

DIMETHYL ETHER – A NEW SYNTHETIC FUEL COMMODITY AND CHEMICAL BUILDING BLOCK

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Abstract

Dimethyl ether (DME) is recognized as a potential next-generation, environmentally benign commodity for energy storage and distribution, as well as a momentous chemical building block. DME can be produced at a competitive price from synthesis gas conveniently generated from a variety of carbon-containing feedstocks, such as coal, natural gas and other fossil methane resources, biomass, methane from anaerobic processes, etc. Expected in the near future, significant progress in DME mass production, as well as development of distribution and consumption technologies, can greatly alleviate the problems concerned with energy safety and lead to significant environmental and industrial benefits.

Keywords: Dimethyl ether, DME, Energy carrier, Energy commodity, Diesel fuel

INTRODUCTION

The world is at the threshold of a new energy economy which will require not only the use of new energy resources but also new energy carriers which will be environmentally benign, energy efficient, “multi-purpose,” and produced at low prices. One intended alternative to fossil fuels is hydrogen; however, its physical properties are mismatched with the requirements of the energy market. Hydrogen production, packaging, storage, transfer, and delivery are very costly and would consume excessive amounts of energy. Furthermore, the future use of hydrogen by consumers has to be limited due to unavoidable, extremely hazardous leaks. Instead of using hydrogen directly, another option which can be realized in the framework of hydrogen economy is the efficient mass production of DME and/or methanol, preferably, via the reaction of hydrogen with carbon dioxide. The hydrogen might be provided by nuclear energy and by varied alternative energy sources (sun, wind, etc.) [1,2]. This approach could bring about a significant decrease in CO₂ emissions.

An exceptionally attractive alternative to hydrogen and methanol is dimethyl ether (DME), the simplest ether, which appeared recently as a winning candidate for the next generation “multi-source multi-purpose” energy-transfer commodity [3] and chemical building block [4]. It can be produced either from fossil fuels or non-fossil-fuel sources [5], and the world demand for this product will increase rapidly within the next few years. The economy of the future DME commodity is valued due to:

- The simplicity and low cost of production processes;
- High energy efficiency;
- Superior performance in various fuel applications;
- Lower transportation and distribution costs than those of LNG; and
- Versatile applications as a chemical building block.

So far, DME is used in limited amounts as a coolant and as an environmentally benign aerosol propellant. However, in the near future, DME will be applied as an excellent substitute for diesel fuel and as a potential fuel for power generation and domestic use, as well as a feed in a variety of chemical syntheses [5]. It is clear that DME can provide a bridge between fossil fuel, and bio-fuel and other renewable fuel economies. Its mass production could eventually lead to the replacement of crude oil and natural gas in the above applications, even though the wide utilization of DME requires further development of the distribution infrastructure and utilization technologies.

At ambient conditions, dimethyl ether is a colorless, flammable, and chemically stable gas with a boiling point of -25.1°C (760 mm Hg). DME is easily liquefied, and its physical properties are so similar to those of LPG (liquefied petroleum gas) that DME can be distributed, stored, etc., as liquid using existing LPG-handling technology.

DME itself breaks down quickly under ambient conditions and is not likely to concentrate in the ecosystem at harmful levels [6]. It is relatively nontoxic and noncarcinogenic. Unlike diethyl ether, DME does not form explosive peroxides upon prolonged exposure to air. Its combustion has very little environmental load because it does not generate sulfur oxides and particulate matter, and nitrogen oxides (NO_x) can be kept at low levels [3]. DME does not cause corrosion of any metals.

DIMETHYL ETHER PRODUCTION

Commercially, DME is manufactured by the dehydration of methanol over solid acid catalysts [7]. Newly developed technologies achieve synthesis of dimethyl ether directly from synthesis gas generated from a variety of carbon-containing feedstocks (Fig. 1), including coal, natural gas, and other methane sources, biomass, municipal solid wastes, and environmentally distressed materials such as petroleum-derived coke/residues, *etc.* [4].

