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HYDROGEN ECONOMY VS. METHANOL ECONOMY

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ABSTRACT

Today, the human civilization is very much dependent on fossil fuels, which make the blood and bone of this modern world. These precious natural resources, which form over the course of hundreds of years, are being consumed swiftly. In this alarming situation, it is very much necessary to think for a replacement, which fulfils the social needs without disturbing the environmental stability. One such approach discussed most over the years is 'Hydrogen economy-Producing and using hydrogen as a clean fuel', but there is no infrastructure for it. As it is a volatile gas, so it needs to be handled and stored at high a pressure. Moreover, it is an inflammable gas, which makes its usage as a transportation fuel difficult. A more potential and reasonable alternative, which is gaining importance is 'Methanol Economy' where methanol can be used as a source for transportation, energy storage and raw material for artificial hydrocarbons and their commodities. It is an excellent fuel. Methanol prices today are competitive with hydrocarbon fuels (on energy basis). Development is noted on the commercial conversion of biomass to methanol by means of thermochemical mechanism. Adequate feedstock of natural gas and coal lies to empower the handling of exhaustible methanol as transition fuel to renewable methanol from biomass. This paper discusses methanol's potential as an alternate of the hydrogen economy.

Key words: DMFC, Methanol economy, Hydrogen economy, Energy security, Transportation.

INTRODUCTION

In present day scenario, there is a heavy dependency on fossil fuels. Almost all the energy that we use comes from fossil fuels; for instance natural gas and oil. The rate at which the fossil fuels are being used today is significant and will become expensive in near future. Therefore, there is a strong need to find and develop new sources and options for overcoming this issue. Most of the fossil fuels that we see today contain hydrocarbons having variation in the ratios of carbon and oxygen. Upon combustion, carbon is oxidized to CO_2 while hydrogen to H_2O. Production of hydrogen and using it as a clean fuel is termed as hydrogen economy.

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There are a number of ways, in which hydrogen can be produced. One of those ways is the electrolysis of water. In this process, no by product is produced as such that's why it is also called as a clean fuel. Some other methods include direct oxidative conversion of natural gas and reductive conversion of atmospheric carbon dioxide with hydrogen.

But it proposes certain challenges:

- Handling of hydrogen is a great difficulty since it is volatile.
- Storage of hydrogen is potentially explosive and any leaks can cause explosion hazards; hence, limiting its use.
- Infrastructure needed for the development of hydrogen economy is not economical.
- Significant amount of energy is required in order to liquefy hydrogen.

A potential alternate to hydrogen economy is methanol economy, which can overcome these drawbacks. Methanol economy can lead to a sustainable future, where methanol is produced from biomass and recycled carbon dioxide (CO_2). Turning biomass into methanol is slightly cheaper and easier to produce. In spite of promoting it, methanol did not succeed on a large scale fuel because of its introduction in a period of rapidly falling petroleum price, and of the absence of a strong encouragement for methanol. Though, it is being used as a transportation fuel in countries like US and China.

There are no methodical glitches involved with methanol regarding supply frame or vehicle usage but it asks for substantial funding in view of large scale methanol distribution in transport division[1]. Manufacturing on a commercial upscale and vehicle use can be established as methanol synthesis can be achieved from coal and natural gas. Its role as an octane booster created a noteworthy initial interest.

Following characteristics of methanol make it advantageous for Internal Circuit Engines:

- It has higher flame speed and efficiency.
- It has higher latent heat of vaporization
- It effectively removes heat from engine- air cooled engines
- Methanol combusts better- cleaner emissions
- It is safer fuel in fires than gasoline.

With these large number of uses and advantages, methanol is now under consideration for being a substitute for fossil fuels.

Production

Efforts are going on to produce methanol in the most economical manner. Methanol can be obtained from different sources depending on the type of industrial application.

Methanol from syngas (synthetic)

The methanol preparation involves two steps. In first step, feedstock is converted into a gas stream, which consists of carbon mono oxide, carbon dioxide, water and hydrogen. Catalytic reforming of feed gas and steam is the most suitable process for the conversion. Another way is the partial oxidation. In the second step, methanol is synthesized catalytically from synthesis gas. There are numerous ways, in which these steps can be performed according to the preferred application.

Synthesis of methanol from syngas over a catalyst[1]:

$$CO + CO_2 + 7\,H_2 \longrightarrow 2\,CH_3OH + 2\,H_2 + H_2O \qquad ...(1)$$

Methanol from formic acid and formaldehyde

Methanol can also be synthesized from formic acid and formaldehyde. When methane is oxidized into methanol, it leads to the production of significant amounts of formaldehyde and formic acid. Only low conversion conditions yield higher selectivity to obtain methanol. The direct oxidation of methane should also be taken into account. It leads to the production of considerable quantities of formic acid and formaldehyde. Further, secondary conversion of formaldehyde or formic acid results in the rapid increment in the products. A significant source of methanol will be provided by recycled carbon dioxide also for the usage of methanol as a fuel[2].

