Methanol Energy Analysis

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The following is a report on the energy required to synthesize Methanol from atmospheric carbon dioxide and hydrogen. Unlike similar analyses associated with the energy balance of Ethanol, this analysis does not quantify fossil fuel inputs into the synthesis of Methanol because, for our process, there are no fossil fuel inputs.

As with an Ethanol energy balance analysis, this Methanol energy balance analysis does not take into account the energy required to manufacture the apparatus necessary for the synthesis of Methanol. We track and quantify the inputs to the synthesis of Methanol as well as the outputs, and compare them to the intrinsic energy content of Methanol.

Our process is based on ICI's low-pressure Methanol procedure introduced commercially in 1966 and on work done by Mr. Michael Specht and Mr. Andreas Bandi from the Center of Solar Energy and Hydrogen Research (ZSW), located in Stuttgart Germany, in the early 1990's.

This process of Methanol synthesis has only three inputs: water, electricity and atmospheric carbon dioxide, and four outputs: Methanol, water, Oxygen and heat. No allowance is made for the production of oxygen.

It is a requirement that the electricity input be from a non-fossil fuel (and carbon-neutral) source such as wind, hydro, solar, bio-mass, geothermal, etc. Even nuclear is an acceptable electricity source as far as this analysis is concerned.

The actual Methanol synthesis process is continuous and under automatic control. And, unlike farming, we maintain that no direct labor inputs are required for Methanol synthesis (though it could be argued that no system is completely automatic and that some human supervision and maintenance personnel are required).

The governing chemical equation for the synthesis of Methanol is:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H = -49.7 \text{kJ/mole} \qquad \textbf{(1)}$$

This reaction is exothermic and takes place at 260 ºC and 1200 psi.

CO_2 is provided in compressed form (approx 850 psi) by the owner of the fermentation processor (i.e. Mogollon Brewing Co.). Hydrogen is obtained by the splitting of water in a commercial electrolyzer such as the H_2 IGEN from Hydrogen Systems.

The hydrogen and carbon dioxide are mixed in a 3:1 molar ratio, compressed to 1200 psi and introduced into a reactor vessel containing a Cu/ZnO-based catalyst. At best, 25% of the feed gases are converted to “wet Methanol” (a mixture of methanol and water).

The products, gaseous Methanol, water and un-reacted CO_2 and H_2 are expansively cooled to about 40 ºC in the knock-out drum where the wet methanol settles. The un-reacted CO_2 and Hydrogen are re-directed to the reactor by a re-cycle compressor; make up gases of H_2 and CO_2 are added to the reactor so that the reactor operates in a continuous manner at a constant flow rate – a space velocity of 8000 liters per hour per liter of catalyst.

The wet methanol is distilled, separating the Methanol and water; the water is fed back to the electrolyzer to produce Hydrogen.

ENERGY GAIN ANALYSIS

The following energy balance analysis will be based on the production of 1 Kg of Methanol. 1 Kg of Methanol is equivalent to 31.25 moles of Methanol (31.25 moles * 32.04 g/mole = 1000 g) so equation 1 can be re-written as:

$$31.25CO_2 + 93.75H_2 \rightarrow 31.25CH_3OH + 31.25H_2O$$

In mass terms:

$$1.375 \text{ Kg of } CO_2 + 0.1875 \text{ Kg of } H_2 \rightarrow 1.0 \text{ Kg } CH_3OH + 0.5625 \text{ Kg } H_2O \qquad \textbf{(2)}$$

Heat is evolved at (ΔH = -49.7kJ/mole) 49.7KJ/mole*31.25 moles = -1.5 MJ

Reaction heat = -1.5 MJ

CO_2 is provided but the Hydrogen must come from the splitting of water:

$$H_2O \rightarrow H_2 + O \quad \text{or re-balancing:} \quad 93.75H_2O \rightarrow 93.75H_2 + 93.75O$$

In mass terms:

$$1.6875 \text{ Kg } H_2O \rightarrow 0.1875 \text{ Kg of } H_2 + 1.5 \text{ Kg O}$$

Since the 0.5625 Kg of H_2O produced in equation 2 is re-cycled, the net water required to produce 1 Kg of Methanol is 1.6875 – 0.5625 kg = 1.125 Kg. 1 Kg of Methanol is equivalent to 1Kg/0.791Kg/liter = 1.264 liters and 1.125 Kg of water is equivalent to 1.125 liters. From this we can conclude:

It takes 0.89 liters of water to produce 1 liter of Methanol.

