The CRI RM Process and Potential 19 Gordon Taylor 2010-05-03

Introduction

The Carbon Recycling International (CRI) 'Renewable Methanol' process was outlined at a Workshop 'Reversing Global Warming: Chemical Recycling and Utilization of CO2', sponsored by the NSF and the Loker Hydrocarbon Research Institute, University of Southern California, on July 9-10, 2008. [1] It uses existing concentrated CO2 streams, H2 produced by electrolysis using low-cost, renewable electricity – hydro and geothermal, hence with very high Capacity Factors - and catalytic synthesis. CRI started operating a pilot plant in 2007 and have 'their own catalyst technology' with two patents. [2] [3] Other processes were mentioned at the Workshop, but none seemed as suitable or likely to be ready in the near-term.

Local Factors

Drivers

Iceland already has the world's highest share of renewable energy, at about 80%. [4] 'As almost all stationary energy in Iceland is produced from renewable sources, measures to reduce emissions are largely focused on mobile sources: Transport and the fishing fleet'. [5] This includes road and air transport as well as marine and accounts for about one third of Iceland's UNFCCC GHG emissions. [6]

Iceland hosted the experimental use of hydrogen fuel cell vehicles – notably three buses. [7] However, elemental hydrogen proved impractical for transport, thus confirming the need for liquid fuels. This lead to considering the use of renewable hydrogen and available CO2 streams to synthesise methanol, as proposed for Iceland and elsewhere by Arnason and Sigfusson and for worldwide use by Olah. [8] [9]

Electricity Availability and Cost

'In 2008, HS Orka signed an agreement with Carbon Recycling International to provide 40 GWh or 5 MWe for the production of methanol from CO2 extracted from geothermal wells at the Svartsengi geothermal plant'. [10]

The electricity costs, both hydro and geothermal, range from about 2.5 to 5 ISK/kWh. [11] At an exchange rate of 125 ISK/1 USD, this would be 0.016 to 0.032 USD/kWh.

CO2 Availability and Cost

'At the plant CO2 emissions of the power plant of HS Orka will be used to produce methanol fuel for cars. While using carbon emissions from a geothermal plant now, the same technology could be used at any carbon emission generating facility, e.g. at the aluminum smelters in Iceland'.

'Based in Iceland, Carbon Recycling International is targeting converting CO2 from emission stacks .. into the renewable fuels methanol and DME. CEO K.C. Tran said the company is initially targeting geothermal plants, but expected the approach to be particularly appropriate for the aluminum and ferrosilicon plants of Iceland'. [12] The Industrial Scale Plant (ISP) will use CO2 from geothermal boreholes, which is already separated from the hot water. There are almost no large combustion flues in Iceland and capturing CO2 from the air would be more costly.

Location

The Industrial Scale Plant site is very near to the HS Orka geothermal plant, while the Commercial Scale Plant is planned to be over the hill. [13]

Hydrogen Production Efficiency

'The electricity required for hydrogen production is 10.3 kWh per kg of methanol'. [14] The 'theoretical' energy required to produce hydrogen by electrolysis is 39.4 kWh/kg. [15]

The equation for using CO_2 and H_2 to synthesise methanol is:
$CO_2 + 3H_2 = CH_3OH + H_2O$
The respective Molar Masses are, in kg/kmol: CO_2: 44, H: 1, CH_3OH: 32 and H_2O: 18.
So the mass balance is: 44 + 6 = 32 + 18.
Therefore to make 1 kg of methanol requires 6/32 kg of hydrogen.
This implies that the electrolysis efficiency is (39.4 x 6/32)/10.3 = 0.72. [16]

For producing hydrogen by electrolysis, 72% is typical of alkaline electrolysers operated for high output, although some current-production designs can achieve 80%. [17]

Overall Efficiency of Methanol Synthesis

From a plot of the cost of methanol versus the cost of electricity, at an electricity cost of 0.027 USD/kWh, the methanol cost is USD 600/t. [18] Of this, the 'fixed' cost is about USD 285/t and the 'variable' cost is about 600 – 285 = 315 USD/t. The latter implies an overall process efficiency of about 0.027 x 22.7 x 1000/(3.6 x 315) = 0.54.

For a second estimate: The Industrial Scale Plant is due to produce 4.2 million liters a year. [19]
The density of methanol is 0.79 kg/l. So 4.2 million liters = 4.2 x 0.79 = 3.32 million kg.
This requires electricity of 40 GWh/y. [20] The Higher Heat Value (HHV) of methanol is 22.7 MJ/kg.
So the overall energy efficiency = 4.2 x 0.79 x 22.7/(3.6 x 40) = 0.52. [21]
However, the electricity value of 40 GWh/y is a round number, and if the efficiency was 0.54, it would be 4.2 million x 0.79 x 22.7/(3.6 x 0.54) = 38.7 Gwh/y.

