\$ 5.45 GJ^{-1} for a DME plant capacity of 2500 TPD; US\$ 4.74 GJ^{-1} for a DME plant capacity of 5000 TPD [26]. Table 3 compares DME prices to those of other common fuels. Using a natural gas price of US\$ 7.00 per MMBTU (April 2005 industrial price), the NKK price of DME would be around US\$ 13.65 GJ^{-1} (US\$ 14.37 per MMBTU) [26]—approximately US\$ 1.87 GJ^{-1} more than diesel (refinery price of diesel as of April 2005 was US\$ 1.59 gal^{-1}).

Because methanol, and consequently dimethyl ether, is not a natural resource, the prices of methanol and dimethyl ether are directly related to the price of the feedstock (e.g.,

Table 3
Price comparison of common fuels

	Natural gas[a]	Gasoline[b]	Diesel[c]	Methanol[d]	Ethanol[d]	DME[e]
US\$ GJ^{-1} (LHV)	4–7	6–12	6–12	5–17	12–17	5–14
US\$ per MMBTU (LHV)	4–7	6–13	6–13	5–18	12–18	5–15

[a] US price range from November 2002 to April 2005 [27].
[b] US price range at refinery from November 2002 to April 2005 [27].
[c] General range from 1993 to 2005 [27].
[d] General range from 1989 to 2005 [27].
[e] Price Range for a 5000 TPD plant with a transportation distance of 3700 miles (natural gas price US\$ 4.00–7.00 per MMBTU) [26].

natural gas). Natural gas is the primary feedstock for producing dimethyl ether—additional feedstocks include coal and biomass. For the case of methanol produced from natural gas, the increase in natural gas price over the past few years has forced methanol producers to relocate production facilities where there is cheap-stranded natural gas. In light of this, research and development efforts for producing dimethyl ether from clean coal and biomass could potentially dampen the price volatility resulting from fluctuations in natural gas prices.

4. Infrastructure

The infrastructure needed to supply an alternative fuel to the end user may include ocean transport, land transport and refueling stations. In the US, the most extensive infrastructures are those of natural gas and gasoline/diesel, followed by the infrastructure for LPG fuels. Depending on the alternative fuel, existing infrastructures may be modified or used as is. For example, the gasoline/diesel infrastructure can be used for ethanol. In the absence of a suitable infrastructure (as is the case for hydrogen), the infrastructure will need to be built. Building an infrastructure requires time and large amounts of capital. The capital investment (production plants and infrastructure) for hydrogen was estimated to be US$ 18 billion, whereas the investment for DME was US$ 4 billion, for methanol US$ 4 billion, and for ethanol US$ 5 billion [28].

Dimethyl ether, having properties similar to LPG fuels, can use the existing land-based and ocean-based LPG infrastructures. Ocean transport of dimethyl ether can use conventional LPG tankers. Dimethyl ether can be offloaded and stored at a receiving station using the same methods and equipment as those used for LPG with minor modifications to the pumps, seals, and gaskets. Similar modifications would be required for the land-based infrastructure. Since there are numerous refilling stations for LPG, a transitioning to dimethyl ether could be less costly than building a completely new infrastructure; additional refueling stations would be built as the demand for dimethyl ether increases.

5. Dimethyl ether as a diesel substitute

Since the mid 1990s dimethyl ether (cetane: #55–60) has been promoted as a diesel substitute (cetane: #55) [7,8,29–40]. With the concerns of diminishing petroleum reserves, dimethyl ether is garnering more attention as a viable alternative to diesel. The advantages of dimethyl ether over conventional diesel include decreased emissions of NO_x, hydrocarbons and carbon monoxide. Dimethyl ether combustion does not produce soot. CIDI engine tests have been performed with diesel and dimethyl ether in order to compare the exhaust emissions [7,31,39–44]. Data are reproduced from McCandless [39] in Fig. 1. The decreased pollutant emissions observed with dimethyl ether will contribute to cleaner air (i.e., no smog). Dimethyl ether fueled CIDI engines are also quieter than conventional diesels.

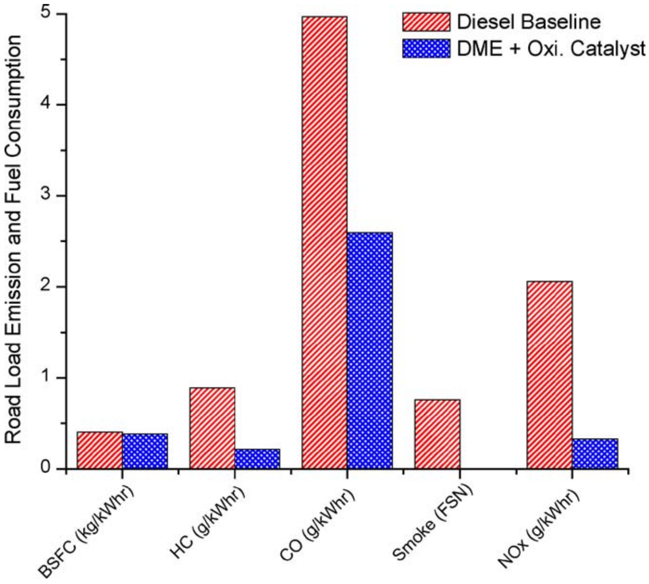

Fig. 1. Road load test data comparing engine emissions using diesel and neat DME. Data reproduced from reference [39].

The operation of a DME engine requires a new storage system and a new fuel delivery system—both have been addressed [35,36,40,45]. The engine itself does not need modification. However, in order to achieve an equivalent driving range as that of a CIDI diesel, a DME fuel storage tank must be twice the size of a conventional diesel fuel tank due to the lower energy density of DME compared with diesel fuel.

The most challenging aspects of a DME engine are related to its physical properties and not to its combustion characteristics. The viscosity of DME is lower than that of diesel by a factor of about 20; causing an increased amount of leakage in pumps and fuel injectors. There are also lubrication issues with DME; resulting in premature wear and eventual failure of pumps and fuel injectors. Additives have been used to increase the lubricity of DME, and the commonly used additives have been those developed for reformulated diesel [35,36,40]. Fundamental research on improving DME wear and lubricity is ongoing [40,46].

6. A comparison of transportation fuels

Because the US transportation sector accounts for 66% of total petroleum consumption, the alternative fuel that addresses this market will have the largest impact on reducing petroleum consumption.

The GREET model, developed at Argonne National Laboratory [1] is a widely used model that performs life cycle analyses (a.k.a. cradle-to-grave or well-to-wheel) for alternative transportation fuels. This model calculates relative perfor-

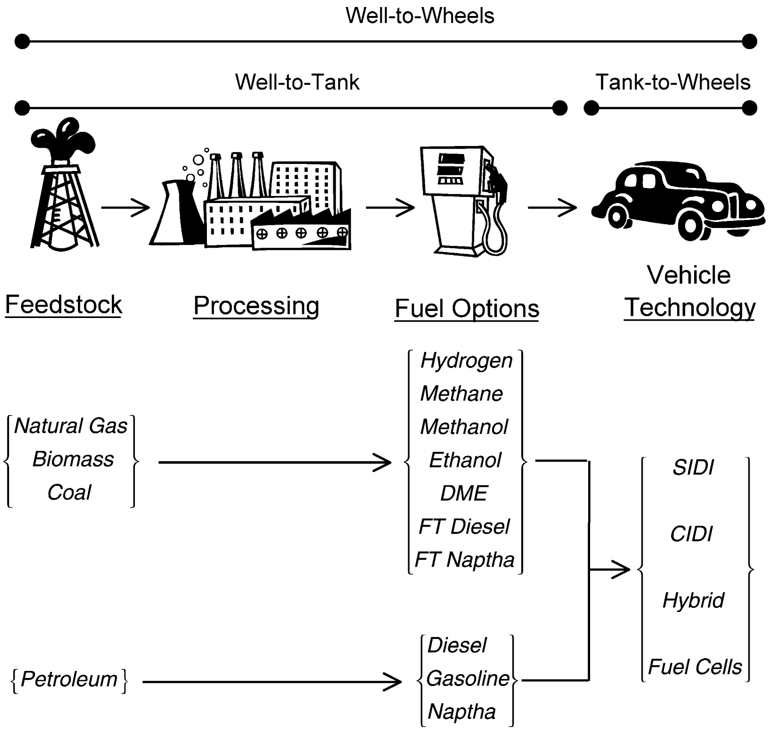

Fig. 2. Feedstocks, fuels, and vehicle technologies that can be implemented in the transportation sector.

mances of various transportation fuels (e.g., Fischer–Tropsch diesel, methanol, etc.) and vehicle technologies (e.g., hybrid, compression ignition, spark ignition, fuel cell vehicles, etc,). A similar approach was performed by L-B-Systemtechnik GmbH [47]. The life cycle analysis modeling approach is shown in Fig. 2.

