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# Improving the Distribution and Use of Biogas by Conversion to Methanol

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## Abstract

In this technology review, the process of turning an average biogas into methanol will be presented. The purpose is to find a better method of transporting the energy contained within biogas so that it may be used in industry as a value added product. The first step is removal of hydrogen sulfide, a corrosive chemical that can breakdown mechanical parts. The second step is carbon capture and conversion of the biogas into hydrogen. The final step is the hydrogenation of carbon dioxide into methanol using a copper catalyst and an alcohol co-catalyst.

## Overview

The businesses that produce the valuable raw materials for biogas production such as manure and decaying organic material are typically located several miles apart. The transport of these materials to a central processing facility is not economical because of poor logistics as well as health concerns over the nature of the material. The biogas that is produced either naturally as is the case of a landfill or in anaerobic digesters is usually considered a waste product of waste treatment and is burned in large flares. The biogas can be purified into bio-methane to power vehicles or used similarly as natural gas. However, the cost of building the necessary processing equipment would raise the price of the bio-methane to well above commonly available natural gas. If bio-methane is obtained, the next problem is getting the final product to market. There are strict regulations for pipeline injection of bio-methane into the natural gas network. Also, since natural gas normally contains a mixture of hydrocarbons such as propane and ethylene there are concerns about bio-methane diluting the energy content within the pipeline.

One concept that currently is being considered for natural gas locations in remote or difficult to access locations is converting the natural gas into methanol. The simplest molecular form of alcohol; methanol is a widely used building block for chemical industries. One example of this is Dimethyl ether (DME) that is used as a propellant, refrigerant, and vehicle fuel. Also it is a valuable liquid fuel that can be used as hydrogen storage for fuel cells. Another advantage is methanol does not require refrigeration or compression when placed into storage. Some drawbacks of methanol are that it is highly toxic and will dissolve certain materials such as plastic within machines.

**Hydrogen Sulfide Removal**

A critical first step in converting biogas into methanol is the removal of hydrogen sulfide. The reason for this is hydrogen sulfide undergoes chemical reactions that yield corrosive substances and the wearing down of machinery. For this technology review, the use of activated charcoal will be focused on. The regeneration of the activated charcoal produces contaminated water or solvent that must be treated in a separate process.[1]

Activated charcoal has three different chemical reactions to remove hydrogen sulfide that are dependent on the pH of the enviroment.[1]

In a pH above 7.0 the hydroxyl (HO) group dominates. The hydroxyl group causes a partial oxidation of hydrogen sulfide to form solid sulfur that gets trapped in the pores of the activated charcoal.[1]

A pH between 7 and 4.5, hydrogen sulfide converts into sulfuric acid as well as sulfur oxides.[1]

When the pH is below 4.5 the formation of sulfuric acid increases significantly. Solid sulfur is formed from the chemical reaction between the sulfuric acid and incoming hydrogen sulfide. This reaction is slower than the other two because it is both pH and concentration dependant.[1]

**Catalytic Activated Charcoal (CAC)**

Catalytic activated charcoal (CAC) is a carbon substrate that has been treated with a nitrogen compound such as urea or ammonia. The CAC unit can be regenerated with a water based method.[1]

**Impregnated Activated Charcoal (IAC)**

Impregnated activated charcoal (IAC) is a carbon substrate that is saturated with a solvent. A few of these are listed below[1]:

- Sodium bicarbonate ($NaHCO_3$)

- Sodium hydroxide (NaOH)

- Potassium iodide (KI)

- Potassium permanganate ($KMnO_4$)

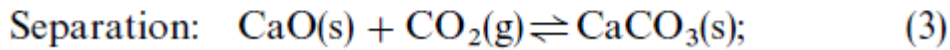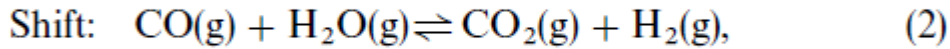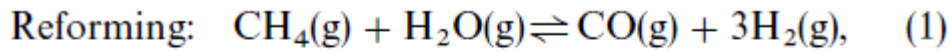The IAC pieces can be regenerated by washing with the original solvent.[1]

Since the composition of biogas is different at each site, additional purification steps such as removal of siloxanes or condensation of water vapor may be necessary.

