



# Dry Reforming of Methane – Review of Feasibility Studies

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Starting from carbon dioxide and methane, the dry reforming of methane produces synthesis gas which is a mixture of hydrogen and carbon monoxide. Although this concept has many environmental and economic incentives, unfortunately, there are no commercial processes for dry reforming of methane. In this paper a review of feasibility studies is presented. Firstly, a comparison between the steam reforming and the dry reforming of methane is performed as well as a study of the production of methanol and sulfur-free diesel from the dry reforming of methane.

Furthermore, a thermodynamic analysis is carried out by the method of equilibrium constants, for defining the thermodynamic limit and the optimum conditions.

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) has been identified as the most significant greenhouse gas arising from anthropogenic activities. It is of great importance to reduce anthropogenic CO<sub>2</sub> emissions in order to counteract global warming. One such method, which is presently being extensively investigated, is the capture and sequestration of CO<sub>2</sub> produced by concentrated sources (such as industry and power stations) and in particular the research of best chemical solvents able to minimize the cost of regeneration and thus that of the capture (Rivera-Tinoco and Bouallou, 2010). However, no one can be sure of the potential influence of CO<sub>2</sub> buried on the ecosystem in the long term. Conversion of CO<sub>2</sub> instead of its sequestration is presently being explored as one potential alternative solution (Abidin et al., 2011). Methane (CH<sub>4</sub>) reforming with carbon dioxide can produce a synthesis gas (a mixture of hydrogen: H<sub>2</sub> and carbon monoxide: CO) having a ratio close to unity H<sub>2</sub>/CO = 1 (Bradford and Vannice, 1999; De Castro et al., 2010).

Today, the industrial application of dry reforming of methane is limited. Indeed, there are only two industrial processes of this kind which produce synthesis gas called CALCOR (Teuner et al. 2001) and SPRAG (Udengaard et al., 1992) respectively. Similarly, there are only two pilot plants for the production of more interesting products such as: hydrogen (H<sub>2</sub>) (Aboudheir et al. 2007) and synthetic fuels (naphtha (C<sub>8</sub>H<sub>18</sub>-C<sub>12</sub>H<sub>26</sub>), kerosene (C<sub>11</sub>H<sub>24</sub>-C<sub>13</sub>H<sub>28</sub>) and gasoline (C<sub>5</sub>H<sub>12</sub>-C<sub>12</sub>H<sub>26</sub>)) (Fuyuki et al. 2004).

This paper will assess whether dry reforming can be viably used as a method of CO<sub>2</sub> mitigation. We will calculate energy and CO<sub>2</sub> balances for a number of all over process scenarios involving the production of synthesis gas followed by the production of some other product (hydrogen, methanol, sulfur-free diesel). Also we will establish a thermodynamic analysis to define the thermodynamic limit of this reaction.

## 2. Methods of analysis

### 2.1 Comparative study between the dry and steam reforming of methane

Steam reforming is a widely used process for producing synthesis gas rich in hydrogen with a high H<sub>2</sub>/CO ratio (> 3). This is an endothermic reaction such as:



that needs to provide heat energy. This energy can be provided by an external source which does not emit CO<sub>2</sub> such as solar or nuclear energy. But generally, this energy is provided by fossil fuels. Otherwise, several authors have proposed to use the CO<sub>2</sub> produced by many industrial facilities: cement plants, blast furnaces ... and to conduct studies on the dry reforming reaction which is:



Dry reforming produces synthesis gas with H<sub>2</sub>/CO ratio equal to 1 which is much lower than the synthesis gas produced by steam reforming. It also appears that the amount of heat to be supplied is greater than that required for steam reforming.

In this study, we calculate the energy balance and CO<sub>2</sub> balance for both reforming namely, the dry reforming and steam reforming, in order to make a comparison between the two processes for producing synthesis gas and hydrogen.

Currently, over 90% of the production of hydrogen is provided from hydrocarbons (Fuyuki et al. 2004) especially the natural gas that consists primarily of methane. In this case, the production of hydrogen occurs in two steps: the first step is to produce synthesis gas and the second involves the WGS reaction: Water Gas Shift (Eq. 3):



In our calculations, we assume that: The energy efficiency of hydrogen production is 88 % (Spath and Mann, 2001), the temperature to calculate the enthalpies of reactions is: 973 K and the remainder of the energy required can be attained from the combustion of natural gas (Eq.4):



The energy calculations are based on PCI and the enthalpies of reactions.