For comparison, Specht and Bandi, 1999, gave the primary energy demand for methanol synthesis from CO_2 and electrolytic H_2, excluding that for CO_2 capture and transport, as 7.58 kWh/l. [22] Relative to the methanol HHV of 17.9 MJ/l, this implies an overall efficiency of 17.9/(3.6 x 7.58) = 0.66.

Hence for a modern methanol synthesis plant using an existing stream of concentrated CO_2 and hydrogen from present-day electrolysers, an overall efficiency of 0.54 is plausible.

CO_2 Analysis

Statistics Iceland publishes a database giving the CO_2 emissions of the geothermal plants up to 2006 and the electricity generation of all the public power plants, geothermal and hydro. [23] The CO_2 emissions of all the public electricity plants have varied over time. With those of hydro electricity as zero, the weighted average of the CO_2 intensity for 2006 - the latest year for which data is given - is 0.0157 kg/kWh. [24]

When substituting methanol for gasoline on an equal volume basis:
The CO_2 for methanol production is 22.7/(3.6 x 0.54) x 0.0157 = 0.183 kg/kg.
The CO_2 reduction for methanol is (1.375 – 0.183)/1.375 = 0.866 or 87%.
The Lower Heat Value (LHV) of methanol is 15.8 MJ/l while that of gasoline is 32 MJ/l.
When substituting methanol for gasoline on an equal energy basis:
The CO_2 reduction for methanol is (1 – (1 – 0.866) x 32/15.8)) = 0.729 or 73%. [25]

An earlier presentation from CRI showed the reduction in life cycle emissions for Renewable Methanol as 65-85%. [26] However, a later presentation gives only 65%. [27] It seems very likely that the higher value is for gasoline being replaced by methanol of equal volume and the lower value for it being replaced by methanol of equal energy - i.e. of about twice the volume.

For the CO_2 reduction in the equal volume case, my value of 87% is close to the CRI value of 85%. However for the equal energy case, my value of 73% is somewhat higher than theirs of 65%. Either way, CRI Renewable Methanol should exceed the required 60% reduction in life cycle GHG emissions, and so be defined as a renewable fuel. Also, it would comply with the 'Direction towards second generation renewable fuels' and thus qualify for 'Double credits for fuels generated from waste and non land use'. [28]

Cost Analysis

a) The electricity prices, both hydro and geothermal, range from about 2.5 to 5 ISK/kWh. [29] At an exchange rate of 125 ISK/1 USD, this would be 0.016 to 0.032 USD/kWh.

b) 'It is no coincidence that the business was founded in 2006: the company makes a profit when its fuel can be sold for over USD 50 per barrel and oil prices passed USD 50 in early 2005. The current price of oil is more than double that amount'. (Posted on 29 April 2008). [30] Sometimes methanol may replace oil/gasoline at equal volume – i.e. a barrel of methanol could replace a barrel of oil/gasoline. 1 US barrel is 159 liters and the density of methanol is 0.79 kg/l. So 1 tonne of methanol = 1000/(159 x 0.79) = 7.96 barrels. Hence oil/gasoline at USD 50 per barrel could be replaced by methanol at 50 x 7.96 = about USD 400/t.

c) From a plot of the cost of methanol versus the cost of electricity, at a methanol cost of about USD 400/t, the cost of electricity is 0.01USD/kWh. [31] This is less than 0.016 to 0.032 USD/kWh. (See a) above).

The data from a), b) and c) above were used to determine the break-even prices of oil for various costs of electricity. The two cases considered are: I) when methanol replaces gasoline at equal volume and II) when methanol replaces gasoline at equal energy (which requires about twice the volume).

The calculation omits the cost of refining oil to gasoline and the value of any carbon credit – both of which would benefit Renewable Methanol.

CRI plan to sell their Renewable Methanol for use as a 3% blend. [32] To replace gasoline with low blends of methanol should require only equal volume. At an electricity price of USD 0.01/kWh, the methanol is just profitable – i.e. breaks even - at an oil/gasoline price of USD 50/barrel. Even with the higher electricity prices, the break-even oil/gasoline prices would be only USD 60 and 83/barrel respectively. [33]

The current (April 2010) oil price is around USD 84/barrel, and gasoline would cost at least as much, so CRI Renewable Methanol from the Industrial Scale Plant should be profitable at all likely electricity prices and still break even at the highest electricity price considered here.