**Conversion of Carbon Dioxide and Methane into Hydrogen**

The current method of hydrogen production is steam methane reforming (SMR). The SMR process operates at approximately 800° to 950°C and 20 atm (20.265 Bar). The system is highly inefficient because large amounts of supplemental fuel must be burned in order to maintain reformer temperature. The material from the reformer then travels through high and low temperature shift reactors. The last step is the removal of carbon dioxide by either anime scrubbing or pressure swing adsorption (PSA). With amine scrubbing the carbon oxides are often reduced further by methanation to achieve trace levels. Using a PSA device the product gas does not need further enrichment, but as much as 20% of the hydrogen generation may be lost during column blowdown and purging. The following reactor design integrates hydrogen production with enrichment in order to simplify the chemical process and conserve energy.[3]

The fixed bed CaO reactor uses a mixture of reforming catalyst and carbon sorbent so that the methane reforming, shift and carbon dioxide separation steps occur at the same time. The end result is a high concentration of hydrogen gas to be collected directly from the reforming system. This reactor also removes the need for a shift catalyst.

The main reactions that occur within a carbon capture reactor are shown below.[3]

Reforming:  $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g),$  (1)

Shift:  $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g),$  (2)

Separation:  $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s);$  (3)

In a standard methane reforming reactor the hydrogen concentration increases with temperature up to 76% at 850°C.  A more efficient approach is the use of a carbon sorbent; with this component hydrogen concentration reaches 96% at 725°C at a conversion efficiency of 88%. The carbon sorbent is no longer effective at temperatures of 850°C or higher. Since the carbon sorption process uses less fuel it is 20 to 25% more energy efficient than the current industry reactors.[3]

Liquid water was injected into the system using a high pressure syringe that is vaporized by an electric heater wrapped around the pipe. Nitrogen was used as a diluent to the feed gas due to the challenges of vaporizing large volumes of water at the reactor pressure of 15 atm (15 Bar).  Feed gas entered into the annular area between the reactor insert and pressure vessel. A furnace surrounded the reactor vessel preheating the gas to the required temperature. The heated gas flows downward through a bed of catalyst and calcinated calcium oxide sorbent. Excess steam is removed and the pressure reduced to 1 atm (1 Bar) using a backpressure regulator.[3]
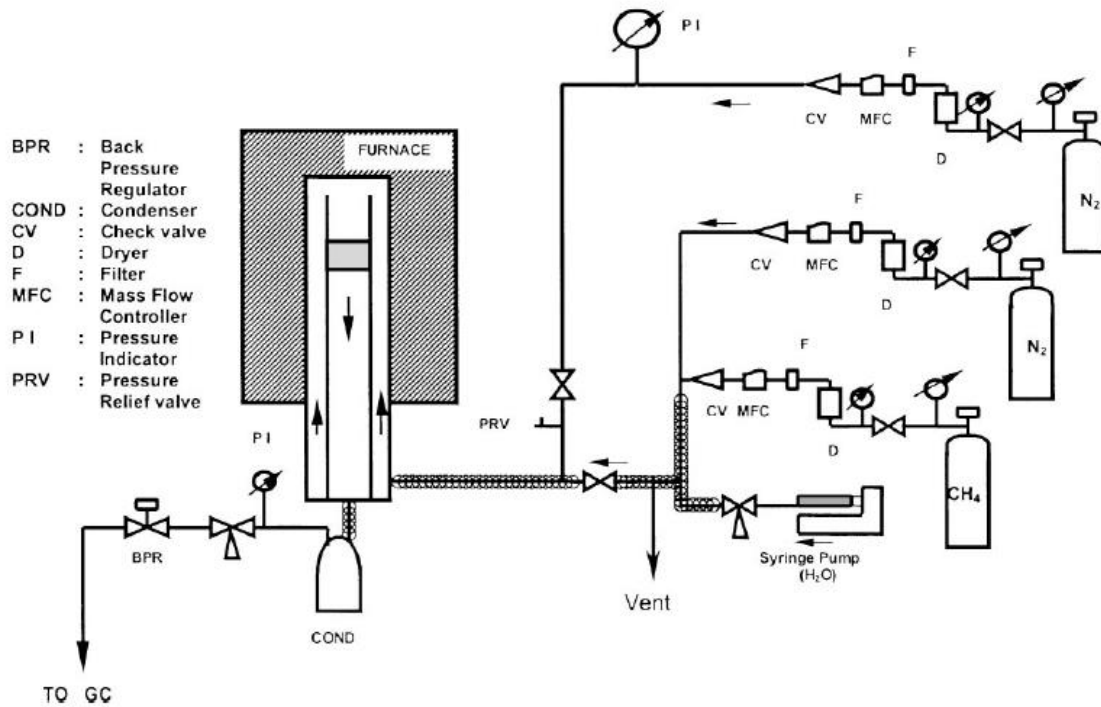
**Figure 1.** Carbon Capture Methane Reformer[3]