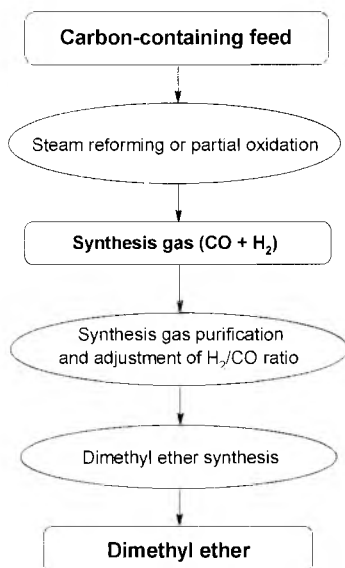
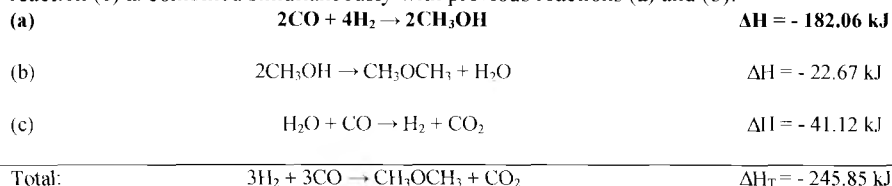


Figure 1. Dimethyl ether production scheme flowchart

Process

The direct DME synthesis involves three reversible and highly exothermic reactions in a one-stage operation achieved by the use of a hybrid catalyst consisting of a methanol synthesis catalyst and a dehydration catalyst [4,7]. These reactions include (a) conversion of synthesis gas to MeOH, followed by (b) dehydration of the latter to yield dimethyl ether (DME). Further

improvement of the economic aspects of the process is accomplished if the water-gas shift (WGS) reaction (c) is combined simultaneously with previous reactions (a) and (b):



Reactions (b) and (c) essentially eliminate unfavorable thermodynamic limitations for methanol synthesis (a). Methanol from the first reaction (a) is consumed in the second reaction (b), forming DME and water. The water, by the WGS reaction, generates CO_2 and H_2 , and the latter enters the methanol synthesis. Thus, one of the products of each step is a reactant for another step in the sequence. This creates a strong driving force for the overall process, allowing very high conversion (> 95%) of synthesis gas in a single-pass operation [8]. Due to its strong exothermic effect, the effective direct DME synthesis requires a relatively low reaction temperature (i.e., 250 to 280°C) and high pressure (i.e., 3 to 7 MPa). Usually applied process conditions include reaction temperature as high as 260°C and reaction pressure as high as 5 MPa [9,10].

Recent research efforts on DME production are concerned with development of highly effective catalysts, as well as efficient reactors which assure excellent mass and heat transfer characteristics.

Catalysts

Up to now, the hybrid catalysts are the most common catalysts employed in DME synthesis processes; however, it is expected that further progress in the DME synthesis process can be achieved by development of highly “synergistic” bifunctional catalysts which combine both methanol synthesis and methanol dehydration functionalities.

