ALCOHOL ENERGY SYSTEMS

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Keywords: alcohol, methanol, ethanol, methanol synthesis, methanol energy, methanol reforming, methanol direct use, methanol - CO_2 reversible tanker

Contents

- Introduction
 Feature of methanol Energy system
 Methanol Energy Systems
 1 CO2 Supply
 2 Methanol Samthasia
- 3.2 Methanol Synthesis
- 3.3 Tanker Transportation
- 3.4 Recovery of Hydrogen from Methanol
- 3.5 Energy Use
- 4. Methanol Direct Use
- 5. Conclusion
- Glossary
- Bibliography
- **Biographical Sketches**

Summary

Among the alcohols, only methanol can be synthesized easily with hydrogen from big scale renewable energy and CO_2 . The methanol synthesis is an almost established technology.

The merits of methanol energy system are: CO_2 can be obtained infinitely from exhausted gas; and the CO_2 problem can be mitigated by CO_2 recycling. Direct use of methanol is the most suitable substitution for oil fuel.

The demerits are: A CO_2 recovery at the present time makes this system uneconomical. However, it will be the most effective system for the counterplan against the greenhouse effect and exhaustion of fossil fuels.

At the present cost, noble use of methanol for vehicle fuel is more than that of hydrogen. It is supported by noble demand equally of gasoline. If CO_2 is successfully recovered from the methanol fuel cell, direct use of methanol becomes completely advantageous.

1. Introduction

For the establishment of global hydrogen energy system using renewable energy, it brings a serious bottleneck for global transportation that gas-hydrogen or liquid-hydrogen has a thin energy density.

A plan called alcohol energy system has been proposed. Alcoholic compounds have the merit that they can be transported and stored easily at normal temperature. Also, they can be induced from CO_2 and hydrogen comparatively easy:

Methanol Synthesis: $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

Ethanol Synthesis: $2CO_2 + 6H_2 \rightarrow C_2H_5OH + 2H_2O$

Methanol synthesis is already a technology ready for industrialization. It has high selectivity, high reaction speed, and high yield rate (RITE, 1993, etc.).

On the other hand, there is a synthetic method and fermentation method to produce ethanol. For ethanol synthesis, effective catalyst was developed recently by Arakawa, Y. (1997). Yet, it has many problems for achieving high selectivity and reaction speed.

The fermentation method has been given satisfactory results from ancient times.

Actually, most ethanol production is by fermentation method. However, it will compete with food production.

So here we will focus on methanol as a carrier to transport hydrogen energy mainly by paying attention to the synthetic method. Today's conventional methanol synthesis is operated industrially. The following reaction via producing "Synthetic Gas" (CO + $2H_2$) from fossil fuel produces 20×10^6 tons of methanol per year. Most of the methanol is synthesized from natural gas.

Methanol Synthesis nowadays: $CO + 2H_2 \rightarrow CH_3OH$

This reaction is similar to a synthetic reaction using CO_2 , at the points of catalyst and reaction speed. It is possible to say that this fossil methanol synthesis is more advantageous because the useless water is not produced.

However, most of the fossil energy can be transported globally without synthesis. So there is no need to transport methanol from fossil fuel because the refinement requires extra process energy and it makes the cost expensive. Today, synthetic methanol from natural gas is not for fuel but for chemical use only. Compared with the energy price, methanol is always as much as two times higher than LNG.

2. Feature of methanol Energy system

Following is the configuration of the global energy system of hydrogen energy using CO_2 . Methanol is synthesized by making synthetic gas by CO_2 , mixing with hydrogen, which is produced by water electrolysis with electric power from renewable energies, subsequently compressing, and elevating temperature.

Methanol is transported to the consumer's area by conventional oil tanker, afterwards it can be used as hydrogen after the decomposition and separation of hydrogen from CO_2 mixing gas (WE-NET. 1995).

The feature of this system is synthesis of alcohol using carbon source like CO_2 as a carrier of hydrogen energy. It makes possible to transport hydrogen energy by tanker globally according to increase energy density to near the level of fossil fuel by converting hydrogen into liquid methanol.



