Converting CO_2 Emissions and Hydrogen into Methanol Vehicle Fuel

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There are new possibilities for transforming the ecological position of the metal-producing industries by utilizing their greenhouse gas emissions with electrolytically produced hydrogen to generate methanol as a replacement for gasoline.

INTRODUCTION

In the last decade, increased CO_2 emissions from cars and vessels as well as newly established or extended metals industries has led to a situation in Iceland where it is difficult to comply with international regulations concerning greenhouse gas emissions. In addition, the rapid economic development of Iceland since World War II has increased the use of imported fuels for the transportation and fishing industries. The nation's current energy mix consists of geothermal energy (38.6%), oil (38.6%), hydroelectric power (19.2%), and coal (3.6%).[1] The transport and fishing sectors share 28% of the total energy consumption, or 70% of the total liquid fossil fuels, which are imported.

Researchers are currently looking at the possibility of utilizing greenhouse gas emissions from the metals industries and electrolytically produced hydrogen to produce methanol for use in the transportation and fishing industries. This could, in principle, add greater value to Iceland's metal producers and, perhaps, serve as a pilot for larger scale development in other countries.

NEBUS AND NECAR

The proton-exchange-membrane (PEM) fuel cell-powered NEBUS and NECAR 3 recently developed by Daimler-Benz AG open up the possibility of running city buses in Reykjavik, the capital city of Iceland, on pure electrolytically produced hydrogen and private cars in Iceland on methanol.[2,3] According to information from Daimler-Benz AG, the mass production of both the NEBUS and NECAR 3 are planned for 2004.[4]

Pilot projects involving the use of hydrogen for powering the bus fleet of Reykjavik are presently being planned. The technology being considered is provided by Daimler-Benz AG,[3] and the fertilizer plant on the outskirts of Reykjavik will produce the required hydrogen. No further purification of the hydrogen is required for use in the PEM fuel cells. In the case of a 100 MW plant and an electricity price of \$0.02/kWh, hydrogen would be about three times more expensive than imported liquid fuels when calculated on the basis of energy content.[5] (The electricity price used is based on a common estimate for large-scale electricity sales from new hydroelectric plants.) When hydrogen is used to power PEM fuel cells, the energy efficiency is about 2–3 times higher than in conventional internal combustion engines. Thus, fuel-cell-based transport and fishing sectors utilizing hydrogen from hydroelectric energy seem competitive as compared to the present fuel economy.

In the NEBUS, the hydrogen is stored on board as pressurized gas in a sufficient amount to operate the bus approximately 250 km on each tank filling, which is the same distance as the Reykjavik city buses are run each day, on the average. The city bus fleet can be operated from one filling station (in this case, the fertilizer plant), which eliminates the need for a complicated infrastructure for fuel distribution.

Onboard storage of pressurized hydrogen gas in hydrogen-powered PEM fuel cell private cars seems unrealistic considering the existing technology, mainly for two reasons: the operating distance on each filling would be much too short, and a complicated infrastructure for fuel distribution would be required. Thus, the concept currently developed to store the hydrogen bound in methanol onboard the cars seems to be the most attractive method.[3]

There are, in principle, no obstacles to developing PEM fuel cells for fishing vessels, provided that fuel cells in the megawatt range become commercially available. To illustrate this, a Japanese fuel cell project is currently underway, where a 1,500 tonne vessel is powered by two 500 kW fuel cells, and the fuel is stored onboard as methanol.[6]

PRODUCING METHANOL

The standard entalphy of combustion of gasoline is 48 GJ/t, while the standard entalphy of combustion of methanol is 24 GJ/t. The present energy efficiency in a gasoline-powered car is approximately 20%. According to information from Daimler-Benz AG and the Ship Building Research Association of Japan, the efficiency of methanol when used to power fuel cells is about 35–40%.[4,6] This means that a gasoline car would need 0.875–1.000 tonne of gasoline to travel the same distance that PEM fuel cell cars could travel on one tonne of methanol.

A gasoline-fueled car emits about 3.1 tonnes of CO_2 for every tonne of fuel. A fuel-cell-based vehicle emits about 1.4 tonnes of CO_2 for every tonne of methanol. Thus, the total emitted CO_2 from a methanol-powered vehicle is about 45–52% of the emission for a conventional gasoline-fueled vehicle.