Methanol from methane

Obtaining methanol from methane is economically advantageous while omitting the synthesis gas. These days, direct routes are gaining the attention of numerous researchers to bring down the cost of reforming[3,4].

Currently study on synthesis of methanol from direct methane oxidation, a solitary exothermic process, is being conducted.

$CH_4 + .5O_2 \rightarrow CH_3OH \qquad \Delta rH^\circ = -128 \text{ kJ mol}^{-1}$ …(2)

It has an advantage that the direct partial oxidation of methane to methanol is implemented in two directions and in a sole step, first is the gas phase homogeneous oxidation and second is the catalytic oxidation. This oxidation of methane is executed in flow quartz reactor in the presence or absence of the catalyst. The oxidant used here is oxygen.

Reactions of synthesis of methanol from methane are as follows[5]:

$CH_4 + H_2O \leftrightarrows CO + 3\,H_2 \qquad \Delta rH^\circ = +\,206 \text{ kJ mol}^{-1}$ ...(3)

$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad \Delta rH^\circ = -\,42 \text{ kJ mol}^{-1}$ ...(4)

$CO + 2\,H_2\,O \leftrightarrows CH_3OH \qquad \Delta rH^\circ = -\,90 \text{ kJ mol}^{-1}$ ...(5)

$CO_2 + 3\,H_2 \leftrightarrows CH_3OH + H_2O \qquad \Delta rH^\circ = -\,45 \text{ kJ mol}^{-1}$ ...(6)

Methanol economy: China

One of the largest consumers of methanol is China. It is mainly used for transportation. Methanol's increasing attraction in China is providing an interesting experiment. Availability of rich feed stocks in China such as coal and natural gas can be a reason for its interest in methanol.

On the other hand, the approach of the central government towards methanol-gasoline is a bit different due to which acceptance of methanol has slackened in certain districts while certain other provinces are encouraging methanol-gasoline blends[6]. Currently, private fuel stations in China are dealing with M5 (five per cent methanol), M10 (ten per cent methanol), M15 (fifteen per cent methanol), M85 (eighty five per cent methanol) and M100 (hundred per cent methanol) in the market. The most familiar among them is M15.

Methanol's significance in transportation

The methanol gasoline will lower down the emissions of many harmful gases like carbon monoxide, nitrogen oxide and hydrocarbon. It will provide better performance specifically with higher pressure. Methanol's favourable economics is the main reason, which enables it to be used as a fuel. Therefore, China is carrying out a large research of methanol for transportation purpose.

DMFC (Direct Methanol Fuel Cells)

DMFC is one of the newest electric power sources, which became increasingly more attractive subject for many researchers because:

- These fuel cells require a compact polymer electrolyte, which operates at a comparatively low temperature.
- Their fuel is cheaper in terms of cost and possesses high energy density making DMFCs more efficient.
- Even a 20% efficient DMFC is more than three times efficient than advanced lithium batteries[7].

Under this electrochemical cell, methanol undergoes oxidation, which produces water and carbon dioxide as stock to produce electricity. This is achieved without producing hydrogen. Due to this oxidation, fuel cell technology is simplified making it practical for many applications like supplying power to cellular devices and ultimately to motor vehicles and commercial electricity producing sites.

Reaction of synthesis of methanol from DMFC[8]:

Anode reaction:

$$CH_3OH + 7\,H_2O \rightleftharpoons CO_2 + 6\,H_3O^+ + 6\,e^- \qquad E^0 = 0.02V \qquad ...(7)$$

Cathode reaction:

$$\frac{3}{2}\,O_2 + 6\,H_3O^+ + 6\,e^- \rightleftharpoons 9\,H_2O \qquad E^0 = 1.23V \qquad ...(8)$$

Overall reaction:

$$CH_3OH + \frac{3}{2}\,O_2 \rightleftharpoons CO_2 + 2\,H_2O \qquad E^0 = 1.21V \qquad ...(9)$$

It has certain advantages:

- Methanol is an appropriate fuel due to its elevated energy density.
- DMFC operates at low and moderate temperatures; till 150ºC.
- DMFC is supplied to water with a dilute aqueous solution of methanol.

- Optimum performance is observed, when cells are in gas phase.
- At higher temperatures, there is an increase in kinetics and methanol crossover is decreased along the gas phase feed.

