

# Optimization of a Water Gas Shift Reaction

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# Optimization of a Water Gas Shift Reaction

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## Abstract

The optimum flow rate of steam ( $H_2O$ ) to the reactor for the purpose of producing hydrogen gas for sale is determined.

## Keywords

hydrogen gas, Fischer-Tropsch process, equilibrium constant, optimum flow rate

## PROBLEM STATEMENT

The continued use of fossil fuels all over the world leads to the increased emission of greenhouse gases such as carbon dioxide into the atmosphere of the earth as it can be read in the following statement from the United States Environmental Protection Agency (EPA) “[greenhouse gases pose] significant risks to humans and the environment”. In the 2015 report the Environmental Protection Agency estimated that an extremely high number of lives would be saved if to increase the efforts to mitigate greenhouse gases [CIRA, 2015; EPA, 2017]. These efforts include activities such as replacement of fossil fuels with alternatives such as sources of biomass and hydrogen, or the use of renewable energy like geothermal, solar, and wind. The other kinds of mitigation are to use production methods that have low emissions and reduce carbon dioxide in the atmosphere through the expansion of forests. Hydrogen is an alternative fuel that has recently gained worldwide support [TT, 2017]. This project focuses on the increasing production of hydrogen in the industry.

The idea of a hydrogen economy has gained popularity over time, and the focus of the consideration of hydrogen as a replacement source of fuel for hydrocarbons is on the increase. Currently, hydrogen is largely produced industrially from reforming the steam; it uses fossil fuels like coal, natural gas, or oil. This project aims to determine the maximizing conditions of the production of hydrogen gas in industries through the use of the water gas shift reaction. According to the United States Department of Energy (DOE), both the transportation and the stationary energy sectors have a great potential for growth if hydrogen is used extensively.

## MOTIVATION

Knowing that fossil fuels are responsible for many forms of pollution, including the high emission of greenhouse gases, the replacement of fossil fuels has recently been under consideration. Given that hydrogen has been known to burn clean, i.e., it does not produce polluting emissions and thus it does not impact negatively the environment. Maximizing its use worldwide can be a considerable improvement for the environment. For instance, in Japan or California, the Honda and Toyota industries have begun leasing fuel cell vehicles to the public. However they face the challenge of high production costs of fuel cells and the lack of a refueling network for hydrogen. These are major issues which the automakers are trying to address. Lack of demand, safety, and cost are some of the reasons that cause oil companies to fail in setting up hydrogen tanks at the existing gas stations.

Ditching of fossil fuels for hydrogen will come with a lot of benefits to the environment in general. In fact, the burning of fossil fuels like natural gas, oil, and coal has been known to take a heavy toll on the environment hence leading to a significant contribution to both global problems like global warming and local problems like raised particulate levels. In addition, the byproducts of running hydrogen-powered fuel cells are a trickle of water and oxygen, neither of these byproducts can cause harm to the health of human beings or the environment. As at now, a high fraction of the hydrogen that is available in the United States is either made by the use of electrolytic processes which are powered by fossil fuels or extracted directly from the fossil fuels, therefore negating real emissions savings or reducing the use of fossil fuels. A dream of a clean hydrogen fuel can be realized if the source of the gas does not involve the use of fossil fuels.

Before hydrogen can replace fossil fuels, the problems associated with its utilization and production need to be addressed, for instance, the shortage of infrastructure for its storage and efficient distribution [Elghawi et al., 2008]. However, in the meantime, short term solution of this problem can be on board production of hydrogen, this kind of production may, however, have its setbacks. For example, the performance of the utilized catalysts during the process and process units' compactness [Cheekatamarla et al., 2008]. One of the processes that can aid in the production of clean hydrogen gas is through the employment of the water gas shift reaction.

In 1780, Felice Fontana, an Italian physicist, discovered the water gas shift reaction and much later, the industrial value of the reaction was realized. Early in the 20th century, hydrogen gas was derived through reaction of steam under extremely high pressure to yield hydrogen, iron oxide, and iron. With time, industrial processes, such as the Haber-Bosch process of ammonia synthesis, that required hydrogen developed and an efficient and less expensive method of producing hydrogen was required in order to save on costs. As a solution to the problem, the water gas shift reaction was put together with coal gasification to produce pure hydrogen.