1. **Hybrid catalysts.** A hybrid catalyst system for DME synthesis constitutes a mechanical mixture of (a) methanol synthesis catalyst component, and (b) methanol dehydration catalyst component.
 - (a) Methanol synthesis catalysts include Cu/ZnO/Al₂O₃, ZnO/Cr₂O₃, sulfided Ca/Pd/SiO₂, etc. [10,11]. Amongst them, the most commonly used catalyst is Cu/ZnO/Al₂O₃, a conventional catalyst employed in methanol synthesis processes. To avoid severe deactivation, this catalyst has to be operated at reactor temperature lower than 280°C. Sulfur-tolerant catalysts, e.g., Ca/Pd/SiO₂, Ca/Pd/SiO₂, and ZnO/Cr₂O₃, are especially applicable in DME production processes utilizing small-scale methane-containing gas sources (e.g., coal seam gas, bio-gas, etc.) and biomass. Their use can simplify or eliminate the synthesis gas desulfurization unit in the DME production facilities [5,12].
 - (b) Methanol dehydration catalysts embrace H-ZSM-5 and H-Y zeolites, γ -Al₂O₃, SiO₂-Al₂O₃, and AlPO₄ [8,13,]. The strength of acid sites present on the surface of these catalysts strongly affects not only their methanol dehydration activity and selectivity, but also the overall synthesis process. H-ZSM-5 zeolite is the most extensively used methanol dehydration catalyst due to its high activity at the optimum DME synthesis temperature. To prevent a secondary conversion of DME to hydrocarbons on its strong acid sites, H-ZSM-5 zeolite has to be subjected to modification by ion exchange with Mg and ammonia, or by rising Si/Al ratio (dealumination), which results in elimination of strong acid sites and an increase in relatively weak acid sites [8,14].
2. **Bifunctional catalysts.** A bifunctional catalyst combines all catalytic functionalities of the two hybrid catalyst components which are applicable in the DME synthesis reactions. In comparison with the hybrid catalyst, the bifunctional catalyst should exhibit a much stronger “synergistic effect,” which is expected to provide higher overall conversion and

selectivity in the production of DME. The reported promising DME synthesis bifunctional catalysts include $\text{Cu-MnO}_x\text{-MO}_x/\gamma\text{-Al}_2\text{O}_3$ ($M = \text{Zn, Cr, W, Mo, Fe, Co or Ni}$), $\text{Cu-MnO}_x\text{-ZnO/Y}$, $\text{Cu-ZnO-Al}_2\text{O}_3/\text{H-ZSM-5}$, and $\text{Cu-ZnO-Al}_2\text{O}_3/\text{H-SY}$ [15-17].

Reactors

Since the DME synthesis reactions are highly exothermic, an effective heat removal from the reactor and reaction temperature control in the reactor is necessary. To achieve these requirements, catalytic reactors which assure excellent mass and heat transfer characteristics, such as slurry and fluidized bed reactors, are employed in this process [18,19]. In the slurry reactors, fine catalytic particles (1 to 10 μm in size) are suspended in an inert liquid (e.g., paraffin oil) agitated by bubbling synthesis gas up through the liquid. The reaction heat is quickly absorbed by the inert liquid, which acts as a high-capacity heat sink and an effective heat conductor. A uniform reactor temperature is easily controlled, even at high synthesis gas conversions, by an internal cooling system which removes excessive heat from the slurry. A fixed bed multi-stage reactor has also been employed in the process developed by Haldor Topsøe Company [20].

DIMETHYL ETHER ENERGY APPLICATIONS

Dimethyl ether is widely used as a coolant and aerosol propellant for spray paints, agricultural chemicals and cosmetics. A wide array of newly recognized potential applications of DME as an energy source is depicted in Fig. 2. They are divided into three categories: (1) direct combustion (diesel fuel, domestic use, and industrial power applications), (2) reformed gas generation from DME (hydrogen for fuel cell and substitute synthesis gas for power generation), and (3) direct conversion into other fuels (gasoline, olefins, dimethoxymethane, *etc.*) [4,18].