Table 1
Ranges of reaction parameters

| | |
|---|---|
| Temperature | 450–750°C |
| $CH_4$ content of feed gas | 6–20 mol% |
| Steam-to-methane ratio | 3–5 |
| Total gas feed rate | 200–1200 cm$^3$(STP)/min |
| Reforming catalyst | 3–7 g |
| Calcium oxide | 7–10 g |

The operating parameters for the Carbon Capture Methane Reformer can be seen in Table 1 above.[3]

After the CaO sorbent has been fully used it can be separated from the catalyst and replaced. The carbon dioxide content of the feed gas entering the reactor as well as the conversion rate will determine how often the sorbent will need to be exchanged.[3]

## Sorption-Enhanced Steam Methane Reforming (SE-SMR)

After the carbon dioxide is removed from the biogas by a molecular filter such as pressure swing adsorption or amide scrubber, a Sorption-Enhanced Steam Methane Reforming Reactor can be used.[2]

The SE-SMR is a process where during reforming carbon dioxide is captured in a sorbent powder that blows through a fluidized bed along with the catalyst particles. A metal oxide, denoted as MO below, is chemically transformed into a metal based carbonate. As a result a separate purification step to remove carbon dioxide at the end of syngas production is unnecessary or significantly reduced. Due to the carbon dioxide capture reaction in equation 4 that is seen below, the syngas reforming reaction can be performed at a temperatures of approximately 600°C .[2]

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \text{Reforming} \qquad (1)$$

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \text{Water-gas shift} \qquad (2)$$

$$CH_4(g) + H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g) \qquad 1+2 \qquad (3)$$

$$MO(s) + CO_2(g) \rightleftharpoons MCO_3(s) \qquad \text{Sorption (MO=solid oxide)} \qquad (4)$$

$$CH_4(g) + 2H_2O(g) \rightleftharpoons MCO_3(s) + 4H_2(g) \qquad \text{Overall, } 3+4 \qquad (5)$$

The metal based carbonate is regenerated in a separate vessel. The temperature required for the reverse of equation 4 depends on the metal sorbent and the partial pressure of the reactor. Common kinds of sorbents are processed CaO (lime) and dolomite; these materials require a temperature of 800°C to 900°C for regeneration.[2]