Vehicles

China is dominating the struggle in the evolution of methanol dedicated and FFV (Flexible Fuel Vehicle):

- Chery Automobile, a Chinese automobile giant, concluded testing of 20 methanol FFV models, for commercial manufacture.
- Shanghai Maple Automotive concluded testing of fleet methanol M100 cars.
- Chang'an Automobile Group announced Ben-Ben car, a FFV[1].

Marketing of methanol

In the present day scenario, many private firms are interested in setting up methanol-gasoline blending centres with a large capacity of around 200 million gallons. Price is one of the dominant reasons for which private gas stations choose to provide methanol-gasoline blends. Since, the retail pricing is controlled by the government; there is an inducement for private retailers to identify fuel additives, which are cheaper in terms of cost. Maximum of the methanol consumed in China is unlawfully combined with gasoline. This unlawful practice makes the scene between the refinery and automobile tank. Recently, Chinese government delayed the approval of M15 because M85 gasoline requires a modified engine, which has restrained market recognition[9].

In spite of the useful nature of methanol, it is pursued for economic reasons, with low production costs and potential.

Limitations (Implications)

Certain environmental and economic implications are associated with the growth of methanol economy in China. The domestic production of coal dependent methanol could be used as a substitute for the imported oil and it would also bring down the regular automobile discharges. Though production of methanol can worsen the problem of water scarcities in coal-abundant but dry areas, cause the instability to the coal process in China and all-inclusive, escalate the greenhouse gas discharges and threaten the user protection.

Water resources also present a challenge to China's Methanol Economy. Surprisingly, around 20 m^3 of fresh water is required to produce one ton coal-based methanol, which also involves releasing of noteworthy amount of wastewater[9]. Also, considerable water resources are consumed during coal mining. Chinese government's major basis for limiting the escalation of the Methanol Economy in the coal-abundant regions is the issue of water shortage.

The jeopardies of leakage and explosion are another serious problem. If used in vehicles, methanol can damage some of the rubber or plastic components inside the automobile's arrangement. It is also capable of corroding metals such as aluminium, magnesium and zinc[2]. Methanol blending is not legal in China, which creates a problem for drivers since they are not able to point the cause of damage of the engine to a particular gasoline station. To protect consumers, a legalized and formally regulated methanol-gasoline standard is required by requiring the blenders to add additives to reduce the degrading and corrosive effects. The solution for the leakage problem can be done by replacement of rubber seal with a material that provides protection for DME (dimethyl ether) and LPG (liquefied petroleum gas)[9]. Retrofitting the cylinders is an effective method for this problem.

Environmental conditions also propose a challenge for Methanol Economy. The emissions of carbon monoxide (CO) and total hydrocarbon (THC) resulted from combustion of methanol-gasoline blends in a spark-ignition are considerably low than for gasoline alone; on the other hand, emissions of nitrogen oxides (NO_X) are similar[10]. In addition to this, there is substantial increase in methanol and formaldehyde on further disintegration of hydrocarbon discharge. The unburned methanol and formaldehyde can be broadly knocked out by the three way catalytic converter present in gasoline-powered vehicles[10].

Conclusion (Future aspects)

Hydrogen is almost the perfect fuel. It has the highest energy content by weight of any fuel. It has almost no emissions, when burned and when used in a fuel cell, the only by-product is water. It is used in fuel cells for power vehicles, making them as efficient as powered vehicles. But Hydrogen Economy is limited by certain factors. For instance, hydrogen requires large amount of space per unit energy. Hydrogen requests to be effectively liquefied or compressed to be used as a fuel and for these processes, large amount of energy is required, which in turn dips the whole energy value of the hydrogen. It liquefies at very low temperature that is almost close to absolute zero, which needs huge sophisticated tanks that are expensive and heavy[11]. Due to which, storage of the fuel and infrastructure needed for transportation and refuelling is convoluted. As the compressing and liquefying of hydrogen is significantly costly and needs such huge sums of energy, it is the right time that we look for other sustainable replacements.

Methanol Economy might demonstrate as an alternative to the Hydrogen Economy since it does not suffer from drawbacks like those of hydrogen. In contrast, methanol enhances the urban quality of air and covers many weak spots as a fuel. Methanol can be easily produced from natural gas encouraging its large scale production of carbon-neutral methanol manufactured from recycled carbon dioxide and biomass. Turning biomass into methanol is a relatively developed technology and is possibly inexpensive and hassle free to produce as compared to cellulosic ethanol[12,13]. Methanol Economy can lead to a sustainable future. While it does possess few difficulties like increasing greenhouse effect and water shortages but accepting and promoting Methanol Economy would invite higher research input to overcome these challenges.

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