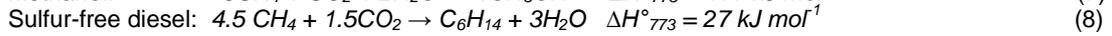
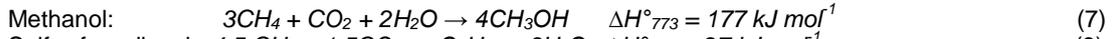
### 2.2 Production of synthetic fuels from dry reforming

Much of the work carried out on dry reforming has been justified by the argument that the reaction offers a pathway for the conversion and valorization of large amounts of CO<sub>2</sub>. The synthesis gas produced by the dry reforming can be used to produce higher value products, especially the sulfur-free diesel (C<sub>6</sub>H<sub>14</sub>) via Fischer-Tropsch synthesis (Eq. 5) and methanol (CH<sub>3</sub>OH) (Eq. 6).



Both of these reactions (Eq. 5) and (Eq. 6), requires H<sub>2</sub> to be added to the reactant synthesis gas feed in order to adjust the H<sub>2</sub>/CO ratio for the Fischer-Tropsch synthesis and methanol production. The hydrogen required is supplied by the steam reforming of methane.

In this study methanol and sulfur free diesel are assumed to be produced in two stages. The first step involves the formation of synthesis gas via the combined dry reforming (Eq. 2) and steam reforming (Eq. 1). Following the reforming step, fuels are synthesized by reacting the resultant synthesis gas (CO and H<sub>2</sub>) in the temperature range [473-573] K and pressure range [10-60] bar according to the reactions (Eq. 5) and (Eq. 6). The overall reaction for each fuel is as follows:

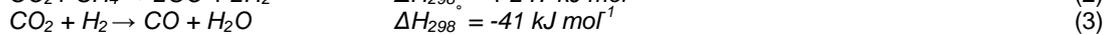


In our calculations, we assume that: CO<sub>2</sub> and steam reforming operate in parallel to form the necessary ratio of synthesis gas, energy efficiency of methanol and sulfur free diesel production is 80 % (Treacy and Ross, 2004), the enthalpies of the processes involved at a temperature of 773 K. This temperature represents a compromise between the low and high temperature steps (the final reaction and the reforming steps respectively) likely to be involved in the all-over process.

### 2.3 Thermodynamic analysis

In order to define the operating conditions and limitations of dry reforming reaction, it was necessary to carry out a thermodynamic analysis.

The effects of temperature, pressure and CO<sub>2</sub>/CH<sub>4</sub> ratio are evaluated by the method of equilibrium constants. We consider the following reactions:



The advancement of these reactions is calculated by solving a nonlinear system of two equations and two unknowns by writing the equilibrium constants in the gas phase, based on advancements with fixed temperature and pressure.

The equilibrium constant, K<sub>(k)</sub>(T) of each reaction (k), is defined by the relation:

$$K_{(k)}(T) = \exp\left(\frac{-\Delta_r G(k)^\circ(T)}{R \cdot T}\right) \quad (9)$$

Where ΔrG (k)<sup>°</sup>(T) is the free enthalpy of the reaction k at temperature T and standard reference pressure:

$$\Delta_r G(k)^\circ(T) = \Delta_r H(k)^\circ(T) - T \cdot \Delta_r S(k)^\circ(T) \quad (10)$$

At thermodynamic equilibrium, this constant is the product of chemical activities, which are the reduced (partial) pressures. For each reaction k, we have the relation:

$$K_{(k)}(T) = \prod_{i,k} (f_i/f^\circ)^{\nu_{(k,i)}} \quad (11)$$

$$f_i = \Phi_i \cdot y_i \cdot P_i \quad (12)$$

$$\sum (y_i \Phi_i)^{\nu_i} = \left(\frac{P}{P^\circ}\right)^{-\sum \nu_i} K_j \quad (13)$$

Where P<sub>i</sub> is the partial pressure of component i, P<sup>°</sup> is the standard reference pressure (1 bar) and ν<sub>(k,i)</sub> is the stoichiometric coefficient of component i (ν<sub>i</sub> > 0 for products, ν<sub>i</sub> < 0 for reagents) for the reaction (k).

