

## A STUDY ON THE DIFFERENT REFORMING TECHNIQUES IN GAS TO LIQUID TECHNOLOGY

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### Abstract

Gas-to-liquid (GTL) is the chemical conversion of natural gas into high-quality liquid products. The most important reforming technologies used are autothermal reforming (ATR), Partial oxidation (POX), and Steam methane reforming (SMR). A process flowsheet based on each reforming technique is designed with parameters and operating conditions obtained from the industry field data and simulated with ASPEN plus V8.6. A comparative analysis is mainly developed for assessing the different reforming technologies based on syngas ratio ( $H_2/CO$ ) that is a favorable value of 2, and the results are documented and provide that ATR and POX techniques have a value equal or close to 2, then an additional comparison between ATR and POX based on Amount of Syngas, amount of heat saving and greenhouse gas emissions. POX is the most influential technique that has a large amount of syngas and heat saving and low  $CO_2$  content and should be expanded use in industry.

**Keywords:** Gas-to-liquid; Steam Methane Reforming; Partial Oxidation; Autothermal Reforming.

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## 1. Introduction

The gas-to-liquid (GTL) technology, it chemically converts natural gas into clean-burning liquid products [1]. This chemical liquefaction technique produces sulfur-free transportation fuels with a high cetane number suitable for blending or as a direct fuel for combustion engines [2-4]. By converting natural gas into liquid fuels, the technology greatly reduces high transport costs which in the past prevented its access to distant markets. It also facilitates fuel transport; thus benefits the environment in two ways. First, the resulting liquid hydrocarbons are pure and burn cleanly. Second, converting gas to liquid allows producers to transport and market associated gas that would otherwise be flared into the atmosphere [5]. Due to the removal of impurities before the gas is converted to liquid, GTL products have superior properties regarding combustion efficiency and emission of some pollutants [6].

A GTL process mainly comprises of three parts as shown in Figure 1. which are reforming of natural gas to syngas ( $CO$  and  $H_2$  mixture) by different technologies, subsequent Fischer-Tropsch reaction of syngas to hydrocarbons (also called syncrude), conversion of syngas into chains of hydrocarbon products takes place on a catalyst surface, and upgrading of syncrude by fractionation, hydrotreating, hydro-cracking, and hydroisomerization to yield products that meet the market specifications Before these three steps of a GTL process, the acid gas removal unit is existed to turn the natural gas feedstock from sour gas to sweet gas. A sulfur compound in sour gas will poison the active sites of catalyst used in the subsequent process [7-8].

## 2. Syngas production for GTL

The most important reforming technologies currently used for syngas production are Steam Methane Reforming (SMR), Partial Oxidation (POX) and Auto Thermal Reforming (ATR). These different technologies are employed by several industries such as Shell which uses POX [3], Rentech which uses SMR [9], and Sasol [10] and Exxon Mobil [4] which use ATR.

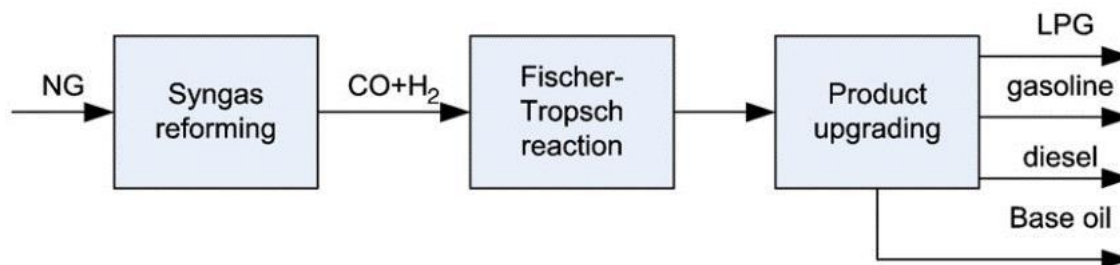


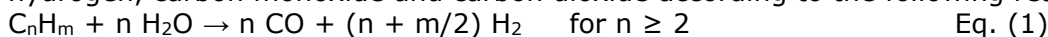
Figure 1. Gas-To-Liquids process diagram

### 2.1. Autothermal reforming (ATR)

During ATR, a mixture of steam, methane, and oxygen is reacted adiabatically over a fixed bed of nickel-based catalyst. ATR has a combination of reactions [2].

To avoid the potential problem that the ATR works as a steam cracker, which produces olefins from higher hydrocarbons in the feed, a pre-reformer is introduced.

In the pre-reformer, all higher hydrocarbons ( $C_{2+}$ ) are converted into a mixture of methane, hydrogen, carbon monoxide and carbon dioxide according to the following reactions [11].



