

# CARBON DIOXIDE REFORMING

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## INTRODUCTION

Carbon dioxide is generated as a waste byproduct in fossil fuels combustion, chemicals production and synthetic fuels manufacturing. Natural gas sometimes contains sizeable concentrations of CO<sub>2</sub>.

The CO<sub>2</sub> produced from fossil fuels is diluted into the atmosphere. New technologies are being developed to prevent or reduce the CO<sub>2</sub> generation at its source, or to capture the generated CO<sub>2</sub> for subsequent sequestration into depleted oil and natural gas reservoirs, deep coal seams, saline aquifers, or the deep ocean.

An alternative is to convert CO<sub>2</sub> into a valuable chemical product such as synthetic gas or syngas as a mixture of hydrogen and carbon monoxide. Hydrogen can be separated as an energy carrier for use in fuel cells in a hydrogen-based economy.

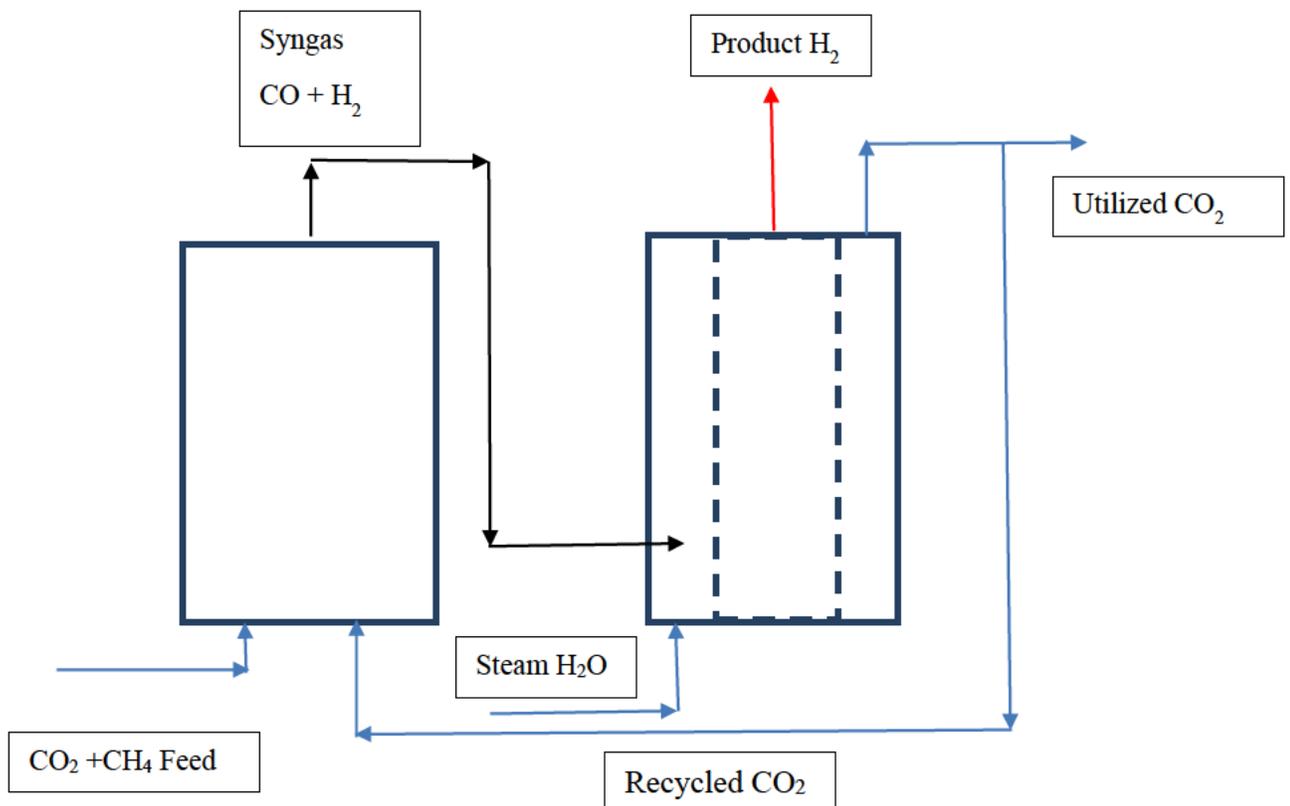


Figure 1. Hydrogen production using the CO<sub>2</sub> dry reforming process.