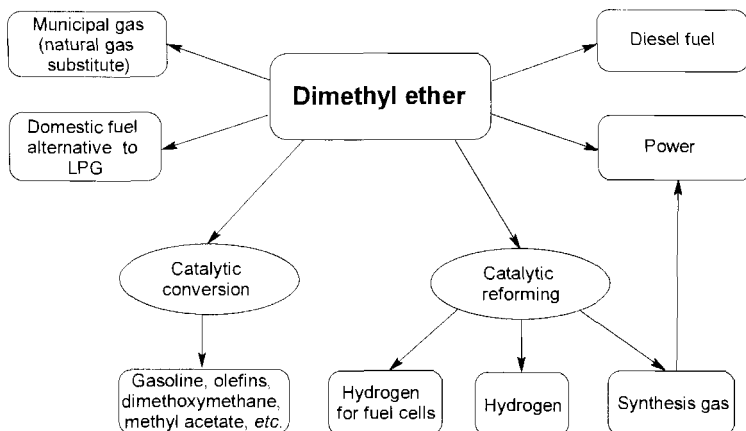


Figure 2. Dimethyl ether applications

Direct combustion applications

DME is easy to handle, giving it broad commercial applications such as a municipal gas, as an alternative to liquefied petroleum gas (LPG), as a transportation fuel alternative to diesel fuel, as a fuel for fuel cells, and as a source of hydrogen energy. Its vapor pressure at 25°C is 0.61 MPa; therefore, it is easily liquefied under light pressure and can be stored and handled in standard LPG facilities. The physical properties of DME are compared with those of similar fuels in Table 1.

Table 1. Comparison of the physical properties of DME with those of other fuels

Property	DME	Propane	Methanol	LNG	Hydrogen
Formula	CH ₃ OCH ₃	C ₃ H ₈	CH ₃ OH	CH ₄	H ₂
Boiling point, °C	-25.1	-42	64.8	-161.5	252.8
Liquid density (@ 20°C, g/cm ³)	0.668	0.49	0.79	-	-
Gas specific gravity (Air 760 Hg = 1)	1.59	1.52	-	0.55	0.07
Saturated steam pressure (@ 20°C, MPa)	0.54	0.93	-	-	-
Auto-ignition temperature (@ 1 atm, °C)	235 - 350	504	470	632	565
Explosion limit, %	3.4 - 17	2.1 - 9.4	5.5 - 36	5 - 15	4 - 74
Cetane number	55 - 60	5	5	0	-
Lower heating value, MJ/kg	28.84	46.47	21.10	50.24	121.1

Diesel fuel

DME has emerged as a prominent alternative diesel fuel with the highest energy efficiency and among the lowest in emissions of carbon dioxide and particulate matter. It fulfills most of the Euro-4 exhaust emission standards coming into effect in 2005 for Europe, and new (Tier 3) emission standards for the USA, and can be used in all compression-ignition engines independent of their size. The unique low autoignition temperature, which assures smooth combustion, resulting in low noise levels, combined with a short delay period between injection and combustion, provides for excellent diesel engine performance. The DME energy density is lower than that of a conventional diesel fuel but their thermal efficiencies are similar [4]. The use of DME does not require modification to the diesel engine itself, however, due to its low boiling point and low viscosity and lubricity, the fuel supply system has to be equipped with an injection pump operating under high-pressure fuel conditions, and the addition of a lubricity-improving agent will be necessary [18]. DME is highly suitable for applications in diesel engines due to the following characteristics [21]:

- Essentially no emissions of particulate matter;
- Low emission of NO_x, CO, and hydrocarbons;
- High cetane number. >55;
- No cold start problems;
- Low engine noise; and
- The same peak output torque/power as for engines on conventional diesel fuel.

Due to the absence of carbon-carbon bonds in the DME chemical structure and of sulfur, particulate matter emissions are near zero. DME also reduces NO_x emissions by 40 - 90%, and with the absence of solid particulates, the emissions of NO_x can be almost completely eliminated by tailpipe emission-control technologies. Methane and nonregulated toxic exhaust emissions, such as acetaldehyde, acrolein, propionaldehyde, and acetone, are very low, whereas emission of formaldehyde is relatively low [22]. The emission of these compounds can be drastically reduced by optimization of the DME injection/combustion systems and by the application of a suitable exhaust gas oxidation catalyst [18].