A catalyst / sorbent blend used in the reactor shown below, is 20% $Ni/NiAl_2O_4$ and 80% calcined dolomite.[2]
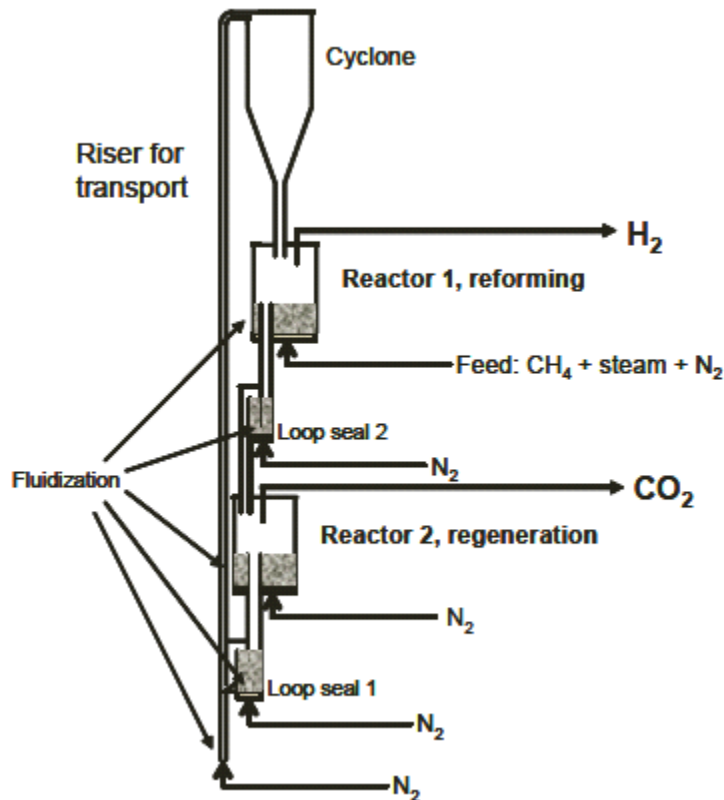


**Figure 2.** The Sorption-Enhanced Steam Methane Reformer using a circulating fluidized bed.[2]

In both reactor 1 and 2, nitrogen gas enters from the bottom at a speed necessary to fluidize the powder mixture. The loop seals prevent the mixing of gas from reactor 1 and reactor 2. The powder mixture gets blown from reactor 1 down an overflow pipe and eventually into reactor 2 for regeneration. The regenerated powder mixture travels further down to the riser which transports the powder back to the top of the cyclone for further reforming. In order to extract the product gas and keep the reactor powder from escaping, cyclone separators are used. The gas is bubbled through water tanks for additional purification and to capture any particles that have not been collected by the cyclones. The final step is to condense the water vapor from the product gas. The startup period for this reactor is one hour for the temperature and particle circulation to have stabilized. New reactor powder is added after several cycles in order to maintain optimum performance.[2]