## FIXATION OF CO<sub>2</sub> AS A CHEMICAL

An option for the reduction of CO<sub>2</sub> emissions is its fixation as a chemical product. The advantage of CO<sub>2</sub> fixation over its disposal is that the production of chemicals with an economic value is possible.

Aresta et. al. [1, 2] have described the possibility of production of materials such as carbamic esters, urea and methylamines from CO<sub>2</sub> feed-stocks.

Through the process of dry reforming, CO<sub>2</sub> can be converted into synthetic gas; a mixture of hydrogen and carbon monoxide.

## DRY CO<sub>2</sub> REFORMING PROCESS

Synthesis gas (syngas), is a mixture of H<sub>2</sub> and CO and is a building block for several important chemicals.

The CO<sub>2</sub> dry reforming of natural gas produces syngas from the equation [3]:



Syngas can be produced by reforming natural gas with CO<sub>2</sub> or steam. Partial oxidation of natural gas and heavier hydrocarbon feed-stocks is another means of producing syngas.

Reforming of natural gas with CO<sub>2</sub> can produce syngas with a H<sub>2</sub>/CO ratio of unity at 1,652-1,832°F (900-1,000°C) and 1-20 atmosphere pressure.

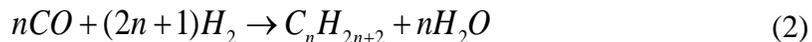
Group VIII metals such as nickel, Co, rhodium and ruthenium or Mo<sub>2</sub>C are suitable as catalysts for natural gas CO<sub>2</sub> reforming. Nickel has a high tendency of coking under most reforming conditions, but is still a preferred option. Palladium and platinum offer a compromise between costs and good functionality.

Alumina, magnesia, silica, zirconia, and titania have been considered as supports to the catalysts.

Syngas can be produced with imported CO<sub>2</sub> or from captured and recycled CO<sub>2</sub>. Syngas itself can then be converted into other products such as methanol, sulfur-free green diesel fuel and carbon.

## HIGHER VALUE PRODUCTS

Synthesis gas is an equimolar mixture of CO and H<sub>2</sub>. By adding H<sub>2</sub> to the reactant gas feed to establish the correct reactants ratio, it can be used to produce higher value products, most notably sulfur-free diesel using the Fischer-Tropsch process:



It can also be used to produce methanol:



The required additional H<sub>2</sub> would be supplied by the steam reforming of CH<sub>4</sub> through the reaction:



or through High Temperature Electrolysis (HTE) of water:



or other thermochemical processes.

The dry reforming reaction is highly endothermic and so energy has to be supplied to drive it.

Methanol is produced by the Syntex or ICI process in the temperature range 473-573 K, while reforming reactions are usually carried out in the temperature range 973-1,223 K.

The steam reforming of CH<sub>4</sub> produces CO<sub>2</sub> making the electrolysis process a better choice.

## **FISCHER TROPSCH, FT SYNTHESIS**

### **INTRODUCTION**

The Fischer-Tropsch (FT) process dates back to the 1920s when Fischer and Tropsch discussed the reaction of H<sub>2</sub> and CO using Co, Ni and Fe catalysts to produce paraffins, olefins, waxes and oxygenates.

The most likely long term application of the FT process concerns the conversion of natural gas to liquid transportation fuels as low sulfur green diesel fuel.

Green diesel fuel has a higher cetane rating compared with conventional diesel fuel. Green diesel also contains virtually no sulfur compounds. It is low in aromatics, greatly reducing soot and particulate emissions.

The FT process is highly exothermic. The heat released per mole of CO is about 1,000 kJ, for an end product as C<sub>6</sub>H<sub>12</sub>.

The highly exothermic reaction causes a number of problems in the design of an effective FT reactor. As a solution, if the heat generated can be rapidly transported from the reactor to heat exchangers it can be used to provide energy to the endothermic CH<sub>4</sub> reforming reactions.

The overall reforming and FT process is slightly endothermic with ΔH = 23 kJ. A small amount of CH<sub>4</sub> combustion is required to drive the process.

This approach is carbon neutral in that the fixated carbon in the green diesel will eventually be burnt in an engine releasing it back into the atmosphere.

