Carbon Dioxide Reduction Metallurgy
Edited by: Neale R. Neelameggham, and Ramana G. Reddy
TMS (The Minerals, Metals & Materials Society), 2008

CHEMICAL UTILIZATION OF SEQUESTERED CARBON DIOXIDE AS A BOOSTER OF HYDROGEN ECONOMY

Michael S. Moats[1], Jan D. Miller[1], and Wlodzimierz W. Zmierczak[1]

[1]Department of Metallurgical Engineering, University of Utah
135 South 1460 East, Rm 412, Salt Lake City, UT 84112

Keywords: Dimethyl Ether, Liquid Fuels, Carbon Sequestration

Abstract

For many, hydrogen in a pure hydrogen economy would be like natural gas in today's energy economy. Unfortunately, hydrogen's physical properties are unsuited to the energy market's requirements in terms of packaging, storage, transfer, and delivery. In this paper, a hybrid energy economy that packages hydrogen chemically on carbon atoms from various sources including recycled carbon dioxide is introduced and discussed. For this new hybrid energy economy to become a sustainable reality, the ability to recycle carbon dioxide and use hydrogen to create an appropriate energy product, such as dimethyl ether (DME), is needed. DME is recognized as a potential next generation, "beyond-petroleum", environmentally benign commodity for energy storage and distribution. It is expected that to maximize the sustainability of the proposed hybrid energy economy, "green" hydrogen will be utilized. The "green" hydrogen would be created by the electrolysis of water powered by renewable energy sources, such as solar, wind or geothermal heat.

Introduction

With the growing concerns surrounding trends in global warming and increasing concentrations of "greenhouse" gases, such as CO_2 and CH_4, efforts to mitigate the emission of these gases from industrial sources are growing. With respect to CO_2, the demonstrations of various capture and sequestration methods are underway around the world.

The sequestration of CO_2 is mainly focused on storing the gas underground or deep in the ocean. The Intergovernmental Panel on Climate Change (IPCC) estimates that 2000 Gtonnes of CO_2 can be stored underground in depleted oilfields, un-minable coal beds and other geologic features [1]. Additionally CO_2 may be stored at the bottom of the ocean. The lure of storing carbon dioxide in depleted oilfields or un-mineable coal seams is that an economic benefit (enhanced oil or methane recovery) can offset the costs of gas capture, transportation and storage. Unfortunately, all of these storage methods have potential for the release of CO_2 or CH_4 back into atmosphere or creating environmental damage (mobilizing heavy metals, disrupting deep sea ecology).

Thus, it would be beneficial to the world's environment and society to better utilize the CO_2 captured from the burning of fossil fuels. In this paper, a novel process is proposed that combines captured CO_2 with H_2 produced from renewable or nuclear energy sources to create dimethyl ether (DME).

DME is recognized as a potential next generation, "beyond-petroleum", environmentally benign commodity for energy storage and distribution.[2] Significant DME production is being planned in Japan, Iran, Denmark and China as summarized in Table 1 [3]. It is valued due to its simplicity, high energy efficiency, superior performance in various fuel applications, direct applicability as a fuel cell fuel, and versatility as a chemical building block. Combustion of DME has very little environmental load. It does not generate sulfur oxides and particulate matter, and because nitrogen oxides (NO_x) can be kept at low levels, DME has emerged as a prominent clean diesel fuel. Its large-scale production can facilitate shifting to projected super efficient hybrid diesel/electric cars, which will likely utilize only 35% of the gasoline equivalent per mile of today's gasoline engine cars. DME exhibits physical and thermodynamic properties not unlike LPG that should assist in its assimilation in the fuels marketplace and the world demand for this product will increase rapidly within the next few years. DME itself disappears quickly from the ecosystem under ambient conditions because of its speedy consumption by microorganisms, and is not likely to concentrate in the ecosystem at harmful levels. It is relatively nontoxic and noncarcinogenic.