## Plasmatron Reforming

Plasma reforming technology is seen as a way to solve the issues of slow ignition, the requirement of high external temperature sources to provide energy to the reaction and catalyst deactivation by small concentrations of sulfur compounds. Plasma can easily transmit the energy required to form the high density ion cloud using direct current (DC) electric discharges. This reactor has a startup time of a few seconds due to the advantages of partial oxidation of the feed gas. In addition to this, the reactor can accept a wide variety of flow rates and gas forms.[4]
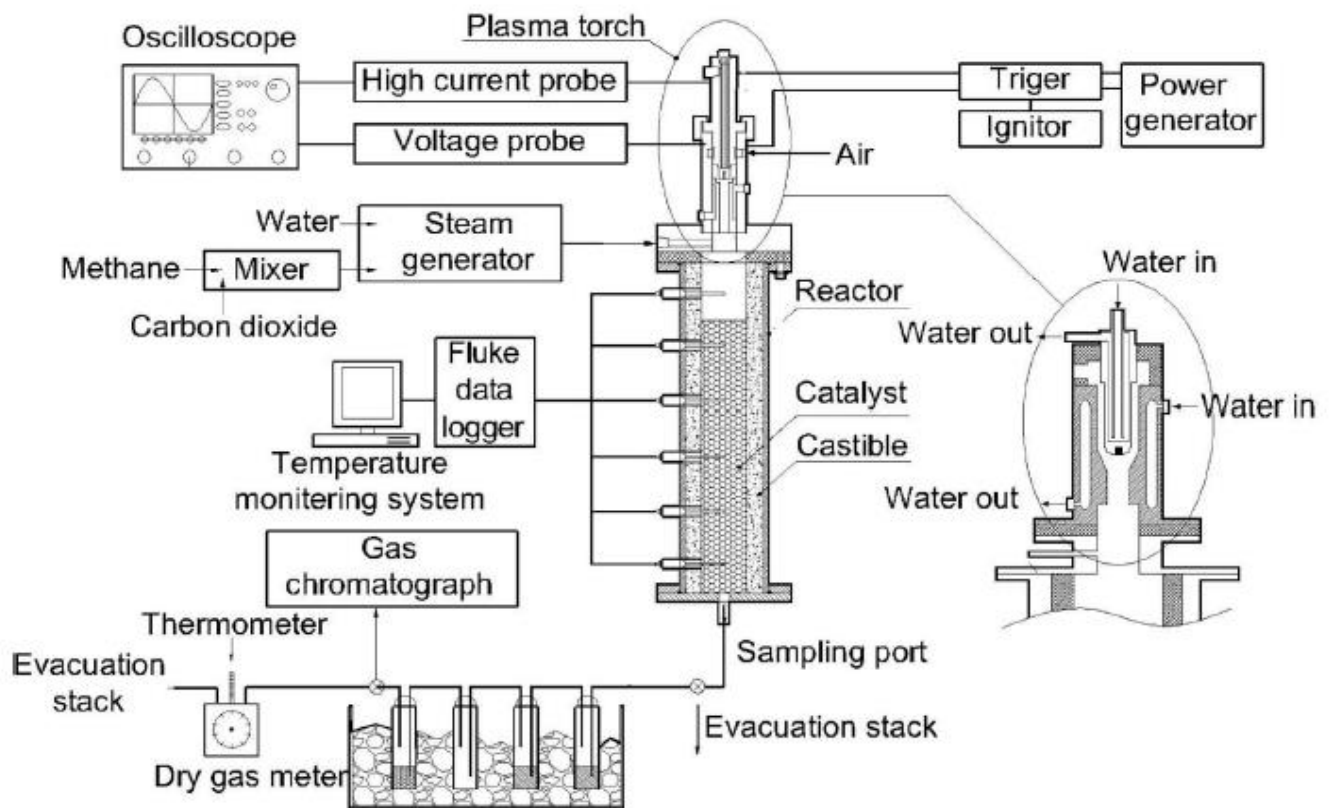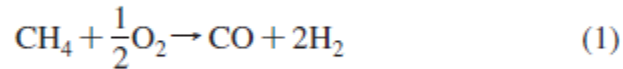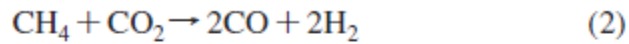


**Figure 3**. The overall layout of a plasmatron methane reformer.[4]

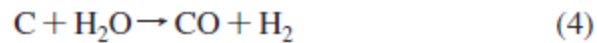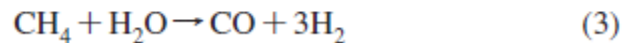Inside a plasmatron a variety of different reactions can take place. Here is a listing of the most common: [4]
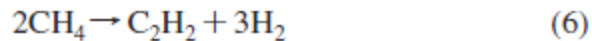
Partial-oxidation-reforming reaction

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (1)$$

Carbon-dioxide-reforming reaction

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (2)$$

Steam-reforming reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (3)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (4)$$