Modern diesel engines are characterized by superior fuel economy, emission performance, specific power and torque, and excellent drivability. Further progress in these areas can be achieved by replacement of conventional diesel fuels with DME. Several prominent car and engine companies, such as Mitsubishi, Isuzu, and Volvo already worked out their firm strategy on development of "eco-friendly" DME-fueled vehicles. In the near future, large-scale production of DME can facilitate shifting to projected super-efficient hybrid diesel/electric cars which will use 35% of the gasoline equivalent per mile of today's gasoline engine cars [23,24].

Power generation

DME can be a convenient clean fuel in gas turbine power plants, especially in remote areas or if market demand is relatively small. Low ignition temperature and fast combustion velocity makes DME an excellent gas turbine fuel, which can be used directly for power generation without

major modifications to the turbines or the combustors [25,26]. Furthermore, DME power generation effects much lower emissions of NO_x , CO, and hydrocarbons as compared to operation with natural gas.

Domestic fuel

In a few years DME will be used as a first-rate replacement of LPG in its domestic applications. Far East Rim countries, especially Japan and China, which are major consumers of LPG, recognize that future supplies of LPG may not be adequate to meet their huge domestic needs and pursue this DME application vigorously [18,27]. The calorific value of liquid DME is considerably lower than that of LPG; however, its density is larger. This makes the liquid DME calorific value expressed per unit volume about 90% of that of LPG. DME flame is visible blue, like that of natural gas. Toxicity of DME combustion products is very low, and they do not contain any aldehydes [4].

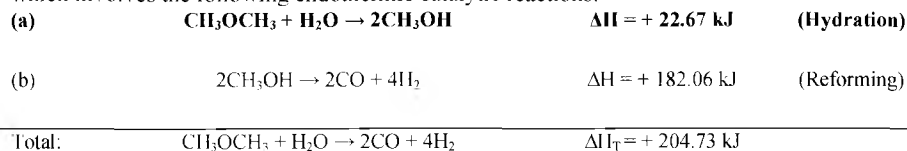
Municipal gas

DME can be distributed as gas in the existing natural gas municipal grids and used for various domestic applications. Its thermal efficiency is almost identical to that of natural gas. DME can replace natural gas for burning in typical natural gas applications with merely a minor burner jet alteration [18].

APPLICATIONS OF REFORMED GAS FROM DME

Indirect power generation

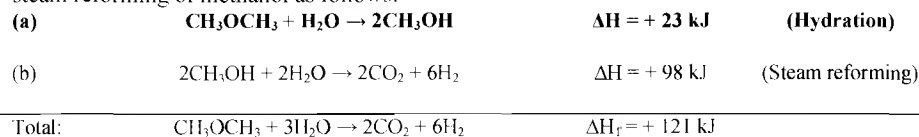
DME can be used in gas turbines indirectly in the chemical recuperation mode. In this approach, waste heat from the gas turbine effluent is utilized prior to firing in the DME reforming process, which involves the following endothermic catalytic reactions:



The process can be carried out at temperatures lower than 300°C and can boost the DME power efficiency by several percent [28,29].

Production of hydrogen

Hydrogen, an alternative energy carrier, is currently produced commercially in high-temperature, highly endothermic natural gas steam reforming processes. The heat required for these processes comes from burning fossil fuels and results in significant CO_2 emissions. Recently production of hydrogen from DME appeared as an alternative to these processes. The catalytic generation of hydrogen from DME occurs at relatively low temperature (200 to 400°C) and pressure through two successive endothermic reactions, i.e., (a) hydration of DME to methanol followed by (b) steam reforming of methanol as follows:



The above reactions are catalyzed either by a hybrid catalyst composed of a solid acid catalyst (hydration) and a steam reforming catalyst, or a bifunctional catalyst [30-32]. The heat required for the catalytic steam reforming of DME can be provided from combustion of fossil fuels or

preferably, from nuclear reactor technology [33]. In the fast breeder nuclear reactor with turbine set upstream of the hydrogen generation unit, the overall energy utilization efficiency is 75%.