No other amounts of water is consumed in the process. Assuming this water is pumped from a depth of 100 meters with 75% efficiency (per Patzek), the energy required to input this water to the electrolyzer is: 1.125kg*100m*9.81m/s/0.75 = 1,472 J.

Water pumping = 0.0015 MJ

Assuming an alkaline electrolyzer such as the H2 IGEN is used, the feedwater is "electrolytically pressurized" and filtered before being split. The energy required to split water is listed as 3.9 KWh/Nm^3 of Hydrogen, equivalent to 14 MJ/m^3 or 156 MJ/Kg H_2.

From equation 2, we need 0.1875 Kg H_2 per Kg of Methanol so the energy cost of the electrolyzer is: (156 MJ/Kg H_2)*(0.1875 Kg H_2) = 29.3 MJ

Electrolyzer Energy = 29.3 MJ

The CO_2 and H_2 must be compressed prior to entering the reactor and the un-reacted gases re-compressed in a cyclic loop. The power required to compress a gas is dependent on the inlet pressure, outlet pressure and flow rate. The H2 IGEN electrolyzer delivers Hydrogen at 375 psi, the CO_2 is assumed to be delivered at 850 psi and the pressure in the knock out drum is a function of drum volume. The required outlet pressure is that of the reactor, 1200 psi.

To simplify calculations and to allow the use of published compressor statistics from Hydro-Pac, Inc. we will conservatively assume that all inlet pressures are at 300 psi and the outlet pressures are 1500 psi.

In this case, the Hydro-Pac Model C1.5-03-140/300LX hydrogen compressor will deliver 10.1 scfm (17.2 Nm^3/Hr) using a 3 hp (2.25 KW) electric motor, which we will assume is 75% efficient.

Equation 2 is converted from a mass equation (at Standard Temperature and Pressure, STP) to a volume equation at STP by using the known densities of CO_2 (1.98 Kg/m^3), H_2 (0.08988 Kg/m^3), Methanol (791 Kg/m^3) and water (1000 Kg/m^3), gives:

0.69 Nm^3 of CO_2 + 2.09 Nm^3 of H_2 $\rightarrow$ 1.26 liters of CH_3OH + 0.56 liters of H_2O **(3)**

Thus, the compressors must compress 2.78 Nm^3 of reactant gases into the reactor. In reality, there are a total of three compressors one for CO_2, one for hydrogen and one for the recirculation of CO_2 and H_2. But since the inlet and outlet pressures are the same and the compressors are assumed identical, we can, for the purposes of calculation, combine them all into one.

Now, 2.78 Nm^3 of gases must be pushed through the reactor and converted into 1 Kg (1.26 liters) of Methanol and 0.56 Kg (0.56 liters) of water. But the reaction is only 25% efficient, so after the initial 2.78 Nm^3 of gas has gone once through the reactor, 75% or 2.09 Nm^3 of the gas remains and must be pushed through the reactor again. This process, in theory never ends (much like a capacitor charging); however, in practice we "stop" the process after 95% to 99% of the gases have reacted. Note that this is just an artifact of producing just 1 Kg of Methanol; in reality the operation is continuous.

Pass	Initial Volume	Final Volume
1	2.78	2.08
2	2.08	1.56
3	1.56	1.17
4	1.17	0.88
5	0.88	0.66
6	0.66	0.50
7	0.50	0.37
8	0.37	0.28
9	0.28	0.21
10	0.21	0.16
11	0.16	0.12
12	0.12	0.09
13	0.09	0.07
14	0.07	0.05
15	0.05	0.04
16	0.04	0.03
17	0.03	0.02
18	0.02	0.02
19	0.02	0.01
20	0.01	0.01
Total	11.09	

Thus, a total of 11.09 Nm^3 of gas runs through our hypothetical compressor, which can pump this gas at a rate of 17.2 Nm^3/Hr using a 3 hp (2.25 KW) electric motor, which we will assume is 75% efficient. This means our compressor runs for 11.09/17.2 = 0.64 hours and consumes (2.25 KW)*(0.64 hours)/.75 = 1.93 KWh's or about 7.0 MJ.