Table 1. Recent plans for DME production [3]

Developer	Commercialization Plan
DME International (led by JFE)	37,000 t/y (planning phase) 910,000 t/y (market research phase)
Japan DME (led by Mitsubishi Gas Chemical	1,830,000 t/y (planning phase), Australia
The Mitsui & Co. Group	2,500,000 t/y (planning phase), Iran, etc.
Topsoe (Denmark)	Benchmark tests underway
Lu Tian Chemical Group Co. LTD (China)	50,000 t/y (commercialized) 1,000,000 t/y (planning phase)

"Green" DME Production

Direct DME synthesis from CO_2 and H_2 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]. 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):

$$\text{(a)}\quad CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H = -56.33\ \text{kJ/mol}$$

$$\text{(b)}\quad 2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H = -21.25\ \text{kJ/mol}$$

$$\text{Total}\quad 2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O \qquad \Delta H = -133.91\ \text{kJ//mol}\ (-126.93\ \text{Btu/mol})$$

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. 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 relatively high conversion of synthesis gas in a single-pass operation [5]. Usually applied process conditions include reaction temperature as high as 230 to 260ºC and reaction pressure as high as 1-5 MPa [6,7].

Hydrogen generated in the framework of these technologies and recycled CO_2 (synthesis gas) would be used for the production of DME. Such a part of the energy economy seems to be especially suitable for development. A general vision of the proposed chemical CO_2 sequestration and production of DME is shown in Figure 1.

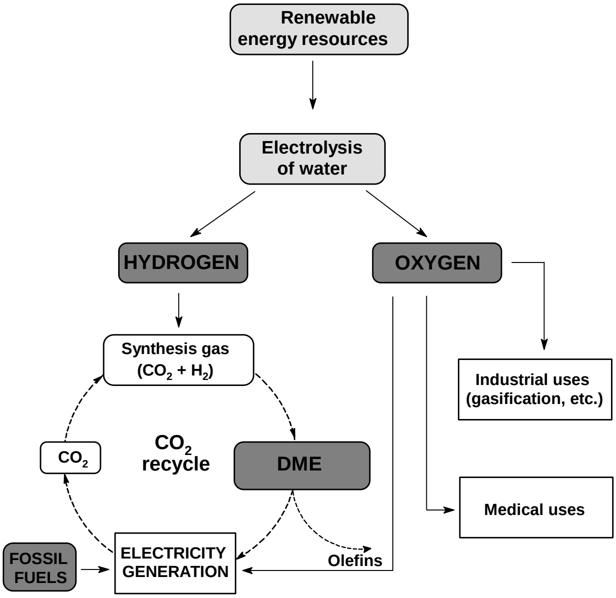

Figure 1. Proposed CO_2 sequestration technology.

This approach includes a recycle of CO_2 generated in combustion processes. DME can be produced from synthesis gas generated by reaction of hydrogen with carbon dioxide. Consequently, this type of economy could eliminate net CO_2 emissions, and would be recognized as benign with respect to the environment as a pure hydrogen economy, and would assure a clean and sustainable energy future. Furthermore CO_2 could be stored by the formation of plastics from olefins derived from DME.

Hydrogen Generation from Renewable Energy

To insure that the proposed DME production method had a net negative CO_2 footprint, hydrogen needs to be generated from a non-carbon based energy source. The ultimate renewable and clean source of hydrogen would be water electrolysis powered by solar or wind energy. Water electrolysis uses electricity to breakdown water into its elemental components, hydrogen and oxygen gases. There are no by-products to the reaction. By using solar or wind as the energy source, water electrolysis can generate hydrogen without environmental contamination.

Electrolysis is the process of water conversion to gaseous O_2 and H_2 by the action of electric current. Three types of electrochemical water splitting systems are used commercially:[8,9]

Aqueous alkaline electrolysis. In this traditional process, potassium hydroxide is added to the water to improve conductivity through the cell. The electrodes are separated by a membrane, which prevents oxygen and hydrogen from mixing.

Solid polymer electrolysis. The sheet-form electrolyte in this case is usually made of Nafion, a solid polymer possessing sulphonic groups attached to its polymeric backbone. The electrodes are deposited on each side of the electrolyte sheet. The H^+ ions formed at the anode, migrate through the polymeric electrolyte to the cathode and produce hydrogen. At the anode the OH^- ions generate oxygen. The solid polymer electrolyzers have relatively low internal resistance and can operate at higher temperatures than alkaline electrolysis units.