The petroleum derived transportation fuels considered were gasoline, diesel, and naptha. Coal is also a feedstock that could be used to produce the listed fuels but was not considered in the modeling studies [1,47]. The modeling studies centered on natural gas and biomass as feedstocks for producing alternative transportation fuels (see Fig. 2). The vehicle technologies available for processing the alternative fuels included conventional technologies (e.g., SIDI, CIDI), hybrid technology, and fuel cell technology.

6.1. Well-to-tank (WTT) analyses

6.1.1. Well-to-tank efficiencies

The well-to-tank efficiencies for producing a variety of alternative transportation fuels using different feedstocks are shown in Fig. 3. The reported values are reproduced from Wang and Huang and L-B-Systemtechnik GmbH. The reference from which the data were taken is in brackets. For many of the fuels there are two efficiencies reported (one from each study)—for example, fuels derived from petroleum, and hydrogen derived from natural gas.

Efficiency represents a measure of feedstock conservation—the more efficient the process, the less feedstock/energy we consume, and therefore the more resources we have for future use. The energy efficiencies in Fig. 3 include fuel recovery, fuel distribution, and fuel manufacturing/processing. Well-to-tank energy efficiency is defined as

$$\eta_{\mathrm{WTT}} = \left(\frac{\mathrm{energy}_{\mathrm{fuel}}^{\mathrm{LHV}}}{\sum \mathrm{energy}_i}\right),$$

$$i = \text{feedstock recovery, fuel manufacturing, fuel distribution, etc.}$$

It is often useful to know how much energy is needed to produce the fuel; the energy input can be derived from the energy efficiency (and vice versa):

$$\mathrm{energy}_{\mathrm{input}} = \frac{1}{\eta_{\mathrm{WTT}}} = \left(\frac{\sum \mathrm{energy}_i}{\mathrm{energy}_{\mathrm{fuel}}^{\mathrm{LHV}}}\right),$$

$$i = \text{feedstock recovery, fuel manufacturing, fuel distribution, etc.}$$

The sum of energies only includes the energy from the well to the tank (Fig. 3).

Petroleum recovery and processing (i.e., gasoline, diesel, and naptha) is currently the most efficient method for producing transportation fuels. The most inefficient process is hydrogen generation via electrolysis. In general, the well-to-tank energy efficiency trend as a function of resource can be

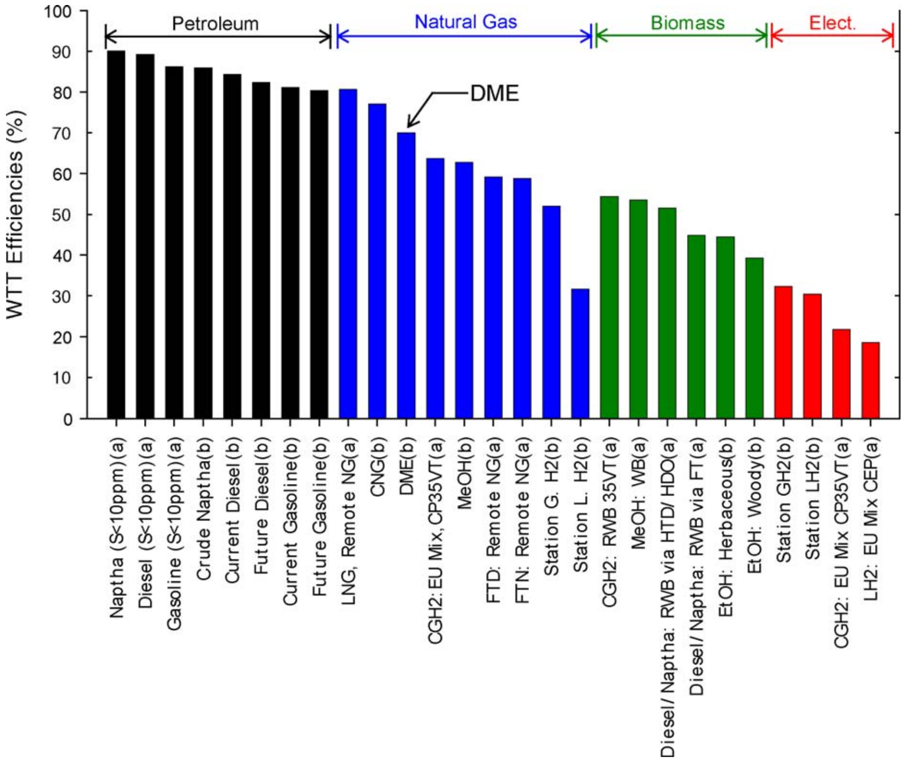

Fig. 3. Well-to-tank energy efficiencies for producing alternative fuels from various resources. Data reproduced from (a) L-B-Systemtechnik GmbH [47] and (b) Wang and Huang [1].

written as

$$\eta_{\mathrm{WTT}}^{\mathrm{petroleum}} > \eta_{\mathrm{WTT}}^{\mathrm{natural.\ gas}} > \eta_{\mathrm{WTT}}^{\mathrm{biomass}} > \eta_{\mathrm{WTT}}^{\mathrm{electrolysis}}.$$

Of the derived alternative fuels (e.g., DME, methanol, diesel, naptha, hydrogen, etc.) from natural gas, biomass or electrolysis, the production of dimethyl ether is the most efficient process. Hydrogen production efficiencies from natural gas vary widely between the two studies.

6.1.2. Well-to-tank GHG emissions

Shown in Fig. 4 are the well-to-tank greenhouse gas (GHG) emissions for various fuels produced from various feedstocks. In the well-to-tank segment of the life-cycle analysis, the GHG emissions are compared for the different fuels (and feedstocks) on a per energy input basis. Excluding fuels produced from biomass, the well-to-tank GHG emissions trend inversely to the well-to-tank efficiencies (Figs. 3 and 4). The GHG emissions for the production of dimethy ether from natural gas ($\sim$25 g MJ^{-1}) are slightly better than those of methanol produced from natural gas.

6.2. Tank-to-wheels (TTW) analyses

6.2.1. Tank-to-wheels efficiencies

The tank-to-wheel efficiencies and tank-to-wheel GHG emissions include everything related to the vehicle (i.e., transmission, engine, etc.), and its operation. In order to calculate tank-to-wheel efficiencies and GHG emissions a vehicle technology (i.e., CIDI, hybrid, fuel cell, etc.) and fuel must be assumed. Shown in Fig. 5 are the results comparing vehicle efficiencies (i.e., tank-to-wheels) for various fuels and vehicle technologies. The results are independent of fuel manufacturing and feedstock. Conventional technology consists of an internal combustion engine (ICE) or a compression ignition engine (CI) with a five speed automatic transmission.

The compression ignition engine fuelled with dimethyl ether has the same efficiency as a CI engine fuelled with diesel. Therefore, the DME markers in Fig. 5 represent the vehicle efficiencies that are expected with DME. Likewise, the vehicle efficiency for a DME fuelled fuel processor will be greater than or equal to the vehicle efficiency of a methanol fuelled fuel processor, based on preliminary DME steam reforming results [48,49].