Fuel cells

Fuel cells are broadly recognized as clean and highly energy efficient power generating electrochemical devices for both stationary and mobile applications. Hydrogen for fuel cells can be derived from high-temperature (600 - 800°C) reforming processes of natural gas, gasoline, hydrocarbon diesel fuel and from low-temperature (150 - 300°C) reforming of methanol. The generation of hydrogen via reforming of methanol, however, is limited due to high cost of its production and toxicity. DME appeared recently as an attractive fuel, feasible for application in different types of direct oxidation fuel cells, such as polymer electrolyte, solid oxide and molten carbonate fuel cells [34-36]. Hydrogen for DME fuel cells is generated in the steam reforming process (See subsection *Production of hydrogen*, above). If process conditions include high temperature, low pressure and high H₂O/DME feed molar ratio, it is feasible to convert almost 100% of DME into a hydrogen-rich product composed of H₂, CO, and CO₂. The CO concentration in the reformed product, which is about 3%, can be reduced by selective CO oxidation to less than 10 ppm. DME in the fuel cell applications is more feasible than hydrogen and methanol due to its following properties [34-38]:

- Low DME steam reforming reaction heat, and favorable overall heat balance, which enable the reforming system to be downsized;
- High electron transfer number of 12 for complete oxidation;
- Complete direct electro-oxidation due to the absence of C - C bonds;
- Low crossover rate;
- Low temperature for start-up;
- Potential storage at high pressure as a liquid and delivery as a gas at low pressure, which allows pumpless portable devices;
- Low toxicity;
- Low explosion limit; and
- Low production cost.

DME fuel cells are expected to be applied particularly for domestic use and in vehicles because of the ease of electrolyte handling, rapid response, and low toxicity. In polymer electrolyte fuel cells, DME provides a high power density and combines the main advantages of hydrogen (low toxicity and pumpless fuel delivery) and methanol (high-energy-density storage).

DME CHEMICAL BUILDING BLOCK APPLICATIONS

DME is a promising intermediate in the synthesis of a wide array of fuels from fossil, biomass, and other carbon-containing feedstocks. In addition, it can be used as a building block for making a variety of high-value hydrocarbons, petrochemicals, oxygenates, etc.

DME-to-gasoline process

The DME-to-gasoline (DTG) process, involving the use of the shape-selective H-ZSM-5 catalyst at about 400°C, is a modification of the Mobil methanol-to-gasoline (MTG) process [39]. Since the first stage of the MTG process is the dehydration of methanol to DME, DME itself has been identified as a more attractive feed than methanol for gasoline production [40]. The high-octane gasoline obtained in this process constitutes a mixture of aromatics, paraffins, and olefins. Their distribution in the DTO product is determined by the process temperature, pressure, space velocity, catalyst SiO₂/Al₂O₃ ratio, and reactor type [41].

DME-to-olefins process

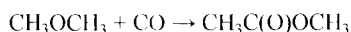
A variation of the DTG process is the DME-to-olefins process. The catalyst used in this process is also H-ZSM-5 and a newly developed H-SAPO-34 [42]. High selectivity to low-molecular weight olefins is obtained by introduction of some changes in the process conditions, *i.e.*, application of a lower acidity zeolite catalyst, a lower DME partial pressure, a higher space velocity, and a higher process temperature (500°C) [41, 43].

Dimethoxymethane synthesis

Dimethoxymethane (DMM) is a diether which can be produced by direct catalytic oxidation of DME. Currently DMM is used as a solvent, as a fuel additive for smoke reduction, and as a building block in the syntheses of polyoxymethylene dimethyl ethers (diesel fuel additives), concentrated formaldehyde, *etc.* [44]. Recently, DMM has been considered as an alternative diesel fuel.