Figure I. Global energy system configuration of methanol (standard); syn. gas: synthetic gas, syn: synthesis, ref: reforming, spn: separation

In methanol synthesis, the reaction heat is extracted from the calorific value that the source hydrogen possessed. Consequently, a calorific value of 85% moves to methanols theoretically. Actually, the loss of process energy should be added to it, making total energy yield rate about 75% as shown below.

 $\begin{array}{l} CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \\ 3 \times 285 \text{ kJ} & 726 \text{ kJ} \end{array}$

In the plan of RITE in Japan, there is a proposal to use CO_2 recovered from the exhaust gas of combustion of fossil fuel at a thermal power generation in the consumer's area as the CO_2 source. The CO_2 is transported to the area of renewable energy production, as return cargo of the methanol tanker.

As for the CO_2 source which can be obtained at the lowest cost and with the lowest energy loss, the use of CO_2 accompanied with natural gas near a renewable energy source is being investigated (RITE. 1999; WE-NET. 1998.3).

As a transitional process, an energy system with a combination of renewable energy and fossil resources, which is the cheapest now, is also being investigated (WE-NET et. al. 1996). This is shown in Figure 2.



Figure 2. Global energy system configuration of methanol by natural energy and coal; gsf: gasification, syn. gas: synthetic gas, syn: synthesis, ref: reforming, spn: separation

This is sometimes called the "semi hydrogen energy system", because the yielding energy is made up of fifty-fifty natural energy hydrogen and the energy introduced from coal. As for the yield rate of energy and the cost, it can be improved over the sum of the methanol produced from each independent system.

Figure 3 shows the methanol energy system configuration by CO_2 recovery (WE-NET. 1997). This system includes a prototype based on the pure hydrogen configuration, that is, the start and goal are hydrogen.



Figure 3. Global energy system configuration of methanol by natural energy and recovered CO_{2} ; syn. gas: synthetic gas, syn: synthesis, ref: reforming, spn: separation

These CO₂ recycling systems include the following processes:

(1) CO_2 supply for preparation of synthetic gas. The CO₂ should be recovered from exhausted gas or natural gas accompanied by CO₂. Sometimes followed by liquefaction, if global transportation is necessary.

natural gas accompanied by $CO_2 (CH_4 + CO_2) \rightarrow pure CO_2$ exhausted gas $(4N_2 + CO_2) \rightarrow pure CO_2$ $CO_2 \rightarrow liquid CO_2$

(2) Production of methanol by synthesis.

 $3H_2 + CO_2 \rightarrow CH_3OH$

(3) *Transporting liquid* CO_2 by LPG tanker from the consumer's area, and transporting methanol by oil tanker from the production area.

methanol \rightarrow tanker transportation \rightarrow consumer's area liquid CO₂ \rightarrow tanker transportation \rightarrow energy production area

(4a) *Regeneration of hydrogen from methanol.* By the following two or three steps:

 $\begin{array}{l} CH_{3}OH + H_{2}O \rightarrow [3H_{2} + CO_{2}] \quad (steam reforming, main) \\ CH_{3}OH \rightarrow [2H_{2} + CO] \quad (decomposition, minor) \\ [2H_{2} + CO] + H_{2}O \rightarrow [3H_{2} + CO_{2}] \quad (shift reaction) \end{array}$

(4b) *Separation of hydrogen from the mixed gas.* There is some energy loss and heat loss.

mixed gas $(CO_2 + 3H_2) \rightarrow pure H_2 gas + CO_2$

(5) *Energy use.* There are two ways: direct use (methanol) and indirect use (hydrogen).

 $\begin{array}{l} CH_3OH+1.5~O_2\rightarrow CO_2+2H_2O+726~kJ\\ 3H_2+3/2~O_2\rightarrow 3H_2O+857~kJ \end{array}$

The energy supply side and the energy demand side an allocated to each process as follows:

- *Energy supply side:* methanol synthesis with CO₂ and hydrogen, and tanker transportation
- *Energy demand side:* methanol use and CO_2 recovery, or: methanol reforming: \rightarrow hydrogen separation \rightarrow hydrogen use and CO_2 tanker transportation if necessary.
- 7

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Biographical Sketches

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