The important trends of Fig. 5 are:

- Conventional technology (i.e., CIDI and SIDI) with petroleum-based fuels have some of the lowest vehicle efficiencies—although the well-to-tank efficiencies for petroleum fuels were the highest (80–90%, Fig. 3).
- CIDI engines have intrinsically higher vehicle efficiencies than SIDI engines.
- The general trend for vehicle efficiency as a function of vehicle technology is

$$\eta_{\mathrm{TTW}}^{\mathrm{FC}} > \left\{ \begin{matrix} \eta_{\mathrm{TTW}}^{\mathrm{FC+hybrids}} \\ \eta_{\mathrm{TTW}}^{\mathrm{FPFC}} \end{matrix} \right\} > \eta_{\mathrm{TTW}}^{\mathrm{hybrids}} > \eta_{\mathrm{TTW}}^{\mathrm{CIDI}} > \eta_{\mathrm{TTW}}^{\mathrm{SIDI}}.$$

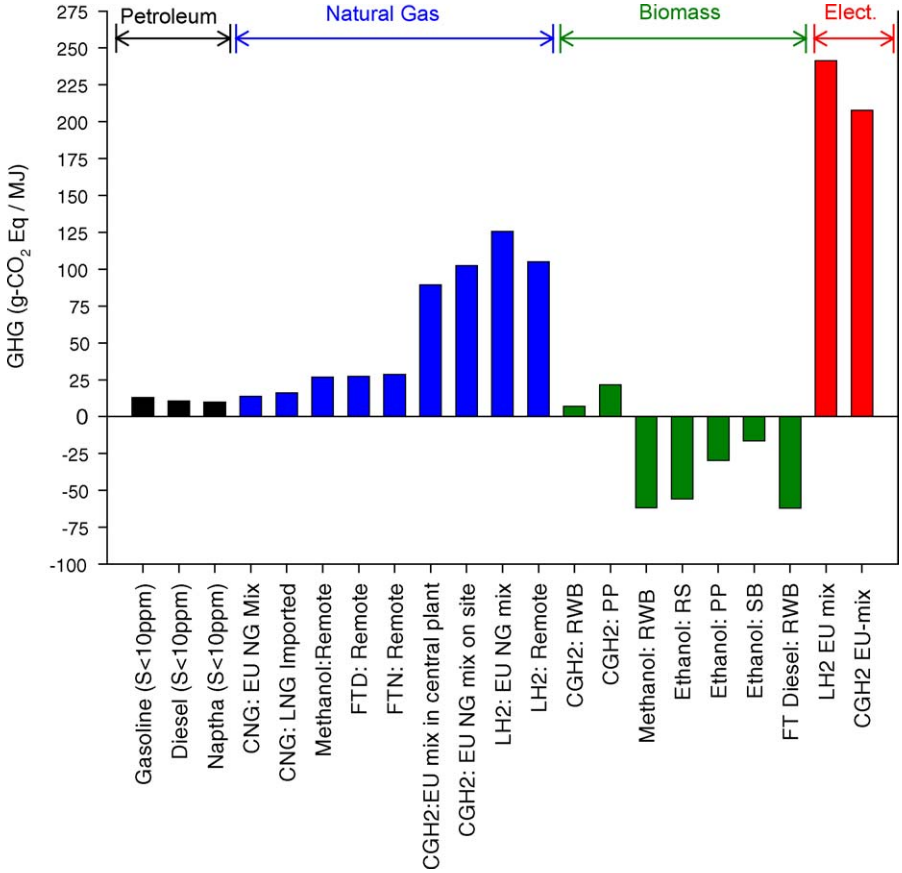

Fig. 4. Well-to-tank greenhouse gas emissions as a function of alternative fuel and feedstock. Data reproduced from reference[47].

- Dimethyl ether ranks among the top in engine efficiency for all vehicle technologies—excluding hydrogen fuel cells.

6.2.2. *Start-up energy*

The fuel processor efficiencies reported in Fig. 5 are steady-state efficiencies. This efficiency does not take into account the start-up energy required to bring the fuel processor from ambient temperature (20 °C) to the steady-state operating temperature. The fuel processor efficiency is a function of the fuel processor operating temperature, which in turn is a function of the fuel being reformed. Methanol requires the lowest reforming temperature whereas methane and natural gas have the highest.

The overall efficiencies when incorporating a drive cycle (33 miles day^{-1}) and the energy required to bring the fuel processor up to steady-state operating temperatures have been calculated [50] and are shown in Table 4. The reformer temperatures were based on thermodynamic equilibrium data, although experimental ATR processing temperatures for methanol and DME are actually lower at about 270 °C. For comparison, modeled fuel processor volumes and start-up energies as a function of fuel are also shown. Methanol and dimethyl ether are clear favorites for on-board fuel reforming for fuel cells in terms of fuel processor volume (and mass) and overall drive cycle efficiency.

6.2.3. *Tank-to-wheels GHG emissions*

The greenhouse gas emissions generated from the vehicle as a function of vehicle technology are shown in Fig. 6. The results are independent of the fuel feedstock and fuel manu-

Table 4
Fuel effects on start-up energy, fuel processor volumes and efficiencies as a function of fuel for automotive fuel cell systems producing 50 kW$_e$

	Methane	Methanol	Ethanol	DME	Simulated gasoline
ATR processing temperature (°C)	827	327	727	427	827
Steady state efficiency (%)	44	44	44	44	44
Efficiencies including start-up energy (%)	33.2	38.3	34.5	38.5	37.0
Fuel processor volume (L)	45.8	25.9	43.7	30.8	42.5
Fuel processor heat duty requirements (kJ)	7592	2712	6632	3423	7068

All fuels were reformed autothermally. Data reproduced from reference[50].

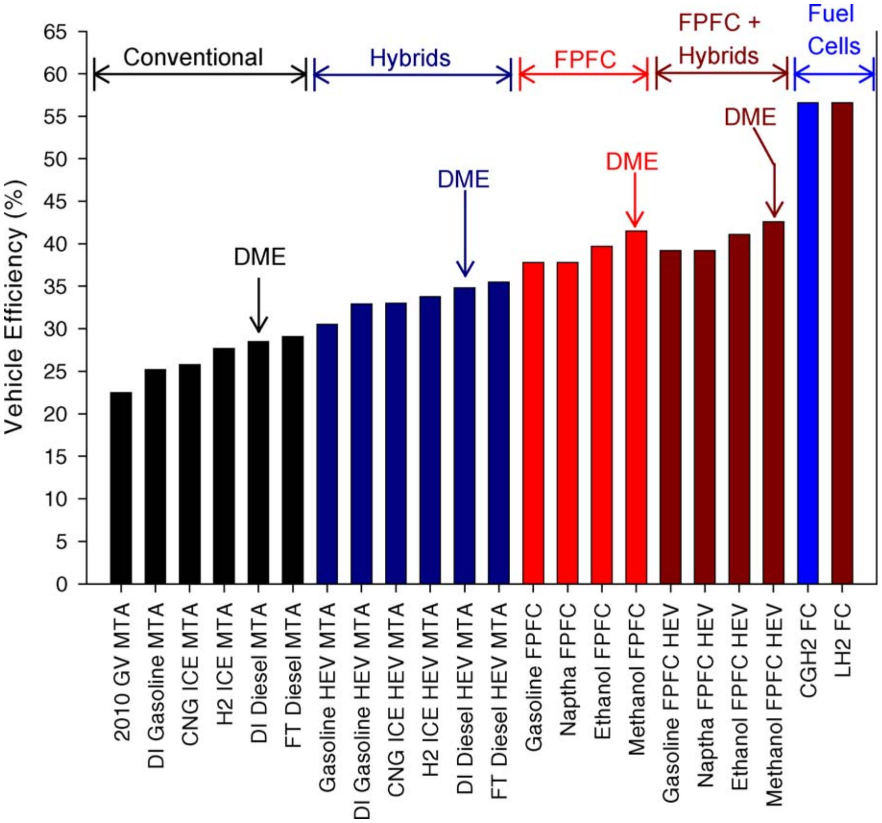

Fig. 5. Vehicle efficiencies for various alternative fuels and vehicle technologies. Data reproduced from reference [47].