However, to replace gasoline with high blends of methanol would require amounts with equal energy. The Lower Heat Value (LHV) of methanol is 15.8 MJ/l while that of gasoline is 32 MJ/l, so on an equal energy or 'gasoline-equivalent' basis, about twice the volume of methanol would be required. At the lowest electricity price, the break-even oil/gasoline price would be only USD 100/barrel so with oil/gasoline at USD 84/barrel, CRI Renewable Methanol would be quite close to being competitive. With the higher electricity prices, the break-even oil/gasoline prices would be USD 120 and 167/barrel respectively. However, the oil price can be expected to rise further as the world emerges from the recession.

Carbon Credit

The price of (fossil-based) methanol has varied between USD 200 and 800/tonne over the last two years and in March 2010 was USD 366/tonne. [34] Hence the current price premium for Renewable Methanol, with a life-cycle GHG reduction (for the equal volume case) of about 85%, is already small at (400 – 366)/366 = 9.2%.

At a CO2 usage of 44/32 = 1.375 t per t methanol, a CO2 reduction of e.g. 85% and a 'Carbon Price' of e.g. USD 20/t CO2, the carbon credit would be USD 1.375 x 0.85 x 20 = USD 23.4/t methanol. This would reduce the current price premium for Renewable Methanol to (400 – 366 – 23)/366 = 3%.

Moreover, since it is made from Natural Gas, the price of which is linked to that of oil, the price of fossil-based methanol can be expected to rise – as it has in the recent past.

Capital Cost and Recovery

'The company has worked the last 3 years hard on making this project possible and the cost for the plant are estimated to be one billion ISK (US$ 8 million)'. [35] This seems remarkably modest, but must be helped by all the favourable local factors. Even so, it shows the scale of investment needed to build a plant large enough to convince themselves and others to follow this example.

The planned production of the ISP is 4,200,000 l/y, which at 159 l/barrel, is 26415 barrels/y. With oil/gasoline at USD 80/barrel and assuming methanol displaces gasoline on a volume basis - as for low blends - this would be worth USD 26415 x 80 = about 2 million a year. Depending upon the electricity price, the profit could be a useful fraction of this, and thus soon repay the USD 8 million cost of the ISP.

Maximum Methanol Production

Two constraints on the maximum methanol production in Iceland are electricity and CO2. The electricity sources considered are hydro and geothermal, which have high capacity factors but are limited, and not wind, which has lower capacity factors but would be almost unlimited. For hydro power, the present usage is 12,400 and the potential is 30,000, so the additional potential is 30,000 – 12,400 = 17,600 GWh/y. For geothermal power, the present usage is 4000 and the potential is 20,000, so the additional potential is 16,000 GWh/y. [36] Hence the total additional potential is 17,600 = 16,000 = 33,600 GWh/y.

'Icelanders need over 400 million liters of gasoline a year'. [37] To replace gasoline of 400 million l/y would require methanol of 400 million x 32/15.8 = 810 million l/y. At a density of of 0.79, this would be 640,000 t/y. At an energy density of 15.8 MJ/l, the energy content would be 810 million x 15.8 = 12,800 TJ, which is 12,800/3600 = 3555 GWh. Assuming a production efficiency of (not 52-54% but) 50%, the required electricity input would be 3555/0.5 = 7110 GWh. Compared to the present Iceland gasoline usage, this would be enough for about 33,600/7110 = 4.7 x.

The CO2 sources considered are industrial and geothermal, which are relatively high concentration but limited, and not atmospheric air, which is low concentration but unlimited. The industrial sources include aluminum smelters, with CO2 concentrations of about 1-2%. [38] The 'power intensive industries that use renewable energy in Iceland (have) the right to emit an extra 1.6 million t CO2/y until 2012'. [39]

Moreover, of the total power potential, 20,000 GWh/y would be geothermal, which would have associated CO2 emissions. The CO2 intensity of additional geothermal power is very difficult to estimate, but as an indication, that for the existing geothermal power in 2006 was 0.0593 kg/kWh. [40] Hence the total associated CO2 emissions might be about 20,000 x 0.0593 = 1.2 million t/y.

Hence the CO2 from power intensive industries and from the total potential geothermal power might be 1.6 + 1.2 = 2.8 million t/y. The methanol synthesis follows: CO2 + 3H2 = CH3OH + H2O, where the molar masses are 44, 6, 32, and 18 respectively. So 2.8 million t CO2/y would be enough for methanol of 2.8 x 32/44 = 2.0 million t/y. Compared to that required to replace the present Iceland gasoline usage, this would be about 2.0 million/640,000 = 3.1 x. This suggests that to match the 4.7 x of the additional potential power from hydro and geothermal, CO2 would have to be captured from the air. However, this is being actively studied and may well be required for geo-engineering to reduce the atmospheric concentration.