### **DESCRIPTION**

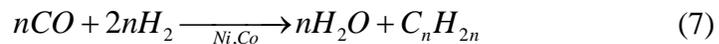
This process was developed in the 1920s by German scientists Franz Fischer and Hans Tropsch. It uses gasified coal or natural gas to produce paraffin wax that can then be refined into diesel, naphtha, and liquid petroleum gases such as butane and propane. Using catalysts such as Ni, Co, Fe, ThO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, MnO, and clays, a series of chemical reactions occur that convert carbon monoxide and hydrogen into various hydrocarbons.

In the Fischer Tropsch industrial process carbon monoxide is reacted with hydrogen to synthesize hydrocarbons. The synthesis conditions are at 150 bar and 700 K in the presence of a catalyst.

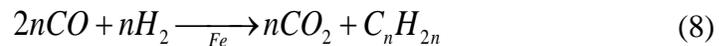
In the case of natural gas methane to liquids applications the suggested basic chemical reaction would be:



With Ni and Co used as catalysts, the following reaction would occur:



If, instead, a Fe catalyst is used the reaction proceeds as follows:

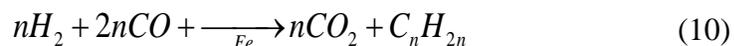


During World War II, Germany being unable to secure sufficient oil supplies, used the process to produce about 600,000 metric tonnes of synthetic gasoline in the year 1943.

When the initial products are generated by the gasification of coal or biomass (CH), the chemical reaction is:



An iron catalyst is then used to catalyze the reaction:



The intermediate mixture of carbon monoxide and hydrogen is commonly referred to as synthetic gas, or syngas in short.

This metastable process yields 200 grams of hydrocarbons from a 1 m<sup>3</sup> mixture of CO and H<sub>2</sub>. The reaction occurs around a pressure of 150 bar and 700<sup>o</sup> K.

The metastability of the reaction requires that the produced hydrocarbons would be destroyed unless they are promptly cooled and their pressure reduced.

## HISTORY OF THE FISCHER TROPSCH PROCESS

During World War II, petroleum-poor but coal rich Germany used the Fischer-Tropsch (FT) process to produce diesel and aviation fuel for their army after the allies curtailed its petroleum imports. In 1944, Germany produced over 90 million tons of synthetic FT oil. When General George Patton's Third Army rolled into Germany, it was fueled by FT diesel; he had to drain fuel from the captured German vehicles and use it on his own after overextending his fuel supply lines.

Synthetic fuels were previously researched in the USA as early as 1925. In the 1940s, a Synthetic Liquid Fuels Act passed by Congress appropriated over \$80 million for research and production. By the 1950s, the USA was producing thousands of gallons of synthetic gasoline a day at a test plant in Missouri, but the discovery of cheap oil, combined with a claimed lobbying effort by the oil industry, resulted in the government abandoning its synfuel research. During the oil crisis in the late 1970s, the federal government briefly pursued synfuel production, but abandoned the idea when the price of oil receded.

The FT process was also used to produce most of South Africa's diesel fuel during its isolation and international sanctions under the Apartheid regime. Since 1955, the South African company Sasol had produced about 1.5 billion barrel of synthetic fuel from around 800 million tons of coal. Currently, Sasol accounts for approximately 29 percent of that nation's fuel.

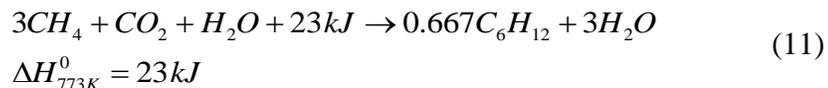
Plants built in response to fuel embargoes in South Africa are estimated to produce around 200,000 barrels of oil per day. Aircraft departing from Johannesburg International Airport have done so using a semi-synthetic blend of 50 percent jet fuel produced from coal by Sasol and 50 percent derived from traditional crude oil refining. Sasol attempted at some point to win final regulatory approval for use of 100 percent synthetic fuel, also derived from coal.

## DISCUSSION

A main characteristic of this reaction is that it is metastable under its pressure and temperature conditions. The produced hydrocarbons would be destroyed unless they are promptly cooled and their pressure reduced.