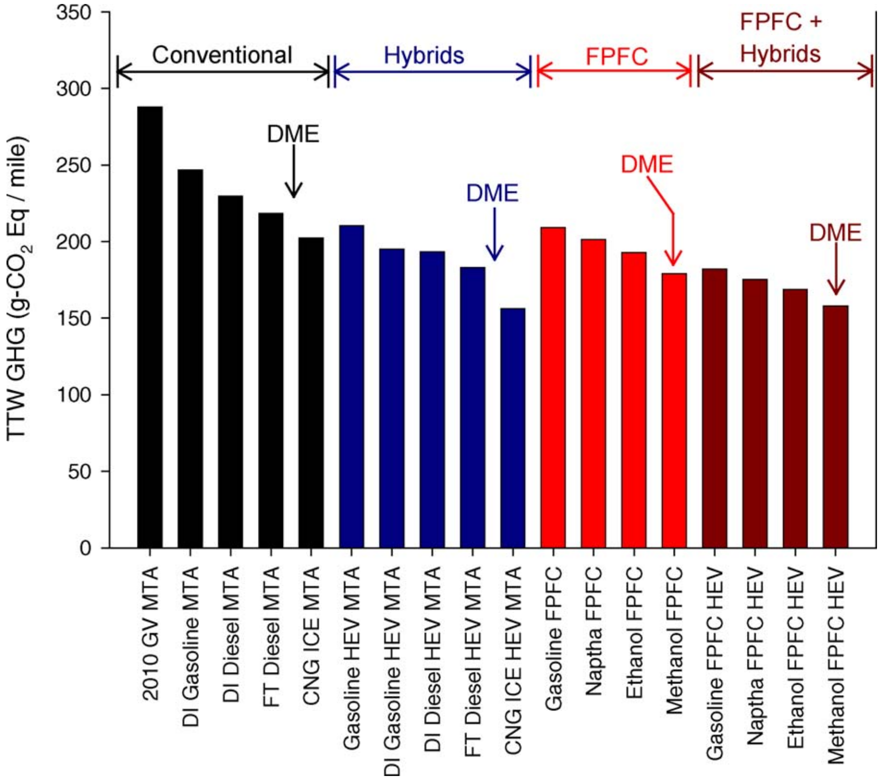

Fig. 6. Tank-to-wheels greenhouse gas emissions for various fuels and vehicle technologies. Data reproduced from reference [47].

facturing process. Tank-to-wheels emissions with hydrogen fuel cells are zero; therefore, they are not plotted. Increasing the TTW efficiency (Fig. 5) decreases the amount of TTW GHG emissions, resulting in the following TTW GHG emissions trend:

$$\mathrm{GHG}^{\mathrm{FC+hybrids}} \approx \left\{ \begin{matrix} \mathrm{GHG}^{\mathrm{hybrids}} \\ \mathrm{GHG}^{\mathrm{FPFC}} \end{matrix} \right\} < \mathrm{GHG}^{\mathrm{conventional}},$$

$$\mathrm{GHG}^{\mathrm{H_2FC}} = 0$$

On a TTW basis, a hydrogen fuel cell is the obvious choice for eliminating GHG emissions, however, this requires the yet to be commercialized fuel cell. Excluding petroleum-based fuels using conventional vehicle technologies, the remaining vehicle technologies generate comparable TTW GHG emissions (Fig. 6). The TTW GHG emissions for dimethyl ether are lower than those produced from gasoline, diesel or FT diesel with current commercialized technology. The placement of the DME markers in Fig. 6 for a CIDI DME and a CIDI-hybrid DME indicate that the values will be somewhere in between the values for FT diesel and CNG.

6.3. *Well-to-wheels analyses*

6.3.1. *Well-to-wheels (WTW) efficiency*

The WTW efficiencies include the contributions of both the WTT and TTW. The WTW efficiencies for the various alternative fuels, feedstocks, and vehicle technologies are shown in Fig. 7. DME ranks among the top in efficiency among the alternative fuels, regardless of vehicle technology.

Compressed natural gas (CNG) edges out DME in conventional technology and hybrid technology, primarily because of the increased WTT efficiency (75–80%). Other studies indicate the WTW efficiencies of a CIDI DME vehicle are either lower or within ~1.0% of a SIDI CNG vehicle [1,7,35,51]. The most notable discrepancy is between CNG and gasoline. Comparing the two fuels with conventional vehicle technologies, the DI gasoline vehicle is more efficient. But, comparing the two fuels with hybrid technology, the CNG ICE-hybrid vehicle is more efficient.

The most efficient WTW processes are petroleum based (i.e., naptha and diesel); WTT efficiencies for petroleum-based naptha and petroleum-based diesel are between 80 and 90%. The least efficient processes are both liquid and gaseous hydrogen fuel cells—hydrogen in both cases is produced from natural gas.

Dimethyl ether using conventional technology has a well-to-wheels efficiency of 18% (cf. 23% for a CIDI diesel). More optimistic DME well-to-wheel efficiencies are reported by Gill and Ofner [35]. They report well-to-wheel efficiencies of 35% for diesel, 27% for dimethyl ether and compressed natural gas, and 21% for methanol and Fischer–Tropsch diesel. The differences in the reported values are the assumptions of total vehicle efficiency—the total vehicle efficiencies for both diesel and DME engines were estimated at 40% [35].

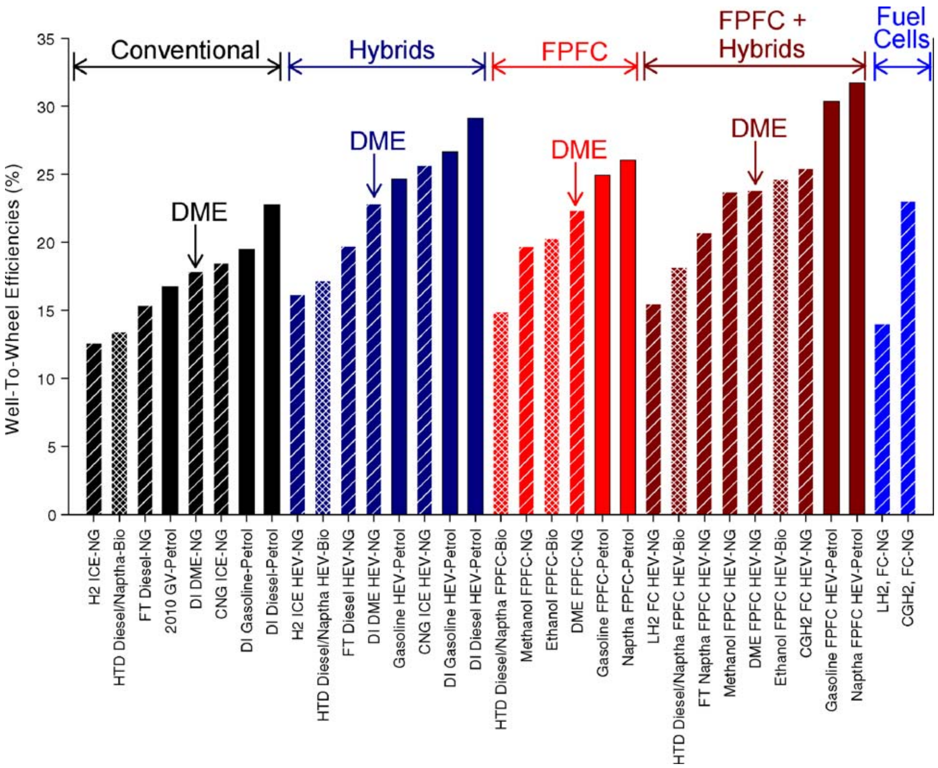

Fig. 7. Well-to-wheel efficiencies for various fuels, feedstocks, and vehicle technologies. Solid bars are petroleum-based fuels, diagonal hatched bars are natural gas-based fuels, and the cross hatched bars are biomass-based fuels. Data reproduced from references [1,47].