All dry reforming reactions operate at low pressures. So we can estimate that the fugacity coefficient of a component in a mixture is equal to 1. (However, we can also study the effect of pressure. The coefficient is estimated by the virial equation (Smith and Van Ness, 2000)). The assumptions that were asked are: The reactions occur in the reformer where the temperature is assumed stationary and uniform, the total pressure P, assumed to be uniform and set by the operating conditions, the balances are calculated and advancement of the reaction is coupled as equilibrium is reached.

## 3. Results and discussion

### 3.1. Comparative study between the dry and steam reforming of methane

Table 1 summarizes the results of the calculations and compares the two methods.

Table 1: Energy and CO<sub>2</sub> balances of dry and steam reforming processes

	Steam reforming		Dry reforming	
	Energy balance	CO <sub>2</sub> balance	Energy balance	CO <sub>2</sub> balance
Syngas production	6.65 MJ / kg (CO+3H <sub>2</sub> )	0.45 kg of CO <sub>2</sub> / kg (CO+3H <sub>2</sub> )	4.35MJ/kg (2CO+2H <sub>2</sub> )	-0.44 kg of CO <sub>2</sub> / kg (2CO+2H <sub>2</sub> )
Hydrogen production	27 MJ/kg of H <sub>2</sub>	7 kg of CO <sub>2</sub> / kg of H <sub>2</sub>	42.7 MJ/kg of H <sub>2</sub>	2.34 kg of CO <sub>2</sub> / kg of H <sub>2</sub>

For the production of synthesis gas and hydrogen, the dry reforming consumes 1.6 times more energy than the steam reforming. However, it has an environmental benefit as it produces much less CO<sub>2</sub>. Therefore, the production of hydrogen by dry reforming appears to be a weak competitor for the steam reforming. However, the dry reforming may be interesting for hydrogen production if we use energy source that does not emit CO<sub>2</sub>, such as nuclear or solar energy.

### 3.2. Production of synthetic fuels from dry reforming

Table 2 summarizes the results of the calculations.

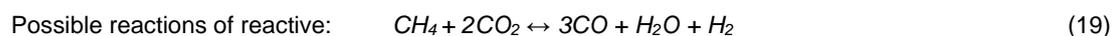
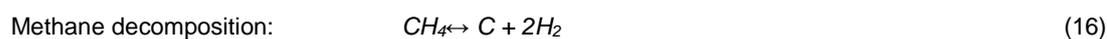
Table 2: Production of methanol and sulfur-free diesel by the combination of dry and steam reforming

	Energy balance	CO <sub>2</sub> balance
Methanol	1.73 MJ/kg of CH <sub>3</sub> OH	-0.25 kg of CO <sub>2</sub> / kg of CH <sub>3</sub> OH
Sulfur-free diesel	0.4 MJ/kg of C <sub>6</sub> H <sub>14</sub>	-0.74 kg of CO <sub>2</sub> / kg of C <sub>6</sub> H <sub>14</sub>

The production of synthetic fuels is an interesting prospect for valorization of CO<sub>2</sub>. Indeed, this alternative consumes CO<sub>2</sub> and appears more attractive for the dry reforming.

### 3.1 Thermodynamic results

The dry reforming reaction described in Eq.2 is highly endothermic. At a temperature lower than 916 K, the reaction Gibbs free energy change is positive,  $\Delta G^{\circ}_{r,T < 916K} > 0$  kJ. From the thermodynamic perspective, CO<sub>2</sub> reforming of CH<sub>4</sub> is not likely to occur spontaneously at a temperature lower than 916 K. Therefore, temperatures higher than 916 K should be employed. However, the chance of side reactions increases at higher temperatures. Our thermodynamic study was limited to studying side reactions that can occur at temperatures above 916 K (Zhang et al., 2008). Side reactions are listed below:



The effects of temperature, pressure on the molar ratios of reagents are illustrated in Figures 1, 2 and 3 respectively.