## SULFUR-FREE GREEN DIESEL

The first step involves the reforming of  $\text{CH}_4$  to produce synthesis gas while in the second step the resulting synthesis gas is reacted to produce the diesel fuel:



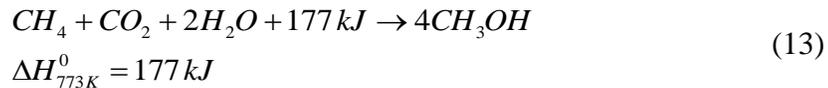
With energy efficiency of 80 percent, the energy required to drive the reaction is 28.8 kJ. This energy can be supplied by burning  $\text{CH}_4$  at the expense of 0.05 moles of  $\text{CO}_2$  per mole of  $\text{CO}_2$  consumed in the Fischer-Tropsch process.

## METHANOL PRODUCTION

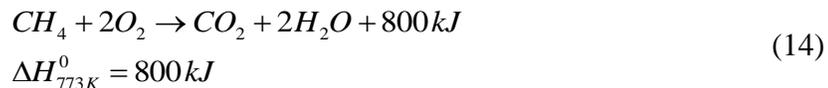
A first step involves the formation of synthesis gas via the combined steam and CO<sub>2</sub> reforming of CH<sub>4</sub>:



Following the reforming step, methanol is synthesized by reacting the resultant synthesis gas. The overall process can be described as:



At a heat efficiency of the system of 80 percent, the energy needed to drive the reaction increases to 221 kJ. For 1 mole of CO<sub>2</sub> to be consumed a heat input of 221KJ is needed from an external source by burning natural gas:



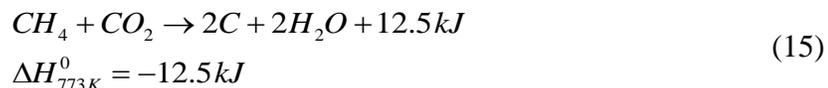
In this case 0.34 moles of CO<sub>2</sub> will be released so as to provide the required energy to drive the overall methanol synthesis reaction. The overall amount of CO<sub>2</sub> consumed in the methanol synthesis process is 0.66 moles per mole of CO<sub>2</sub> consumed by the initial reforming of CH<sub>4</sub>.

Methanol is a useful commodity with a worldwide annual production of 30 x 10<sup>6</sup> million tonnes. Methanol is synthesized in a process where synthesis gas is produced solely by the steam reforming of CH<sub>4</sub>.

If all the methanol production in the world were to be shifted to a process which combined CO<sub>2</sub> and steam reforming, 10 million tonnes of CO<sub>2</sub> could be consumed corresponding to the mitigation of 6.6 x 10<sup>6</sup> metric tonnes of CO<sub>2</sub> annually. Unfortunately, this amount is insignificant in comparison to the global CO<sub>2</sub> emissions. Excluding deforestation and land use change, CO<sub>2</sub> emissions amounted to 23.9 x 10<sup>9</sup> metric tonnes in 1996.

## CARBON PRODUCTION

For carbon production, the steam reforming is not necessary to provide additional H<sub>2</sub> and the process could occur directly according to the reaction:



In this case,  $\Delta H^0 < 0$  for all temperatures and as a result there is no need for additional  $\text{CH}_4$  combustion.

Another approach is through the production of synthesis gas followed by the reduction of CO:



The production of carbon enables 1 mole of  $\text{CO}_2$  to be mitigated per mole of  $\text{CO}_2$  reacted initially in the reforming reaction.

The carbon formed can be used as an adsorbent, as a catalyst support, in the production of synthetic diamonds using Ni/Fe alloys as catalysts.

If the aim is just to remove  $\text{CO}_2$  from flue gases and the cost of  $\text{CH}_4$  required is not a serious factor, the carbon formed can be readily disposed of.

## **TECHNOLOGICAL HURDLES**

A challenge is the development of an economical and stable catalyst suitable for use in commercial scale plants.

An important issue is the cost effective capturing of  $\text{CO}_2$  from  $24 \times 10^6$  metric tons of gas emissions each year from fossil fuels.

If current  $\text{CO}_2$  capturing cost could be reduced by 35-40 percent  $\text{CO}_2$  and natural gas reforming can be potentially sustainable from  $\text{CO}_2$  recovered from flue gases.

## **REFERENCES**

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3. Damien Treacy and Julian R. H. Ross, "The Potential of the  $\text{CO}_2$  reforming of  $\text{CH}_4$  as a Method of  $\text{CO}_2$  Mitigation. A Thermodynamic Study," Am. Chem. Soc., Div. Fuel Chem., 49(1), 127, 2004.