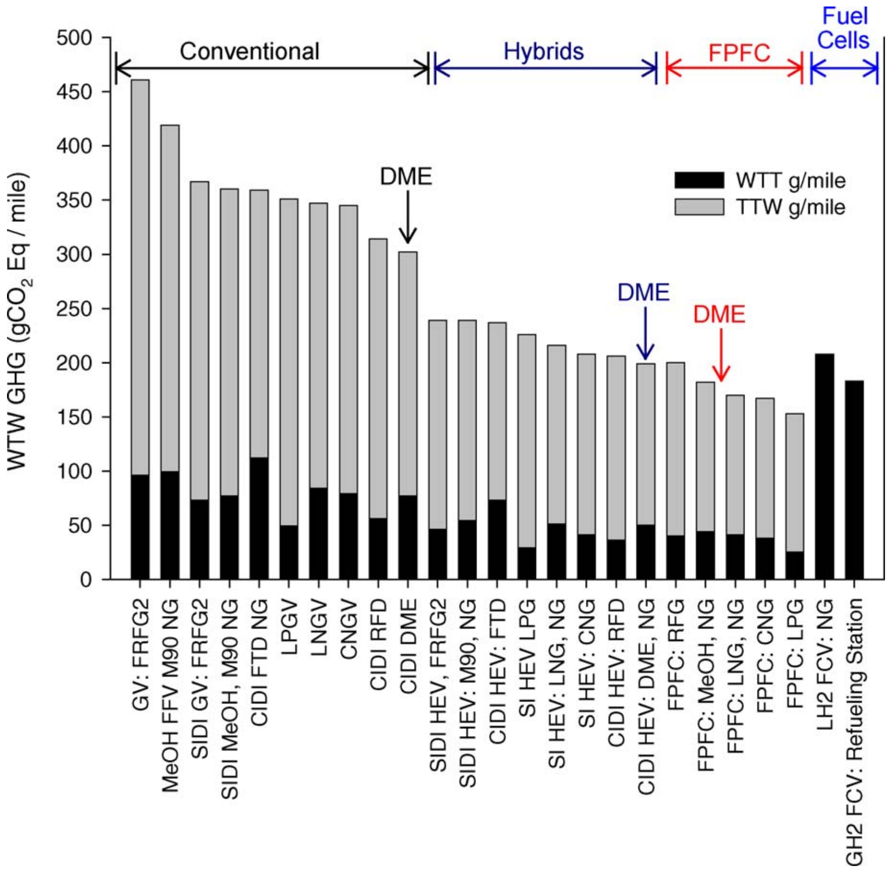

Fig. 8. Well-to-wheels greenhouse gas emissions divided into the well-to-tank and tank-to-wheels contributions for various fuels, feedstock's, and vehicle technologies. Data reproduced from references [1].

The important trends of Fig. 7 are:

- CIDI engines are more efficient than SIDI engines.
- Dimethyl ether has an equivalent or higher WTW efficiency than all other alternative transportation fuels.
- The well-to-wheel efficiency trend as function of vehicle technology is

$$\eta_{\mathrm{WTW}}^{\mathrm{FC+hybrids}} \approx \eta_{\mathrm{WTW}}^{\mathrm{hybrids}} > \eta_{\mathrm{WTW}}^{\mathrm{FPFC}} \approx \eta_{\mathrm{WTW}}^{\mathrm{H_2FC}} > \eta_{\mathrm{WTW}}^{\mathrm{CIDI}} > \eta_{\mathrm{WTW}}^{\mathrm{SIDI}}.$$

6.3.2. *Well-to-wheels (WTW) GHG emissions*

The WTW greenhouse gas emissions for the various alternative fuels, feedstocks, and vehicle technologies are shown in Fig. 8. A CIDI DME vehicle produces the least amount of GHG emissions compared to the other fuels using conventional vehicle technology. A SIDI methanol vehicle is one of the largest GHG producers. Upgrading conventional vehicle technology (i.e., SIDI, CIDI) to include hybrid technology result in some of the largest reductions in GHG emissions—with a DME CIDI hybrid producing the least amount of WTW GHG emissions. Additional GHG emission reductions can be realized with further vehicle improvements, such as fuel processors and fuel cells.

Fuel processor fuel cell vehicles using liquefied petroleum gas, liquefied natural gas, and compressed natural gas produce the least amount of WTW GHGs. Although hydrogen fuel cells produce zero TTW GHG emissions, the WTW GHG emissions can still be high depending on how the hydrogen was produced.

The important trends from Fig. 8 are:

- A CIDI DME engine produces the least amount of WTW GHG emissions compared to the other alternative fuels using conventional technology (SIDI and CIDI).
- A DME CIDI hybrid vehicle produces the least amount of WTW GHG emissions compared to the other fuels using hybrid technology—including fuel cells operating on natural gas derived hydrogen.
- The trend of WTW GHG emissions as a function of vehicle technology is

$$\mathrm{GHG}^{\mathrm{FPFC}} < \mathrm{GHG}^{\mathrm{hybrids}} \approx \mathrm{GHG}^{\mathrm{H_2FC}} < \mathrm{GHG}^{\mathrm{conventional}}.$$

7. DME as an energy carrier

7.1. *Residential Fuel*

Liquefied petroleum gas (i.e., propane and butane) is primarily used as a residential fuel for heating and cooking.

In 2000, Australia exported 1.4 million tonnes of liquefied petroleum gas, with the largest markets being China and Japan. The LPG market in 2000 was 180 million tonnes per annum, and is expected to grow to 260 million tonnes. By 2010, the potential demand for DME as a residential fuel in Asia is forecasted to be 25 million tonnes per annum [34].

Dimethyl ether, having similar methods of storage and handling as LPG fuels, can replace LPG fuels. Dimethyl ether is already being used as a cooking fuel [32]. Pure dimethyl ether gas stove systems require burner tip, storage (∼25% increase), and vaporizer modifications.

7.2. Power generation

India is considering using DME-fired turbines to supply power to its southern region [52]. In 2010, the potential demand for dimethyl ether in Asia has been estimated to be 105 million tonnes per annum; with 50% of the demand being electricity [34]. Power generation via DME- or methanol-fired turbines has been evaluated by general electric [52,53]. For a 700 MW combined cycle power plant using a GE 9E class heavy duty turbine, the heat rate with refrigerated DME at −25 °C would be approximately 1.6% lower than using natural gas and 6.3% lower than using liquid naptha. Of the three fuels, dimethyl ether produced the least amount of NO_x and CO [54].

7.3. DME, hydrogen, and fuel cells

There are four processes for generating hydrogen-rich fuel-cell feeds from hydrocarbon fuels: decomposition, steam reforming, partial oxidation, and autothermal reforming. Decomposition and partial oxidation result in high yields of carbon monoxide and are generally not suited for fuel cell applications owing to their lower efficiencies as compared to the other reforming techniques. Steam reforming produces the highest hydrogen yield with the least amount of carbon monoxide. The shortcoming of steam reforming is that the process is inherently endothermic and hence requires longer start-up times. For many transportation applications, the start-up time is critical for consumer acceptance.

Autothermal reforming combines the endothermic steam reforming reaction with the exothermic partial oxidation reaction. Intrinsically, autothermal processing has decreased start-up times and a faster response to a change in load than the other processes. However, the reformate from autothermal processing has a lower hydrogen concentration than steam reforming.

Methane, methanol, ethanol, and gasoline are the most widely researched fuels for automotive fuel cells [55–90]. Methane, ethanol, and gasoline all require high temperature autothermal processing (>700 °C). Ethanol and gasoline tend to form carbon resulting in durability issues [55,58,91]. Carbon formation can be suppressed with the addition of water, but for realistic conditions (i.e., 1.2 < S/C < 1.5) carbon formation remains a critical challenge [55,58,91]. Methanol is a low temperature (∼280 °C) reforming fuel that exhibits high carbon dioxide selectivities (>98%), and high hydrogen yields (>70%).

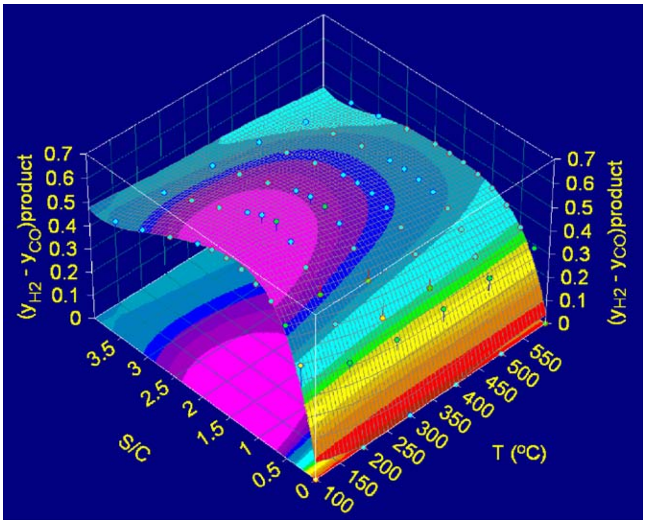

Fig. 9. Plot of the difference in thermodynamic equilibrium product mole fractions of hydrogen and carbon monoxide on a wet basis as a function of steam-to-carbon ratio and temperature for dimethyl ether-steam reforming. Data reproduced from reference [93].