Methyl acetate synthesis

Methyl acetate can be obtained from DME by CO insertion at a temperature of 225°C and atmospheric pressure according to the following reaction [45]:



The bifunctional catalyst for this reaction contains both acidic and carbonylation functionalities. In turn, methyl acetate can be used as feed in:

- Its hydrogenolysis to ethanol;
- Its carbonylation to acetic anhydride, which further can be converted to acetic acid;
- Its conversion to ethylidene diacetate (precursor to vinyl acetate and polyvinyl acetate), *etc.*

DME co-feeding

Co-feeding studies have shown that dimethyl ether can considerably influence conversions of synthesis gas to hydrocarbons [46] and higher alcohols [47], both in terms of yields and selectivity. DME is thought to be capable of building up surface complexes, which facilitate first C - C bond formation, are very similar to those naturally occurring during FT synthesis. Diethyl ether undergoes rapid reaction, probably deoxygenation to ethene, which in turn initiates hydrocarbon synthesis.

The examples of DME applications presented above show only a small fraction of its potential use as a chemical building block in other processes leading to the production of a variety of valuable chemicals.

DME PRODUCTION COMMERCIALIZATION

Far East Rim countries including Japan, North Korea, China, and India, as well as Australia, Iran and Sweden, show especially great interest in development of the DME economy. They have succeeded in developing core technologies which realize low-cost, mass production of DME, and are endeavoring to commercialize DME for its mass use (~ 400 million metric tons per year) in the early part of the 21st century [48]. There are already several DME production plants under construction. They are exemplified by:

- **Papua New Guinea.** Oil Search Company plant to produce and supply DME as a diesel fuel substitute to Japan (capacity: 14.8 million barrels of oil equivalent from natural gas per year). Technology and capital are provided by Mitsubishi Gas Chemical and Itochu Corp.

- **Iran.** Zagros Petrochemical Company plant (capacity: 800,000 million tons of DME from natural gas per year). Technology is provided by Petrochemical Research & Technology Company of Iran, and Haldor Topsøe.
- **China.** Several plants to utilize low-rank coals.

Initial development efforts indicate that this DME energy carrier can be produced at a competitive price. In particular, the production cost *per* unit of heating value is reduced by 20% compared to methanol synthesis. Expected plant investment is very low, and, therefore, the largest impact to the production cost will be that of the feed materials.

There representative examples of promising DME production technologies are as follows:

- **DME from natural gas.** In the very successful direct DME synthesis process proposed by NKK Corporation (Japan), the natural gas is: (a) desulfurized; (b) converted in the auto-thermal reformer to synthesis gas which, with the help of recycled by-product CO₂, is adjusted to a ratio of H₂/CO=1; and (c) conversion of synthesis gas in the slurry reactor to DME and water [49]. The DME product purity obtained in this process exceeds 99.5%.
- **DME from coal.** Production of DME in the framework of an integrated gasification combined cycle (IGCC) technology can be one of the key components in the mitigation of climate change. The IGCC technology includes gasification of coal, purification and adjustment of the H₂/CO ratio of the obtained synthesis gas, co-capture of CO₂ and H₂S for long-term underground storage, and use of the synthesis gas to produce DME and power generation [50].
- **DME from small dispersed feedstocks.** The University of Utah has recently initiated the development of processes for the direct catalytic production of DME from synthesis gas derived from various dispersed carbon-containing feed-stocks (methane from coal beds, oil wells, and anaerobic processes, as well as bio-oil, black liquor, wood, straw, etc.). It is expected that this process can be performed in a small portable facility which will reduce high transportation costs of the feed-stocks. In the framework of this DME production program, the following factors are considered: use of nitrogen containing synthesis gas (5-50% of N₂) without any previous H₂/CO ratio adjustment, and high single-pass operation conversion (>90% conversion of CO) to eliminate recycle loops. Development of a highly effective direct DME synthesis catalyst and development of a low-volume, and low-cost, highly efficient catalytic slurry gas-sparged reactor, newly patented by the University of Utah will facilitate to meet these objectives.

In the near-future energy market, DME is expected to appear as a strong competitor, in the following sequence: (1) as an LPG supplement and replacement; (2) as fuel for power generation; and finally (3) as super clean diesel fuel [48].

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