

Environmental Fossil Fuels Sciences & Technology Group

In cooperation with Envirotech Consulting Inc. (ECI)

D) DME's Potential for the Hydrogen Economy

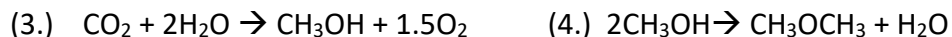
In the 1950s the United States government embarked on a project to evaluate hydrogen's potential for replacing the combustion of fossil fuels. The project was carried out at the US Bureau of Mines. In the 1960s it was concluded that catalytic dehydrogenation of coal at near ambient temperatures enabled generation of large volumes of hydrogen at an acceptable cost. The second phase of the project was aimed at identifying the optimal solutions for hydrogen utilization and handling including storage and transportation - pipelining and shipping in particular. No satisfactory solutions for hydrogen handling were identified.

In October 2004, US Los Alamos National Laboratory issued a report [1] on steam reforming and hydrolysis of DME (Dimethyl Ether; $\text{CH}_3\text{-O-CH}_3$). DME offers a relatively simple solution for hydrogen generation, storage and transportation. Reforming DME with steam (equation 1), as opposed to natural gas reforming (equation 2), can be carried out under mild conditions and results in releasing relatively large volumes of hydrogen, as shown below:



A preliminary review of the scientific and technical information on the hydrogen economy does not indicate that, following the publication of LANL Report 14166 [1] other new and promising concepts have been developed on hydrogen generation, storage and transportation. The cost of DME production by direct synthesis [2] has been estimated by the Japanese technology developers at US\$60-90 per ton (2007 US\$).

DME has been identified and patented in Canada [3] as presently the most effective solvent for in-situ bitumen recovery. DME production cost is of key significance in potential utilization of this compound as a hydrogen donor. DME's impact on the environment and human health has been tested extensively by the US EPA [4]. The results indicate that the suitability of this solvent for storage, transportation and utilization leaves little to be concerned about. The production cost of DME could be significantly reduced by employing a $\text{CO}_2/\text{H}_2\text{O}$ (1:2 molecular ratio) blend for methanol synthesis (equation 3.) followed by dewatering to DME (equation 4.); (see synopsis B).



Reaction (3.) is based on catalytic photosynthesis and takes place at ambient temperature and atmospheric pressure in the presence of Cu_2O catalyst [5]. Additional experimental work is required to confirm that the reaction (equation 3.) can be scaled-up and its kinetics accelerated. Reaction (4.) is a low cost commercially applied methanol dehydration to DME.

The Report LA 14166 [1] reveals that optimal conditions for DME steam reforming highlighted in equation (1.) are: a steam-to-carbon ratio of 1.5, a pressure of 0.1 MPa, and a temperature of 200°C. The report concludes that “thermodynamically, the DME processed with steam can produce hydrogen-rich fuel cell feeds - with hydrogen concentrations exceeding 70%.” Utilization of hydrogen for energy generation offers realistic and practical solutions for resolving all problems associated with climate change. Low cost DME may significantly contribute to the emergence of a low-cost industry for hydrogen production and handling.

The Alberta bitumen industry has acknowledged that SAGD has to be replaced in order for the industry to rebuild itself [6]. So far the best option for the industry is to replace SAGD with the DME extraction. To optimize the DME extraction technology the cost of DME production shall be maximally reduced. By maximally reducing the DME production cost via scaling-up the catalytic photosynthesis of CO₂/H₂O blends (equation 3.), the Alberta bitumen industry shall be able, down the road, to play a key role in the transition from fossil fuels to a hydrogen economy. At this time the ammonia (NH₃) concept developed in Germany appears to be the only known option that could potentially compete with DME in terms of hydrogen generation and handling.

At ambient temperature DME can be readily liquefied by applying a low pressure of only about 0.45 MPa. Liquid DME can be readily pipelined and/or shipped either by LPG tankers, tankers equipped with pressurized containers or a vapors recirculating system. The DME handling infrastructure is identical to that developed for LPG storage and handling. DME delivered to overseas markets can be utilized for a variety of applications including the replacement of Diesel or cooking fuel, or as diluent to effectively reduce the price of LPG. It can be subjected to water reforming thus yielding a blend composed of a large volume of hydrogen diluted with some CO₂. There is no need to separate the CO₂ from hydrogen because the CO₂ accounts for 2vol% only of the product gas generated by steam reforming of the CH₃OCH₃.

Shipping the DME in tankers offers another opportunity. Such tankers can be equipped with a propulsion system powered by electricity generated by oxy-combustion of DME in a low-speed 2-stroke Diesel engine equipped with a re-burning boiler and cryogenic CO₂ condensation. The electric propulsion system is capable of eliminating any CO₂, SO_x and NO_x and reducing carbon micro-particulates emissions by 95%.

DME and natural gas net calorific values are 4,620 and 5,040 Kcal/L or 14,200 and 8600 Kcal/Nm³, respectively. As compared to DME, the natural gas destined for overseas export has to be cooled down to -162°C to be converted into LNG. The cooling requires a lot of energy. The LNG product has to be shipped by employing specialty LNG tankers. At the final destination the LNG has to be converted back into natural gas and unloaded from the tanker by employing rather complex procedures and over a relatively long time. Reforming natural gas requires pressures of 0.3-2.5 MPa, temperatures in the range of 700-1000°C and typically a Ni-based catalyst. Steam reforming of natural gas is endothermic and, again, requires a lot of energy.

DME is a perfect Diesel fuel (Cetane # 55-60); natural gas has a Cetane # of 0. In terms of explosion limits both DME and natural gas are comparable. According to some experts the export of DME from Canada to the Pacific Rim makes more economic and environmental sense as compared to generating and exporting the LNG, especially if the LNG is to be reformed instead of combusted.

By being involved in developing the technology for producing the lowest cost DME, the bitumen industry could not only produce bitumen at a rock-bottom cost but would also emerge as a major supplier of DME that can be readily stored, pipelined and shipped using existing technology, readily and inexpensively converted into hydrogen, if required, thus implementing the hydrogen economy era.

References:

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