High temperature steam electrolysis. Steam electrolysis units operate at temperatures of 700 – 1000 ºC. Consequently a significant part of the energy to drive the reaction is in the form of heat energy rather than electric energy. At 1000 ºC, 46% of the energy could be in the form of heat. O^{2-} ions are transported through the ceramic electrolyte, which usually is yttria-stabilized zirconia. Currently, steam electrolysis is in the development stage.

It appears likely that the use of solid polymer electrolysis will be favored in the future due to their higher efficiency and ability to operate under adjustable loads. The Department of Energy has set 2010 targets for hydrogen production at \$2-3 per kg H_2.[10] Recent project reviews indicate that some companies have operating costs between \$3 per kg H_2 if energy costs are \$0.035/kWh[11]. Wind energy currently produces electricity at \$0.05-0.06/kWh[12]. Thus, renewable hydrogen should be an economic and environmental benign feed source for the proposed DME production process.

Research needs

With the production costs of hydrogen on the decline, the manufacturing economy of the direct catalytic production of DME will be highly dependent on the efficiency of two basic elements of the process, i.e., the catalyst and a reactor used for its synthesis process.

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.

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, will have to be employed in this process [13,14].

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.

The University of Utah has invented a novel, low-volume, high-pressure catalytic slurry gas-sparged cyclone reactor (CSG-SCR) for conversion of syngas. [15]. The CSG-SCR can be modified to convert CO_2 to DME using the developed "faster" bi-functional catalyst. Demonstration of this technology will occur as funding becomes available.

Summary

DME production holds the promise of combining captured carbon dioxide with “green” hydrogen to produce a more energy efficient, less polluting fuel and more benign chemical feedstock. The proposed chemical utilization of captured CO_2 could reduce the world’s dependence on fossil fuels by recycling carbon and lead to the production of “green” olefins and plastics.

References

1. Burke, M., Chemistry and Industry, (3), 21-23 (2007).
2. Miller, J.D., Zmierczak, W., Proceedings of 4th International Conference OILS & ENVIRONMENT, Gdansk, 265-274, (2005).
3. Ohira, T., Science & Technology Trends (17), 48-62 (2005).
4. Petkovic, L.M., Rollins, H.W., Ginosar, D.M., and Burch, K.C., Preprints of Symposia – American Chemical Society, Division of Fuel Chemistry (2006), 51(2), 853.
5. Mao D., Yang W., Xia J., Zhang B., Song Q., Chen Q., Journal of Catalysis, 230, 140-149 (2005).
6. Ogawa T., Inoue N., Shikada T., Ohno Y., Journal of Natural Gas Chemistry, 12(4), 219-227 (2003).
7. Jia M., Li W., Xu H., Hou S., Ge Q., Applied Catalysis A: General, 233(1-2), 7-12 (2002).
8. Czuppon, T.A., Knez, S.A., and Newsome, D.S., in “Encyclopedia of Chemical Technology”, 4th ed. (Kirk-Othmer, Ed.), vol 13, p. 837-894, Wiley, New York, 1991.
9. Bockris, J.O’M., Energy Options: Real Economics and the Solar Hydrogen System, John Willey & Sons, Inc., New York, 1980, p. 314.
10. “DOE Announces New Hydrogen Cost Goal”, July 14, 2005. http://www1.eere.energy.gov/hydrogenandfuelcells/news_cost_goal.html
11. Cropley, C., et al., “Low-Cost, High-Pressure Hydrogen Generator” presented at 2007 Hydrogen Fuel Cells Technology Infrastructure Review Meeting, May 15, 2007.
12. Wiser, R. and Bolinger, M., “Annual Report on U.S. Wind Power Installation, Cost and Performance Trends:2006”, DOE, May 2007.
13. Ohno Y., Inoue N., Ogawa T., Ono M., Shikada T., Hayashi H., NKK Technical Review No. 85 (2001).
14. Lu W.Z., Teng L.H., Xiao W.D., Chemical Engineering Science, 59, 5455-5464 (2004).
15. “Catalytic Slurry Gas-Sparged Cyclone Reactor,” Miller, J.D., Hupka, J., Zmierczak, W., *Patent pending.*