The Fischer-Tropsch process was developed originally by Hans Tropsch and Franz Fischer during the early 1920s, it consists of a series of chemical reactions which involve the conversion of carbon monoxide and hydrogen into hydrocarbons of the liquid state by employing the use of a catalyst. The process also leads to the production of synthetic fuel and lubrication oil such as biomass, coal, and natural gas which are of a general higher quality as compared to those obtained from means of the convention with no aromatics or Sulphur. It has therefore gained importance as a huge source of low-sulfur fuel and also in addressing the supply and cost of hydrocarbons that are derived from petroleum. The conditions of the FT process are normally to favor the production of liquid fuels with a higher molecular weight, it also involves some side

reactions, and this is where the predominance of the water-gas-shift reaction is found. The equation is as follows:



Based on the process employed, catalyst, and the temperature, a range of hydrocarbons from methane to paraffin and higher molecular olefins can be obtained. Although the Fischer-Tropsch synthesis employs the usage of several catalysts, the most common catalysts used include cobalt, nickel, iron, and ruthenium transition metals. The selection of these catalysts is however determined by the production of the diesel fuels and linear alkanes of a high molecular weight. The tendency of Nickel to promote the formation of methane makes it less used, cobalt is preferred over ruthenium since ruthenium has a higher cost, and also, cobalt is generally more active. Iron has a relatively lower cost and a higher water-gas-shift activity, thus suitable for deriving synthetic gas that has low hydrogen/carbon monoxide ratio. Promoters like potassium, copper, and silica or alumina which are known to be high surface area binders and also inclusive of the active metal that makes up the catalyst. The catalysts are prone to get poisoned if sulfur compounds exist in synthetic gas.

The produced hydrogen has an energy content which is much less in comparison to that of the original fuel, some energy is lost in the form of excessive heat in the process of production, the process of steam reforming also results in emissions of carbon dioxide. 4 % of hydrogen in 2004 is produced through the process of electrolysis that involves the use of water and electricity.

## MATHEMATICAL DESCRIPTION AND SOLUTION APPROACH

The water gas shift reaction leads to the production of carbon monoxide (CO) together with hydrogen which requires separation so as to derive pure hydrogen suitable for polymer electrolyte membrane fuel cell (PEMFC) in order to avoid anode corrosion and enhance the efficiency of the fuel cell. The water gas shift reaction (WGSR) is just but one of the many methods that are used in purification of the hydrogen produced from reforming of hydrocarbons and has therefore proven to be the most feasible method of purification technologically [Barbieri et al., 2008]. It involves the reaction between steam ( $H_2O$ ) and carbon monoxide ( $CO$ ) to form carbon dioxide and hydrogen in accordance with the following equation:



To begin, the water gas shift reaction can be assumed to operate close to equilibrium, in which case the moles of reactants and products are related by the equilibrium expression:

$$K = \frac{n_{H_2} \times n_{CO_2}}{n_{CO} \times n_{H_2O}} . \quad (3)$$

This Equilibrium expression is the ratio of the concentration of the products over the reactants, where  $n_{H_2}$ ,  $n_{CO_2}$ ,  $n_{CO}$ , and  $n_{H_2O}$  are the moles/sec of hydrogen, carbon dioxide, carbon monoxide and steam leaving the reactor, respectively. The feed into the reactor consists only of  $CO$  and  $H_2O$ . At the start, there is a basis of 1 mol/s of  $CO$  and  $S$  mols/s of steam entering the reactor. The reactor is operated at 300 °C degrees, and the value of the equilibrium constant is 40. The task is to find the value of  $S$  that will maximize the profit of the production of hydrogen.