It has been suggested that peat or other forms of biomass could be used to produce methanol.[7] In Iceland, these carbon sources suffer from the fact that the subarctic climate limits the primary production of biomass, and the available biomass resources are not environmentally feasible. Another disadvantage is the disruption caused by mining.

The production of methanol from CO or CO_2 and hydrogen can be described by the reactions:

$$CO + 2H_2 \rightarrow CH_3OH$$
$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

The chemical equations show that methanol produced from CO_2 requires 1.5 times more hydrogen than methanol produced from CO.

When looking for carbon-containing resources to use in producing methanol, a potential candidate is the carbon emitted during metals production. In fact, both aluminum smelting and ferrosilicon production emit vast amounts of carbon-oxide-containing gasses.

Ferrosilicon is produced by the reaction of iron ore and quartz with coke by electric-arc heating using a Söderberg process. The overall silicon-forming reaction can be described as

$$SiO_2 + 2C \rightarrow Si + 2CO$$

The emitted gas is blended with excess ambient air, converting all of the CO into CO_2. According to information obtained from the ferrosilicon plant at Grundartangi, Iceland, the measured composition of the gas emitted from a ferrosilicon furnace, before dilution with air, is CO, 70–75 vol.%; H_2, 12–17 vol.%; H_2O, 8–12 vol.%; CO_2, 2.5 vol.%; and CH_4, 1.5 vol.%.[8]

The R&D teams at Elkem and Icelandic Alloys are designing a new 42 MW furnace at Grundartangi. By closing the top of the furnace to ambient air, the emitted gasses can be collected undiluted. By purification of the carbon-oxide gasses in this new furnace and with the addition of 10,000 tonnes of hydrogen, it would be possible to produce 87,000 tonnes of methanol per year. From this single furnace, these 87,000 tonnes of methanol, if used to power PEM fuel cell cars, could, theoretically, replace 76,000–87,000 tonnes of gasoline presently used to power cars in Iceland. The total gasoline import in 1995 was 137,000 tonnes.

Aluminum is produced by the low-voltage, high-current electrolysis of bauxite by using carbon electrodes using the Hall-Héroult process:[9]

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

According to the Boudouard reaction

$$CO_2 + C = 2CO$$

and the side electrochemical reaction

$$Al_2O_3 + 3C \rightarrow 2Al + 3CO$$

the carbon oxides in the gas emitted from the electrolytic cells are expected to be a mixture of CO_2 and CO, which, according to K. Grjotheim et al.,[9] ranges between 50–90% CO_2 and 10–50% CO. For this discussion, the average values of 70% CO_2 and 30% CO are used.

As is the case for the gasses emitted from the ferrosilicon plant, the gasses emitted from the electrolytic cells in the aluminum smelters are presently diluted with ambient air, converting all of the produced CO into CO_2. Assuming that the electrolytic cells of the aluminum smelters could be enclosed, the carbon oxides in the emitted gas could be used with additional hydrogen to produce methanol. The economic feasibility of such a drastic reuse of the emitted gasses from the aluminum industry has yet to be confirmed.

The actual consumption of carbon in aluminum production is in the range of 420–550 kg per tonne of aluminum.[9] In this projection, it is assumed that the carbon consumption is in the lower part of the range. The theoretically possible production of methanol from the Icelandic industries is based on 342,000 tonnes of carbon dioxide being emitted from the aluminum industry, 200,000 tonnes of carbon dioxide being emitted from the two existing ferrosilicon furnaces, and 76,000 tonnes of carbon monoxide being emitted from the new ferrosilicon furnace. Adding hydroelectrically produced hydrogen, 542,000 tonnes of CO_2 and 76,000 tonnes of CO could result in up to 450,000 tonnes of methanol per year. This amount of methanol could, in turn, when powering the fuel-cell-based transport and fishing industries, replace 394,000–450,000 tonnes of imported fuels. The total amount of imported liquid fossil fuel in 1995 was 668,000 tonnes. Replacing the imported fuels with 450,000 tonnes of methanol would result in up to a 55% reduction of anthropogenic CO_2 emissions. Additional electric power totaling 410 MW would be needed to produce the 68,000 tonnes of hydrogen needed in the methanol-conversion process, leading to 450,000 tonnes of methanol in the most extensive of scenarios. In this way, 68,000 tonnes per year of hydrogen would be needed to convert emitted gasses from existing and already decided metals industries into methanol.

Further studies are needed in order to decide the feasibility of and the steps for introducing such scenarios in Iceland and other countries that are concerned with alternative fuels and greenhouse emissions.

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