Thermodynamically, the processing of dimethyl ether with steam indicates the complete conversion of dimethyl ether to hydrogen, carbon monoxide, and carbon dioxide [92,93]. Fig. 9 shows the optimal conditions for producing the largest amount of hydrogen, while minimizing the amount of carbon monoxide. The global maximum occurs at a steam-to-carbon ratio of 1.50 and a temperature of 200 °C.

Dimethyl ether steam reforming occurs via a two step reaction sequence [48,49,94–97]. The first step is the conversion of dimethyl ether to methanol via DME hydrolysis, followed by methanol steam reforming over Cu or Cu/ZnO.

- DME hydrolysis:

$$CH_3OCH_3 + H_2O \underset{\text{catalyst}}{\overset{\text{acid}}{\rightleftharpoons}} 2CH_3OH,$$

$$\Delta H_R^\circ = +37\,\text{kJ}\,\text{mol}^{-1}$$

- MeOH-SR:

$$2CH_3OH + 2H_2O \overset{\text{Cu/Zn}}{\rightleftharpoons} 6H_2 + 2CO_2,$$

$$\Delta H_R^\circ = +49\,\text{kJ}\,\text{mol}^{-1}$$

- Net reaction; DME-SR

$$CH_3OCH_3 + 3H_2O \rightleftharpoons 6H_2 + 2CO_2,$$

$$\Delta H_R^\circ = +135\,\text{kJ}\,\text{mol}^{-1}$$

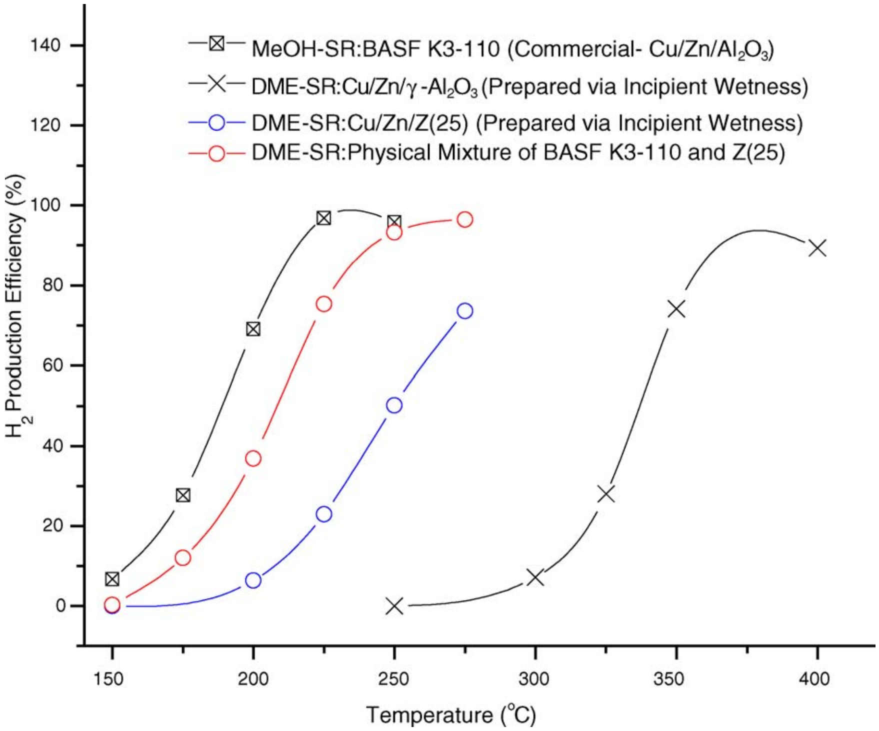

Fig. 10. Comparison of methanol steam reforming to dimethyl ether steam reforming over various catalsyts. Data reproduced from references [48,49].

Most DME reforming studies [94–96,98] used alumina as the acid catalyst for DME hydrolysis. Turnover frequencies as high as 4.2×10^{-6} moles of dimethyl ether per gram of catalyst per second ($T = 275\,°\text{C}$, $\tau = 1.0\,\text{s}$) have been observed with the complete conversion of dimethyl ether to hydrogen, carbon monoxide, and carbon dioxide [48,49].

Fig. 10 compares the performances of methanol steam reforming and dimethyl ether steam reforming over various catalysts [48,49]. Dimethyl ether can be reformed at low temperatures generating hydrogen-rich fuel-cell feeds.

Autothermal reforming will most likely be the process implemented for on-board vehicle fuel processing. Thermodynamic modeling of the autothermal process using various fuels has been conducted to determine the optimal operating conditions (i.e., T, S/C, and O/C) for producing the highest quality reformate (i.e., high hydrogen content and low carbon monoxide content) [99]. Table 5 presents the most optimal conditions that can be expected for methane, methanol, ethanol, dimethyl ether, and simulated gasoline when processed autothermally. The temperatures in Table 5 represent the idealized cases with the ideal catalysts—in practice the temperatures are higher.

The values shown in Table 5 were produced by excluding methane as a product in the model. Ethanol can be a viable reforming fuel if the issue of methane selectivity at low temperatures (∼300 °C) can be addressed. However, high reforming temperatures are currently required for ethanol reforming due to the production of methane. Hence, higher temperatures are required in practice than given in Table 5 in order to maintain a high degree of hydrogen production efficiency for both ethanol and gasoline (∼ 700 °C). However, the reforming of DME and methanol are selective to hydrogen and carbon dioxide at low reforming temperatures (∼ 270 °C).

Table 5
Optimal thermodynamic conditions for the autothermal processing of methane, methanol, ethanol, dimethyl ether, and simulated gasoline

Fuel	Temperature (°C)	S/C	O/C	Conversion (%)	y_{H_2}	y_{CO}	Difference ($y_{H_2} - y_{CO}$)
Dimethyl ether	187	1.167	0.293	99.50	0.615	0.024	0.591
Methanol	227	1.000	0.248	100.00	0.602	0.013	0.589
Ethanol	307	1.167	0.211	99.50	0.534	0.041	0.492
Simulated gasoline	527	1.270	0.569	100.00	0.430	0.125	0.306
Methane	727	4.000	0.410	99.80	0.327	0.044	0.283

Data reproduced from reference[99].

8. Conclusions

Current transportation fuels are based on petroleum, a resource that is being depleted, and whose importation has political and societal ramifications. Hydrogen is viewed by many as the ultimate ‘end-game’ fuel. A transition from petroleum to DME to hydrogen may be more cost effective than a step change to hydrogen. DME can be introduced and exploited with existing technologies, and enable the eventual implementation of advanced technologies, such as fuel cells.

Because dimethyl ether is produced from natural gas, coal, or biomass, dimethyl ether can increase the energy security of the US by displacing petroleum derived fuels. The prominent advantages of dimethyl ether as a fuel and energy carrier are:

- Dimethyl ether can be used in the most efficient engine technology currently produced (i.e., CIDI). Dimethyl ether demonstrated lower NO_x and SO_x than conventional diesel; is sootless.
- Using existing engine technology, dimethyl ether produces the least amount of well-to-wheel greenhouse gas emissions compared to FT diesel, FT naptha, biodiesel, bionaptha, methanol, methane, and ethanol.
- Excluding natural gas, dimethyl ether has the highest well-to-wheel efficiencies of all non-petroleum based fuels using conventional, hybrid, and fuel processor fuel cell vehicle technologies.
- Dimethyl ether can be used as a residential fuel for heating and cooking.
- Dimethyl ether as a turbine fuel demonstrates an increase in efficiency, and decreased NO_x and CO compared to methane and liquid naptha.
- On-board automotive fuel processors using methanol and dimethyl ether exhibit the lowest start-up energies and the lowest fuel processor volumes—correlating to higher overall efficiencies as compared to ethanol, methane, and gasoline fueled fuel processor fuel cell vehicles.
- Dimethyl ether can produce hydrogen-rich fuel-cell feeds with hydrogen yields equivalent to those of methanol at comparable operating temperatures.
- The infrastructure of dimethyl ether is less cost intensive than that for hydrogen because dimethyl ether can use the existing LPG and natural gas infrastructures for transport and storage.
- Dimethyl ether is non-toxic, non-teratogenic, non-mutagenic, and non-carcinogenic.
- Dimethyl ether has a global warming potential of 0.1 (cf., 1.0 for CO_2) for a 500-year time horizon.