Plasma (cracking) reforming reaction

$$CH_4 \rightarrow C + 2H_2 \qquad (5)$$

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \qquad (6)$$

$$2CO \rightarrow C + CO_2 \qquad (7)$$

Water–gas-shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (8)$$

CO oxidation

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad (9)$$
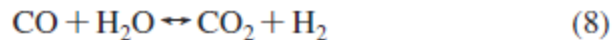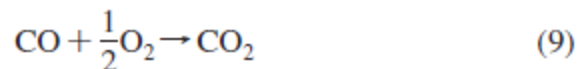
Catalytic surface reactions

$$CH_4 + NiO \rightarrow C_{(s)} + H_2 \qquad (10)$$

$$C_{(s)} + O_{(ad)} \rightarrow CO \qquad (11)$$
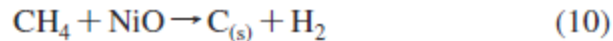
As you can see above, the end product of a plasmatron is hydrogen, carbon monoxide, and carbon dioxide. A plasmatron is essentially a plasma torch and power system with an enclosed reaction vessel. The power system is composed of a power generator, igniter, and trigger system. The input power is 6.4 kW (160 V and 40 A) with a startup voltage of 30 kW. The electrodes are cooled by a stream of cold water. A steam generator set at 335°C and feed gas intakes are also included. The reactor is brought up to 650°C before the feed gas is introduced. Partial oxidation occurs with the feed gas raising the reactor temperature further to 1100°C.[4]

Table 2. Syngas Concentration Dry Volume Percentage.[4]

| syngas concentration (dry vol %) | | | | | | CH₄ conversion rate (%)$^a$ | H₂/ CO | hydrogen yield (%)$^b$ | reformer thermal efficiency (%)$^c$ |
|---|---|---|---|---|---|---|---|---|---|
| H₂ | CO | CO₂ | C₂H₂ | CH₄ | N₂ | | | | |
| 45.4 | 6.9 | 1.5 | 1.1 | 0.9 | 45.1 | 99.2 | 6.6 | 78.8 | 63.6 |

In order to give an example of reactor performance, the product gases formed from a flow rate of 1.8 to 5.1 L/min using only methane gas and the input power of 6.4 kW is shown in Table 2.[4]

The higher the concentration of carbon dioxide in the feed gas the lower the hydrogen concentration in the product gas. As can be seen in equation 8, the higher carbon dioxide level shifts the equilibrium to producing $H_2O$ and carbon monoxide. With a carbon dioxide content of 14.2% the maximum hydrogen production was 33.5%. In contrast when steam was introduced into the chamber the level of hydrogen increased. This is due to the shift of equation 8 to produce hydrogen gas and carbon dioxide. Also, equations 3 and 4 are reaction pathways to produce hydrogen and carbon monoxide. The highest value of hydrogen gas, 50.4%, was obtained with pure methane and a steam flow of 30.2%. The operator of the production plant can balance the system based on the composition of the feed gas using the knowledge of these two reactions.[4]

## Low Temperature Methanol Production

In a conventional methanol production process a carbon conversion of only 10 to 15% of the carbon monoxide and hydrogen feed gas (syngas) gets converted into methanol. This is due to the thermodynamic limitations of the direct reaction of carbon monoxide and hydrogen gas. Therefore, several cycles through a reactor at 5.0 - 10.0 MPa (50 to 100 Bar) and 523- 573°K (249.85 to 299.85°C) is necessary to completely utilize the syngas. In comparison, the use of a alcohol promoter also known as a co-catalyst allows for a 70-100% one pass conversion of syngas at 5.0 Mpa (50 Bar) and 443°K (169.85°C).[7]

Using a Cu/ZnO and Cu/Al$_2$O$_3$ catalyst at 423$^o$K (149.85$^o$C) ethanol is added to the chamber to act as a solvent and co-catalyst. As the concentration of ethanol increases in the chamber the yield of methanol and ethyl formate also increase when syngas is added. When using carbon dioxide the reaction gradually increases up to a CO$^2$ content of 7.5%. When carbon monoxide and hydrogen gas is used the only product is ethyl formate unless water vapor is also present. Ethanol has a carbon conversion of 11.35% but also one of the lowest formate yield of 1.13%.[7]