Compressor energy = 7.0 MJ

The wet Methanol has been liquefied by the expansive cooling that takes place when the hot, high pressure vapor is de-pressurized in the knock out drum – no external energy is needed. But the wet Methanol, consisting of a mixture of 1.26 liters of Methanol and 0.56 liters of water needs to be distilled to extract pure Methanol.

To distill the wet Methanol, the mixture, initially at 40 ºC must be raised to a minimum of 65 ºC. This requires lifting 1Kg of Methanol 25 ºC:

(1Kg)*(2510 J/Kg ºC)*(25 ºC) = .06 MJ

plus raising 0.56Kg of water 25 ºC: (0.56Kg)*(4184 J/Kg ºC)*(25 ºC) = 0.06 MJ.

Then to boil off 1Kg of Methanol requires vaporization energy:

(1Kg)*(1.23 MJ/Kg) = 1.23 MJ

Finally, the gaseous Methanol must be cooled/condensed to a liquid state either by convective cooling, forced air cooling, evaporative cooling, or a closed loop system consisting of a fan, radiator, pump and coolant. We note that, while wasteful of water, evaporating ½ Kg of water would be sufficient to condense 1 Kg of Methanol and would add a miniscule 650 J to the pumping energy. But we will assume another method consuming 0.35 MJ is used for condensing out the Methanol.

Total for distillation: 1.7 MJ

Summing all the energy costs, we have:

Water pumping:	0.0015 MJ
Hydrogen Production (Electrolyzer energy)	29.3 MJ
Compressor energy	7.0 MJ
Distillation	1.7 MJ
Reaction heat	-1.5 MJ
Total Energy Costs for 1 Kg of Methanol:	**36.5 MJ**
Energy Content of 1 Kg of Methanol	**22.7 MJ**
Energy Balance (22.7/36.5)	**62%**

To put these numbers in perspective, it is useful to compare Methanol to liquid Hydrogen. To obtain the same energy content of 1 Kg (1.26 liters) of Methanol one needs 0.167 Kg (1.86 m^3) of Hydrogen. If this Hydrogen is produced by the same electrolyzer, we require (3.9 KWh/m^3)*(1.86 m^3) = 7.25 KWh or 26 MJ of energy.

This 1.86 m^3 of Hydrogen can be condensed into 2.35 liters of liquid Hydrogen (density 70.8 g/l) but the liquefaction process imposes a minimum 30% energy cost of 8 MJ. Thus the total cost of liquid Hydrogen with the same energy content of 1 Kg of Methanol is 34 MJ and the energy balance is 22.7/34 = 67%.

In comparison to Methanol, liquid Hydrogen requires twice the volume per energy content and a cryogenic storage system, which will experience boil-off losses of between 1 and 5% per day (depending on the size of the tank).

Appendix

Methanol, also called methyl alcohol or wood alcohol, is a colorless, water soluble liquid with a mild alcoholic odor. It freezes at -97.6 ºC, boils at 64.6 ºC and has a density of 0.791 at 20 ºC.

Properties of	Methanol	Hydrogen	Water
Chemical formula	CH_3OH	H2	H2O
Molecular weight g/mole	32.04	2.0	18.0
Melting point ºC	-97.6	-259.1	0
Boiling point ºC	64.6	-252.9	100
Density @ 20 ºC Kg/m^3	791	0.08988	1000
Energy content MJ/Kg	22.68	135.8	
Energy of vaporization MJ/Kg	1.23		2.26
Specific heat J/Kg ºC	2510		4184

Some useful conversion factors:
1 KWh = 3.6 MJ
1 calorie = 4.184 J
1 hp = 746 Watts
1 Watt = 1 J/sec
1 BTU = 252 calories