Selling the Methanol

'The (Industrial Scale) plant that will be built on this site will produce approximately 4.2 million liters of methanol ...'. [41] Compared with over 400 million liters a year, it is only about 1% on a volume basis and about 0.5% on an energy basis. 'Production will start in about one year and then all gas(oline) sold by Icelandic gas station chain Olís will be a blend of gas(oline) with methanol'. [42] CRI plan to sell their Renewable Methanol for use as a 3% blend. [43]

'The company combines captured and cleaned CO_2 with hydrogen from electrolysis. The resultant methanol could be used for fuel cells or blended into gasoline. In a 10 percent blend, Tran said the gas(oline) would get the same mileage as 95 octane fuel'. [44] This implies that they have done tests with RM10 and that at such low blends, it replaces gasoline on an equal volume basis. Hence - compared with the initial 1% - RM 10 could increase their share of the local 'gasoline' market ten-fold. This would equal the output of one Commercial Scale Plant, which is planned to have 10 times the capacity of the ISP.

Flex-Fuel Vehicles (FFVs) are designed to use gasoline blended with ethanol up to 85% by volume – E85 – and there are already many such vehicle models available in e.g. USA, Sweden, and France. They should be able to use blends of gasoline with methanol up to M55 without modification. (This assumes the same volumetric flowrate of fuel and reflects the volumetric energy densities of gasoline, ethanol and methanol). However, at such high blends, methanol would replace gasoline on an energy basis. Hence if all Icelandic 'gasoline' vehicles were such FFVs, then – compared with the initial 0.5% - the local 'gasoline' market could absorb about 55/0.5 = 110 times as much methanol. This would require about 11 Commercial Scale Plants.

Spark ignition internal combustion engined vehicles can be designed to be flex-fuel up to M85 or even tri-flex, using any blend of Gasoline, Ethanol and Methanol up to M100. [45] Such vehicles would enable Renewable Methanol to displace even more of the gasoline demand and 100% would require about 20 Commercial Scale Plants. There would be corresponding savings of foreign exchange and CO_2/GHG emissions. Since it would take around 15 years to renew the passenger car fleet, the Icelandic Government could help speed the transition to renewable fuel by encouraging or even mandating the purchase of only such FFVs, able to use M55 then M100, in readiness for such volumes of methanol becoming available.

A forecast of hydrocarbon use for Iceland shows that additional transport fuel is required for the Icelandic fishing fleet and for International aircraft, with the latter becoming the largest after about 2022 and rising until nearly 2050. [46] Hence these demands might justify adding plant to upgrade Renewable Methanol to diesel fuel and aviation kerosene.

Conclusions

Iceland uses the world's highest proportion of renewable energy. Hydro-electricity and geothermal heat and power supply most stationary applications and there are huge resources remaining, while transport still accounts for one third of greenhouse gas emissions. After first-hand experience of hydrogen fuel cell vehicles, they were found to be impractical. This lead to the plan to use renewable hydrogen, together with available concentrated CO_2 streams, to synthesise methanol for use in transport.

Carbon Recycling International have chosen – and further developed – processes with low technical risks. Also, they are following a classical chemical engineering progression – from Pilot to Industrial to Commercial scale plants. Compared with the present Icelandic gasoline demand, the additional hydro and geothermal power potential could be enough for over four times the methanol (by energy), and the industrial and geothermal CO_2 emissions for over three times. So as well as meeting the Icelandic 'gasoline-equivalent' demand, much more methanol would be available for conversion to diesel fuel and aviation kerosene, or for export. Thus Iceland provides an ideal first market for Carbon Recycling International's Renewable Methanol, and a showcase for much wider application. Such solutions could well provide much of the answer to the climate and resource challenges for the transport sector worldwide.

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3 (See http://www.carbonrecycling.is/Videos/overview.pdf Slide 5).
4 (See http://unfccc.int/resource/docs/natc/isl_nc5.pdf p 19).
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7 (See http://www.h2net.org.uk/PDFs/RN_1/Iceland_presentation.pdf).
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10 (See http://www.geysirgreenenergy.com/media/banners/GGE_Annual-Report_2008.pdf Page 30).
11 (See http://energy.balticresponse.com/assets/Gudni-A-JohannessonVilnius.pdf Slide 14).
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20 (See http://www.geysirgreenenergy.com/media/banners/GGE_Annual-Report_2008.pdf Page 30).
21 (See the spreadsheet 'CRI_Effys.xls').
22 (See 'The Methanol Cycle – Sustainable Supply of Liquid Fuels', Specht M. and Bandi A., 1999. http://www.methanol.org/pdf/ZSWMethanolCycle.pdf p 9).
23 (See http://www.statice.is).
24 (See the spreadsheet 'CRI_CO2_Int.xls').
25 (See the spreadsheet 'CRI_CO2.xls').
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