## Supercritical Phase Methanol Synthesis Process

This reaction is another indirect path for methanol synthesis using syngas. During the production process steam, alcohol promoter, and a copper oxide based catalyst are the main materials needed. The environmental conditions for the reaction are 40 to 55 Bar of pressure and 423-443$^o$K (149.85 to 169.85$^o$C.). The kind of alcohol will affect the conversion rate of syngas to methanol due to the molecular structure, 2-butanol or 2-propanol are commonly used due to their high performance.  A conventional fixed bed reactor equipped with a vaporizer and a cooled high pressure trap form the reactor equipment. A supercritical fluid such as n-hexane or n-pentane can be used inside the reactor to increase reaction efficiency. These materials increase the ability to rapidly remove the heat generated. This method allows for milder conditions than other reactors; for example another kind of methanol reactor operates with a Cu/ZnO catalyst under 50 -100 Bar and 523-573$^o$K (249.85 to 299.85$^o$C).[6]
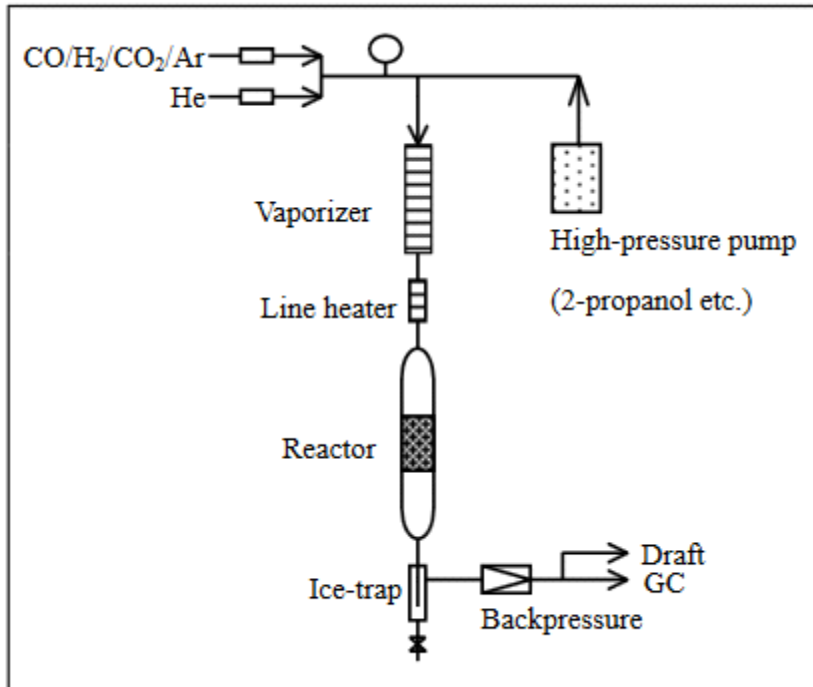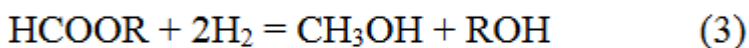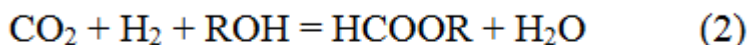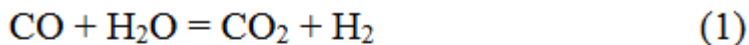
**Figure 4.** Supercritical Phase Methanol Synthesis Reactor. [6]

As shown in the formula below, the reaction process has three steps that occur within the one chamber reactor. The letter R in the formula represents the alcohol present in the reaction. The first reaction (1) is a water gas shift reaction, an esterification (2) and the formation of methanol from the hydrogenation of the ester (3).[6]

$$CO + H_2O = CO_2 + H_2 \qquad\qquad (1)$$

$$CO_2 + H_2 + ROH = HCOOR + H_2O \qquad (2)$$

$$HCOOR + 2H_2 = CH_3OH + ROH \qquad (3)$$

---------------------------------------------------------

$$CO + 2H_2 = CH_3OH \qquad\qquad (4)$$

The table below shows the total carbon conversion for different reaction promoters. Helium gas caused only 5.7 total carbon conversion. The supercritical fluid 2-butanol was able to more than double the carbon conversion than n-hexane alone due to the esterification.[6]