Hydrogen fuel cells show unprecedented efficiencies, but with the current technical challenges of hydrogen storage, hydrogen production efficiencies, fuel cell durability, high infrastructure costs, and high fuel cell costs, there is little likelihood that automotive fuel cell systems will significantly penetrate the commercial market in the near future.

As an alternative fuel, dimethyl ether can address energy security, energy conservation, environmental concerns, and the pragmatic realization of depleting petroleum reserves. Most importantly, these concerns can be addressed immediately in a cost-effective manner with current commercialized technology (i.e., CIDI and hybrid), and do not rely on future technologies (fuel processors or fuel cells) where the time-frame of market penetration is uncertain. As fuel processors and fuel cells are introduced to the public, dimethyl ether can be further exploited as a non-toxic, non-corrosive, environmentally benign hydrogen carrier produced from domestic resources.

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References

[1] M.Q. Wang, H.S. Huang, A full fuel-cycle analysis of energy and emission impacts of transportation fuels produced form natural gas, ANL/ESD-40 1999.
[2] J.G. Speight, Perry’s Standard Tables and Formulas for Chemical Engineers, McGraw-Hill, New York, 2003.
[3] B. John, Hansen S, Fuels and Fuel Processing Options for Fuel Cells 2nd International Fuel Cell Conference, Lucerne, CH, 2004.
[4] D.A. Good, J.S. Francisco, A.K. Jain, D.J. Wuebbles, J. Geophys. Res. 103 (1998) 28181–28186.
[5] D.A. Good, J. Hanson, J.S. Francisco, Z.J. Li, G.R. Jeong, J. Phys. Chem. A 103 (1999) 10893–10898.
[6] T. Fleisch, Prospects for DME as a multi-purpose fuel IBC Gas to Liquids Conference, Milan, Italy, 2002.
[7] T.H. Fleisch, A. Basu, M.J. Gradassi, J.G. Masin, Stud. Surf. Sci. Catal. 107 (1997) 117–125.
[8] A.M. Rouhi, Chem. Eng. News 73 (1995) 37–39.
[9] Y. Ohno, N. Inoue, T. Ogawa, M. Ono, T. Shikada, H. Hayashi, Slurry phase synthesis and utilization of dimethyl ether, NKK Technical Review No. 85, 2001.
[10] J.W. Guo, Y.Q. Niu, B.J. Zhang, Pet. Sci. Technol. 16 (1998) 555–566.
[11] J. Haggin, Chem. Eng. News 69 (1991) 20–21.
[12] M.L. Jia, W.Z. Li, H.Y. Xu, S.F. Hou, C.Y. Yu, Q.J. Ge, Catal. Lett. 84 (2002) 31–35.
[13] O.S. Joo, K.D. Jung, S.H. Han, Bull. Korean Chem. Soc. 23 (2002) 1103–1105.
[14] H.J. Kim, H. Jung, K.Y. Lee, Korean J. Chem. Eng. 18 (2001) 838–841.
[15] S. Lee, M. Gogate, C.J. Kulik, Fuel Sci. Technol. Int. 13 (1995) 1039–1057.
[16] S.H. Lee, W. Cho, W.S. Ju, B.H. Cho, Y.C. Lee, Y.S. Baek, Catal. Today 87 (2003) 133–137.
[17] J.L. Li, X.G. Zhang, T. Inui, Appl. Catal. A: Gen. 147 (1996) 23–33.
[18] X.D. Peng, A.W. Wang, B.A. Toseland, P.J.A. Tijm, Ind. Eng. Chem. Res. 38 (1999) 4381–4388.
[19] G.X. Qi, J.H. Fei, X.M. Zheng, Z.Y. Hou, React. Kinet. Catal. Lett. 73 (2001) 245–256.

[20] A. Sardesai, A. Gunda, T. Tartamella, S.G. Lee, Energy Sources 22 (2000) 77–82.

[21] T. Shikada, Y. Ohno, T. Ogawa, M. Ono, M. Mizuguchi, K. Tomura, K. Fujimoto, Kinet. Catal. 40 (1999) 395–400.

[22] K.P. Sun, W.W. Lu, F.Y. Qiu, S.W. Liu, X.L. Xu, Appl. Catal. A: Gen. 252 (2003) 243–249.

[23] O. Takashi, I. Norio, S. Tutomu, O. Yotaro, J. Nat. Gas Chem. 12 (2003) 219–227.

[24] Z.L. Wang, J. Diao, J.F. Wang, Y. Jin, X.D. Peng, Chin. J. Chem. Eng. 9 (2001) 412–416.

[25] Z.L. Wang, J.F. Wang, J. Diao, Y. Jin, Chem. Eng. Technol. 24 (2001) 507–511.

[26] O. Yotaro, A new DME production technology and operation results, in: 4th Doha Conference on Natural Gas, Doha, Qatar, 2001.

[27] P.L. Spath, D.C. Dayton, Preliminary Screening-Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas, NREL/TP-510-34929, 2003.

[28] S. Jones, Hydrogen Distribution and Transmission, UK Hydrogen Energy Network-Hydrogen Storage Workshop, 2005.

[29] M. Alam, O. Fujita, K. Ito, Proc. Inst. Mech. Eng. Part A: J. Power Energy 218 (2004) 89–96.

[30] M. Alam, O. Fujita, K. Ito, Proc. Inst. Mech. Eng. Part A: J. Power Energy 218 (2004) 89–95.

[31] E.M. Chapman, S.V. Bhide, A.L. Boehman, L.I. Boehman, F. Waller, Engine performance and emissions from fuel blends of dimethyl ether (DME) and diesel fuel, in: AICHE Spring National Meeting, New Orleans, LA, 2002.

[32] T. Fleisch, IDA-The International DME Association prospects for DME as a multi-purpose fuel IBC Gas to Liquids Conference, Milan, Italy, 2002.

[33] T. Fleisch, IDA-The International DME Association: Promoting New Marketes for Methanol World Methanol Conference, Rome, Italy, 2002.

[34] T. Fleisch, R. Sills, Beyond GTL-FT: large-scale gas conversion through oxygenates, in: 7th Natural Gas Conversion Symposium, Dalian, China, 2004.

[35] D.W. Gill, H. Ofner, DME as An Automotive Fuel 9th IEA Workshop, Paris, May, 2001.

[36] J.B. Hansen, S. Mikkelsen, DME as a Transportation Fuel, 2001.

[37] International Energy Agency, DME Newsletter 3: “Dimethyl Ether as Automotive Fuel”, 1999.

[38] International Energy Agency, DME Newsletter 4: “Dimethyl Ether as Automotive Fuel”, 2000.

[39] J. McCandless, DME as an Automotive Fuel: Technical, Economic and Social Perspectives Energy Frontiers Conference, 2001.

[40] S.C. Sorenson, J. Eng. Gas Turbines Power-Trans. ASME 123 (2001) 652–658.

[41] E.W. Kaiser, T.J. Wailington, M.D. Hurley, J. Platz, H.J. Curran, W.J. PITZ, C.K. Westerbrook, J. Phys. Chem. A 104 (2000) 8194–8206.

[42] J. Song, Z. Huang, X.Q. Qiao, W.L. Wang, Energy Convers. Manage. 45 (2004) 2223–2232.

[43] H.W. Wang, L.B. Zhou, Proc. Inst. Mech. Eng. Part D: J. Automobile Eng. 217 (2003) 819–824.