To find the number of mols/s of  $CO_2$  that react, let  $CO_2 = x$ . Using the process of Stoichiometry, the number of moles for each compound in the reaction can be obtained:



We can summarize the results given by equation (4) as follows:

- 1) for every  $x$  moles of  $CO$  and  $H_2O$  that react,  $x$  moles of  $H_2$  and  $CO_2$  are formed;
- 2) for every  $x$  moles of  $CO_2$  produced,  $1-x$  moles of  $CO$  react;
- 3) for every  $x$  moles of  $CO_2$  produced,  $S-x$  moles of  $H_2O$  react;
- 4) for every  $x$  moles of  $CO_2$  produced,  $x$  moles of  $H_2$  are also produced.

Using the number of moles found, an equation for the profit can be obtained. In order to have a profit, from the sales of  $H_2$  we should subtract the cost of steam:

$$\text{Profit} = \text{Sales of } H_2 - \text{Cost of Steam} \quad (5)$$

This could be also written in the following form:

$$\frac{\$}{\text{mol } H_2} \times n_{H_2} - \frac{\$}{\text{mol } H_2O} \times n_{H_2O}, \quad (6)$$

where  $\frac{\$}{\text{mol } H_2}$  has the meaning of cost of  $H_2$  per mole produced, which is 8 times the cost of  $H_2O$ ,

$n_{H_2}$  is equal to  $x$  as found from Equation (1),  $\frac{\$}{\text{mol } H_2O}$  is equal to the cost of  $H_2O$  per mole, and

$n_{H_2O}$  is equal to the amount of steam (i.e.  $S$ ).

The equation for the profit could be simplified:

$$P = 8 \times \text{Cost of } H_2O \times x - \text{Cost of } H_2O \times S . \quad (7)$$

Therefore:

$$P = 8x - S . \quad (8)$$

Equation (3) has to be solved for the equilibrium constant which [is] was given in order to substitute into equation (8). We have:

$$40 = \frac{x^2}{(1-x)(S-x)} . \quad (9)$$

We can now solve for  $S$ :

$$S = \frac{x(40-39x)}{40(1-x)} . \quad (10)$$

Equation (8) now reads as:

$$P(x) = 8x - \frac{x(40-39x)}{40(1-x)}. \quad (11)$$

With this information, the maximum value of the profit can be found by taking the derivative of the function  $P(x)$ :

$$P'(x) = \frac{281x^2 - 562x + 280}{40(1-x)^2}. \quad (12)$$

We can now solve the quadratic equation in order to obtain the stationary points:

$$x^2 - 2x + 280/281 = 0. \quad (13)$$

We obtain two roots of Equation (13):

$$x_1 \approx 1.0597, \quad (14)$$

$$x_2 \approx 0.9403. \quad (15)$$

The value given by (14) is not consistent as we cannot have a reaction with more than we feed on  $CO$ . It follows that the only reasonable value for  $x$  is given by (15). We can now use it to find the value of  $S$  from (10):

$$S = \frac{0.9403(40-39 \times 0.9403)}{40(1-0.9403)} \approx 1.31. \quad (16)$$

Now, this implies that for every 0.9403 moles of  $CO$  and  $H_2O$  that react, 0.9403 moles of  $CO_2$  and hydrogen gas are formed. And for every 0.9403 moles of  $CO_2$  moles that are produced,  $(1 - 0.9403)$  moles = 0.0597 moles of carbon monoxide and  $(S - x \Rightarrow 1.31 - 0.9403)$  moles = 0.3697 moles steam react. Also, for every 0.9403 moles of carbon dioxide produced, 0.9403 moles of hydrogen gas are also produced.

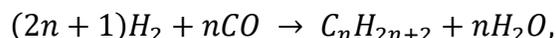
These are the amounts of each substance that should take part in the reaction water gas shift reaction to ensure the attainment of maximum profits.

The production of maximum amounts of oxygen is required in order for maximum profits to be obtained by the company, we have seen that for this to be achieved, the application of

calculus is essential in the calculation of the values of the number of substances that are taking part in the reaction to obtain maximum hydrogen gas, thus maximum profit. Through the use of the maximum profit formula in Equation (3), the value of the maximum profit that can be attainable by the company can then be calculated.