Table 3. Efficiency of Syngas Conversion into Methanol[6]

| Supercritical fluids | Total carbon conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|
| | | MeOH | HCOOR | HCHO | CH$_4$ |
| No | 5.7 | 96.8 | 0.0 | 3.2 | 0.0 |
| $n$-Hexane | 21.4 | 98.1 | 0.0 | 0.0 | 1.9 |
| 2-Butanol | 48.1 | 90.7 | 9.3 | 0.0 | 0.0 |

T = 538 K, P(total) = 55 bar, W(ICI) = 0.5 g, W/F(CO/H$_2$/CO$_2$) = 10 g.h.mol$^{-1}$, P(CO/H$_2$/CO$_2$) = 10 bar.

## Removal of the Methanol Product

Distillation is the process of separating chemical compounds by using a combination of temperature and pressure to vaporize the desired material. To remove the methanol from the alcohol co-catalyst a multistage distillation column is needed. The first step is to add water to decrease the flammable nature of pure alcohol solutions. A process is then carried out similar to the diagram below.[6] A Barg is the amount of gauge pressure in the measurement of a Bar.
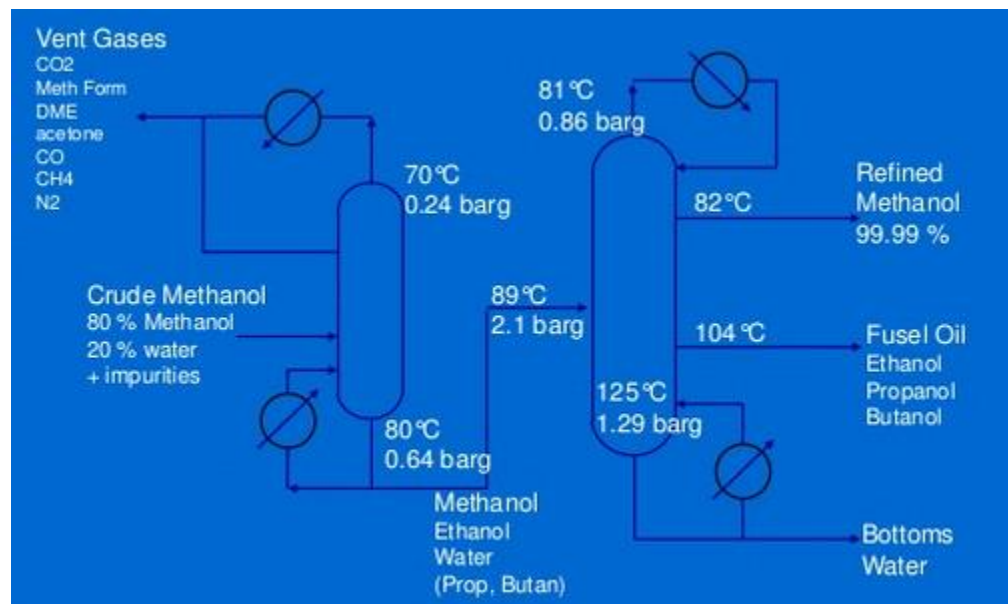


**Figure 5.** Methanol distillation flowchart.[5]

## Conclusion

The main focus of this article has been to convert biogas into a form that is easier to store and transport while having a high value to the industrial sector. The generation of hydrogen, carbon monoxide and carbon dioxide, commonly called syngas, is an important step to provide the raw materials for methanol production. The three syngas reformers provided in this article were selected for fast start-up times and compatibility with already constructed anaerobic digesters. The methanol synthesis reactor presented in this article was selected because it showed the greatest energy efficiency and simpler operation than large scale industrial plants. After distillation the methanol can be stored on site similar to other fuel alcohols or shipped to the end user with currently available transportation vehicles.

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