[44] T.C. Zannis, D.T. Hountalas, Energy Fuels 18 (2004) 659–666.

[45] McCandless, Jim S, AFFORHD Project Update 6th IDA Meeting, Phoenix, AZ, 2003.

[46] H.W. Wang, L.B. Zhou, D.M. Jiang, Z.H. Huang, Proc. Inst. Mech. Eng. Part D: J. Automobile Eng. 214 (2000) 101–106.

[47] L-B-Systemtechnik GmbH, GM Well-to-Wheel Analysis of Energy Use and Greenhouse Gas Emissions of Advanced Fuel/Vehicle Systems—A European Study, 2002.

[48] T.A. Semelsberger, R.L. S Borup, Hydrogen Production from the Steam Reforming of Dimethyl Ether and Methanol 205th Electrochemical Society Meeting, San Antonio, TX, 2004.

[49] T.A. Semelsberger, R.L. Borup, J.I. Tafoya, Steam Reforming of Low-Temperature Fuels: Methanol and Dimethyl Ether, Fuel Cell Seminar, San Antonio, TX, 2004.

[50] T.A. Semelsberger, R.L. Borup, Int. J. Hydrogen Energy 30 (2005) 425–435.

[51] N.-O. Nylund, A. Lawson, Exhaust emissions from natural gas vehicles, IANGV Emission Report, 2000.

[52] G.R. Jones, H. Holm-Larson, D. Romani, R.A. Sills, DME for Power Generation Fuel: Supplying India’s Southern Region PetroTech Conference, New Delhi, India, 2001.

[53] General Electric, Feasibilty of Methanol as Gas Turbine Fuel, 2001.

[54] A. Basu, J.M. Wainwright, DME as Power Generation fuel: Performance in Gas Turbines, PetroTech Conference, New Delhi, India, 2001.

[55] R.L. Borup, M.A. Inbody, T.A. Semelsberger, J.I. Tafoya, D.R. Guidry, Fuel composition effects on transportation fuel cell reforming, Catal. Today 99 (2005) 263–270.

[56] S.F. Abdo, K.V. vanden Bussche, D. Sioui, Abstracts of Papers of the American Chemical Society, vol. 224, 2002, p. U565.

[57] S. Ahmed, M. Krumpelt, Int. J. Hydrogen Energy 26 (2001) 291–301.

[58] R. Borup, W.L. Perry, M. Inbody, J.I. Tafoya, Abstracts of Papers of the American Chemical Society, vol. 224, 2002, pp. U564–U565.

[59] S.G. Chalk, J.F. Miller, F.W. Wagner, J. Power Sources 86 (2000) 40–51.

[60] S.H. Chan, H.M. Wang, Int. J. Hydrogen Energy 25 (2000) 441–449.

[61] S.H. Chan, H.M. Wang, Fuel Process. Technol. 64 (2000) 221–239.

[62] R.M. Charnah, Fuel cell drives for road vehicles, J. Power Sources 86 (2000) 130–133.

[63] A. Docter, A. Lamm, J. of Power Sources 84 (1999) 194–200.

[64] N. Edwards, S.R. Ellis, J.C. Frost, S.E. Golunski, A.N.J. van Keulen, N.G. Lindewald, J.G. Reinkingh, J. Power Sources 71 (1998) 123–128.

[65] R. Kumar, S. Ahmed, M. YU, Abstracts of Papers of the American Chemical Society, vol. 206, 1993, 94-FUEL.

[66] J. Llorca, N. Homs, J. Sales, P. Ramirez de la Piscina, Efficient production of hydrogen over supported cobalt catalysts from ethanol steam reforming, J. Catal. 209 (2002) 306–317.

[67] P.G. PATIL, J. Power Sources 37 (1992) 171–179.

[68] L.J. Pettersson, R. Westerholm, Int. J. Hydrogen Energy 26 (2001) 243–264.

[69] J.R. Rostrup-Nielsen, Phys. Chem. Chem. Phys. 3 (2001) 283–288.

[70] J.R. Rostrup-Nielsen, J. Sehested, Catalyst Deactivation 2001, Proceedings, vol. 139, 2001, pp. 1–12.

[71] C.S. Song, Abstracts of Papers of the American Chemical Society, vol. 221, 2001, p. U493.

[72] C.E. Thomas, B.D. James, F.D. Lomax, I.F. Kuhn, Int. J. Hydrogen Energy 25 (2000) 551–567.

[73] D.L. Trimm, Catal. Today 49 (1999) 3–10.

[74] X. Wang, R.J. Gorte, Appl. Catal. A: Gen. 224 (2002) 209–218.

[75] S. Cavallaro, Energy Fuels 14 (2000) 1195–1199.

[76] J. Comas, F. Marino, M. Laborde, N. Amadeo, Chem. Eng. J. 98 (2004) 61–68.

[77] F. Frusteri, S. Freni, V. Chiodo, L. Spadaro, G. Bonura, S. Cavallaro, J. Power Sources 132 (2004) 139–144.

[78] A. Kaddouri, C. Mazzocchia, Catal. Commun. 5 (2004) 339–345.

[79] J. Llorca, P.R. de la Piscina, J.A. Dalmon, J. Sales, N. Homs, Appl. Catal. B: Environ. 43 (2003) 355–369.

[80] J. Sun, X.P. Qiu, F. Wu, W.T. Zhu, W.D. Wang, S.J. Hao, Int. J. Hydrogen Energy 29 (2004) 1075–1081.

[81] J. Agrell, M. Boutonnet, J.L.G. Fierro, Appl. Catal. A: Gen. 253 (2003) 213–223.

[82] J.P. Breen, J.R.H. Ross, Catal. Today 51 (1999) 521–533.

[83] Y. Choi, H.G. Stenger, Appl. Catal. B: Environ. 38 (2002) 259–269.

[84] J.K. Lee, J.B. Ko, D.H. Kim, Appl. Catal. A: Gen. 278 (2004) 25–35.

[85] B. Lindstrom, L.J. Pettersson, Int. J. Hydrogen Energy 26 (2001) 923–933.

[86] B. Lindstrom, L.J. Pettersson, P.G. Menon, Appl. Catal. A: Gen. 234 (2002) 111–125.
[87] T. Numaguchi, Oil Gas-Eur. Mag. 27 (2001) 35–38.
[88] S. Ohyama, Appl. Catal. A: Gen. 180 (1999) 217–225.
[89] B.A. Peppley, J.C. Amphlett, L.M. Kearns, R.F. Mann, Appl. Catal. A: Gen. 179 (1999) 21–29.
[90] B.A. Peppley, J.C. Amphlett, L.M. Kearns, R.F. Mann, Appl. Catal. A: Gen. 179 (1999) 31–49.
[91] R.L. Borup, M.A. Inbody, B.L. Morton, L.F. Brown, Abstracts of Papers of the American Chemical Society, vol. 222, 2001, p. U479.
[92] T.A. Semelsberger, R.L. Borup, Thermodynamics of Hydrogen Production from Dimethyl Ether Steam Reforming and Hydrolysis, LA-14166, 2004.
[93] T.A. Semelsberger, R.L. Borup, Thermodynamic equilbrium calculations of dimethyl ester steam reforming and dimethyl ether hydrolysis, J. Power Sources, Corrected Proof, in press, 2005.
[94] V.V. Galvita, G.L. Semin, V.D. Belyaev, T.M. Yurieva, V.A. Sobyanin, Appl. Catal. A: Gen. 216 (2001) 85–90.
[95] K. Takeishi, H. Suzuki, Appl. Catal. A: Gen. 260 (2004) 111–117.
[96] Y. Tanaka, R. Kikuchi, T. Takeguchi, K. Eguchi, Appl. Catal. B: Environ., Corrected Proof, in press.
[97] K. Yomada, K. Asazawa, H. Tanaka, Dimethyl ether reforming catalyst. Patent No. 6,605,559 (2003).
[98] A. Bhattacharyya, A. Basu, Process for hydroshifting dimethyl ether. Patent No. 5,498,370 (1996).
[99] T.A. Semelsberger, L.F. Brown, R.L. Borup, M.A. Inbody, Int. J. Hydrogen Energy 29 (2004) 1047–1064.