## Discussion

The water gas shift reaction discussed is used in the Fischer-Tropsch reactor to adjust the ratio of Carbon monoxide to Hydrogen gas while producing liquid fuels. Utilization of the water gas shift reaction in the production of hydrogen, therefore, plays a vital role in the Fischer-Tropsch reactor since hydrogen is one of the input gases. This process involves the combination of hydrogen and carbon monoxide which are produced from natural gas, biomass, or coal in the gasification process; it then turns the gases into a synthetic fuel and synthetic lubrication oil. This process produces a wide variety of hydrocarbons (with the general formula  $C_nH_{2n+2}$ ) through the occurrence of a series of chemical reactions that lead to the production of alkanes as shown in the following formula:



where the value of  $n$  ranges between 10 and 20. Most alkanes that are produced through this process are usually straight-chain and mostly used as diesel fuels. In addition, competing reactions result in the formation of alcohols, alkenes, and even oxygenated hydrocarbons. The conversion of the combination of  $CO$  and  $H_2$  into the different products is a multi-step reaction that also produces several intermediates. The  $C-O$  bond in carbon monoxide is split and thus a new bond of the form  $C-C$  is formed. For the production of one  $-CH_2-$  group through the reaction  $CO + 2H_2 \rightarrow (CH_2) + H_2O$ , the following reactions should take place:

- Adsorption of  $CO$  associatively;

- The splitting of the  $C-O$  bond in carbon monoxide;
- Adsorption of  $2H_2$  associatively;
- Formation of  $H_2O$  through the transfer of  $2H$  to the oxygen;
- $H_2O$  desorption;
- Formation of  $CH_2$  through the transfer of  $2H$  to the carbon.

The product becomes incorporated with alcohol if isotopically labelled alcohol is added to the feed stream.

## CONCLUSION AND RECOMMENDATIONS

For profit maximization to occur in a company, maximum production of hydrogen gas is required. For instance, if the reactor operates at a temperature of  $300\text{ }^\circ\text{C}$  and an equilibrium constant  $K$  of 40, the number of moles of steam required for the water gas shift reaction as calculated above is 1.31 moles. Given that when one mole of hydrogen is sold it yields 8 times the cost of one mole of steam required for the feed, then the producing company can obtain more steam which can in turn facilitate production of more hydrogen, required in large amounts for more profits.

The water gas shift reaction, as it has been seen, yields carbon dioxide as one of its products. Since the latter is a gas that may contribute to global warming, it would be relevant to study other means of reducing the emission of carbon dioxide. An efficient method is through dissolution in water at a pressure of approximately ten atmospheres. Carbon dioxide can also be solidified to form dry ice and then used in this form as a refrigerant, this can then play a big role during the shipping of perishable products. The formation of dry ice takes place when liquefied and compressed carbon dioxide at a temperature of  $-57\text{ }^\circ\text{C}$  or even lower is subjected to

expansion till atmospheric pressure is attained. Spontaneous cooling will therefore occur and the liquid will freeze to a solid, usually referred to as dry ice.

According to the results obtained above, the better results would be obtained if the use of catalysts that are impregnated under vacuum conditions are used as opposed to those impregnated under atmospheric conditions. Also, the optimum reaction temperature for the water gas shift reaction process is found to be 500 °C, either operating at 550 °C or at 450 °C. This process should therefore be carried out at its optimum conditions in order to obtain maximum output, i.e. more hydrogen gas, which will in turn increase the profits.

For future research, it is recommendable to study the ratio of steam to carbon monoxide and also that of hydrogen gas to carbon dioxide be varied in the experiments in order to correctly find out the rate of dependence on the concentration of steam, carbon dioxide and hydrogen gas.

## NOMENCLATURE

SYMBOL	DESCRIPTION
$CO_2$	Carbon dioxide
$CO$	Carbon monoxide
$H_2$	Hydrogen
$H_2O$	Steam
$K$	Equilibrium constant

$^{\circ}\text{C}$	Degrees Celsius
WGSR	Water gas shift reaction
$P$	Profit
$S$	Steam
$n$	Number of moles
$x$	$\text{CO}_2$

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