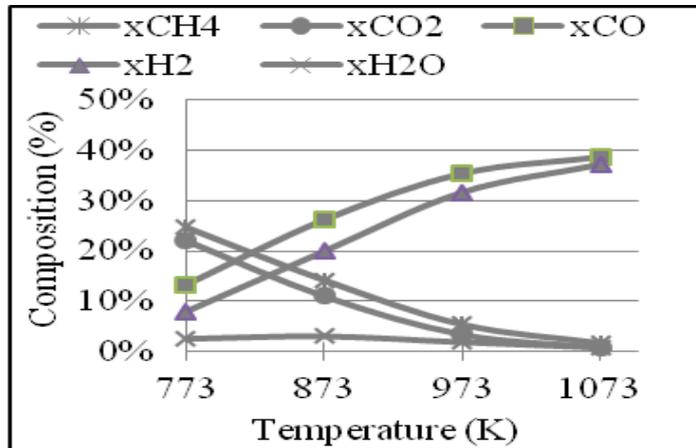


Figure 1: Variation of equilibrium composition with temperatures; ( $P=1$  bar and an initial ratio  $CH_4/CO_2=1/1$ )

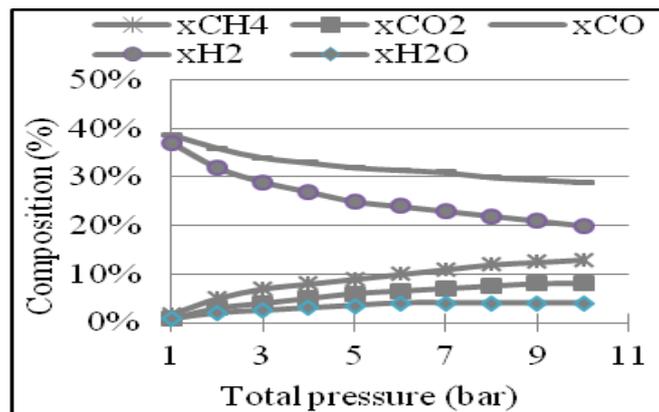


Figure 2: Effect of total pressure on equilibrium composition; ( $T = 1023$  K and  $CH_4/CO_2 = 1$ )

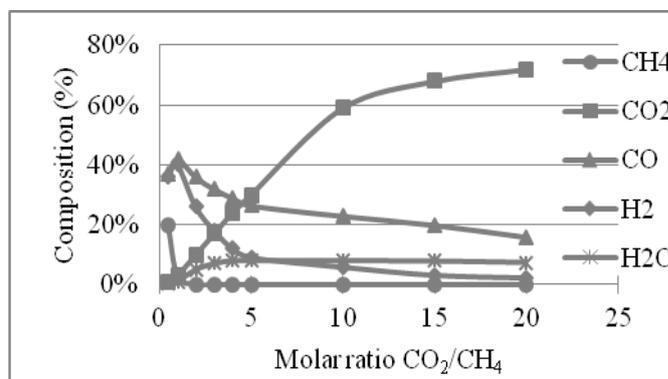


Figure 3: Effect of molar ratio  $CO_2/CH_4$  on the equilibrium composition; ( $P=1$  bar;  $T=1023$  K)

High temperatures and low pressures favour the dry reforming reaction. Higher reactant conversion and high product yield can be achieved at higher reaction temperatures particularly at a temperature range [916, 1300] K and a pressure close to atmospheric pressure. However, high reaction temperature and high pressure can alleviate the carbon formation problem, which is believed to be the major cause of catalyst deactivation in CO<sub>2</sub> reforming of CH<sub>4</sub> (Zhang et al., 2008). Therefore, the operation conditions are proposed based on thermodynamic analysis: T = 1023 K, P = 1 bar and CH<sub>4</sub>/CO<sub>2</sub>=1/1.

#### 4. Conclusion

As far as environmental issues are concerned, the dry reforming of methane can be used to produce higher value products. In this paper, processes that produce from a greenhouse gas (CO<sub>2</sub>) synthetic fuels were examined and studied. This study has been devoted to the feasibility and the limitations of dry reforming of methane. Therefore, to produce hydrogen, dry reforming consumes more energy and emits less CO<sub>2</sub> than steam reforming. However, the dry reforming is more interesting for the production of synthetic fuels because it can consume CO<sub>2</sub> while promoting the reduction of greenhouse gases emissions. Moreover, high temperatures and low pressures favour higher reactant conversion and high product yield. In addition, the high temperature of the reaction can alleviate the problem of carbon formation which is considered the main cause of catalyst deactivation.

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