Equilibrium reaction (exothermic):



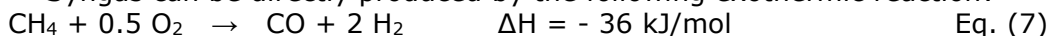
The key part of the syngas unit is the autothermal reformer [12-14]. The chemical reactions carried out in this option are below:



### 2.2. Partial oxidation (POX)

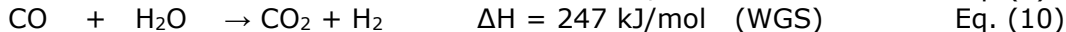
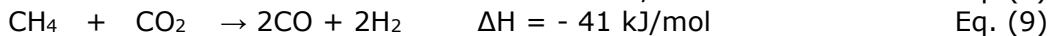
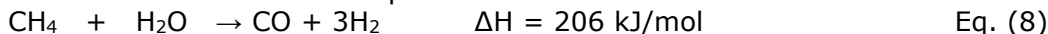
This reforming technique employs an air separation unit because nitrogen-free oxygen is required in the feed. The partial Oxidation can be catalytic or noncatalytic [15-16]. Efforts have been made to achieve the partial oxidation at low temperatures (for range between 300 and 1000°C with a rhodium catalyst [16] or using platinum as catalyst with a temperature lower than 1200°C [17]) because the high reaction temperatures that are currently used (between 1200 and 1500 °C) the operating cost is high and soot formation is observed [18].

Syngas can be directly produced by the following exothermic reaction:



### 2.3. Steam Methane Reforming (SMR)

SMR is a widely practiced technology for hydrogen-rich syngas production. This reaction is strongly endothermic. Thus the major challenge, and often the limiting factor in the selection of the SMR process, is providing sufficient heat into the reactor system to maintain the required reaction temperature [19]. This Reforming Technique is a catalytic process which carried out in a multitubular reactor commonly packed with a catalyst. Most commercial steam reforming catalysts are nickel-based and use carriers such as alumina, zirconia, etc. [18, 20]. The chemical reaction carried out in this option is below



A water-gas shift (WGS) reaction is part of this process [20].

### 3. Simulation and analysis

#### 3.1. Feed conditions and specifications

The case study deals with a feedstock of natural gas. Table 1 lists the characteristics of the natural gas fed to the process.

Table 1. Typical feed gas conditions for the case study [21]

|                    |                     |
|--------------------|---------------------|
| Flowrate (kmol/hr) | 3 000               |
| Temperature (°C)   | 22                  |
| Pressure (bar)     | 63                  |
| Component          | Composition (mol %) |
| Methane            | 92.4                |
| Ethane             | 3.6                 |
| Propane            | 1.6                 |
| N <sub>2</sub>     | 1.0                 |
| CO <sub>2</sub>    | 1.3                 |
| H <sub>2</sub> S   | 0.1                 |

#### 3.2. Modeling environment

The Aspen plus V 8.6. Simulation tool has been used to develop a process model to determine the best Reforming technique according to technicality analysis.

Natural gas is sweetened for acid gas removal then preheated and sent into a reformer to react with steam and/or oxygen.

#### 3.3. Simulation of Acid Gas Removal Process

The model consists of an absorber and a stripper. Moreover, a simulation of this unit is modeled by aspen technology and check for the model is achieved as shown in results which the sweet gas contains a traces of H<sub>2</sub>S and CO<sub>2</sub> less than the standard requirements.

Table 2. Key simulation results of acid gas removal

| Process stream      | CO <sub>2</sub> mole fraction | H <sub>2</sub> S mole fraction |
|---------------------|-------------------------------|--------------------------------|
| Gas in              | 0.013                         | 0.001                          |
| Gas out             | 164 ppm                       | 1.25 ppm                       |
| CO <sub>2</sub> out | 0.9                           | 0.07                           |

#### 3.4. Simulation of syngas production by different reforming routes

As mentioned earlier, there are currently three reforming technologies used on a commercial scale, namely SMR, POX, and ATR.

##### 3.4.1. Design basis and specifications

Peng Robinson equation of state was used as the property method for the physical property calculations. The reformer is simulated with the ASPEN Plus REquil model which is an equilibrium-based calculation.

##### 3.4.2. Simulation of syngas production by ATR technology

The process flow diagram for ATR (including the acid gas removal process) is shown in Figure 2.

###### 3.4.2.1. Process description

The sweet gas leaves from the top of the absorber column with a temperature of 45°C and pressure of 63 bar at the flowrate of 2 965 kmol/hr. After reducing the pressure to 30 bar through a valve and preheating the temperature to 455°C, the sweet gas entered the pre-reformer with steam and recycled CO<sub>2</sub> stream (both at 455°C and 30 bar). All hydrocarbons heavier than methane are converted to CO and H<sub>2</sub>.

The exit temperature of pre-reformer is usually lower than the desired ATR inlet temperature. Thus a heater is needed to increase the outlet stream temperature to a desired level (655°C in this work). The oxygen stream from the cryogenic air separation unit (ASU) section is blown to the burner of ATR reactor at a temperature of 200°C.

The ATR converts the methane into syngas by reacting with steam and oxygen; all the reactions reach equilibrium. Because of the large heat released by the partial oxidation reaction, the overall reaction of ATR is exothermic, and the hot syngas leaves the reactor at 1300 K that is cooled to ambient temperature of 28°C for the removal of water and CO<sub>2</sub> then the syngas is ready to enter the FT Reactor.

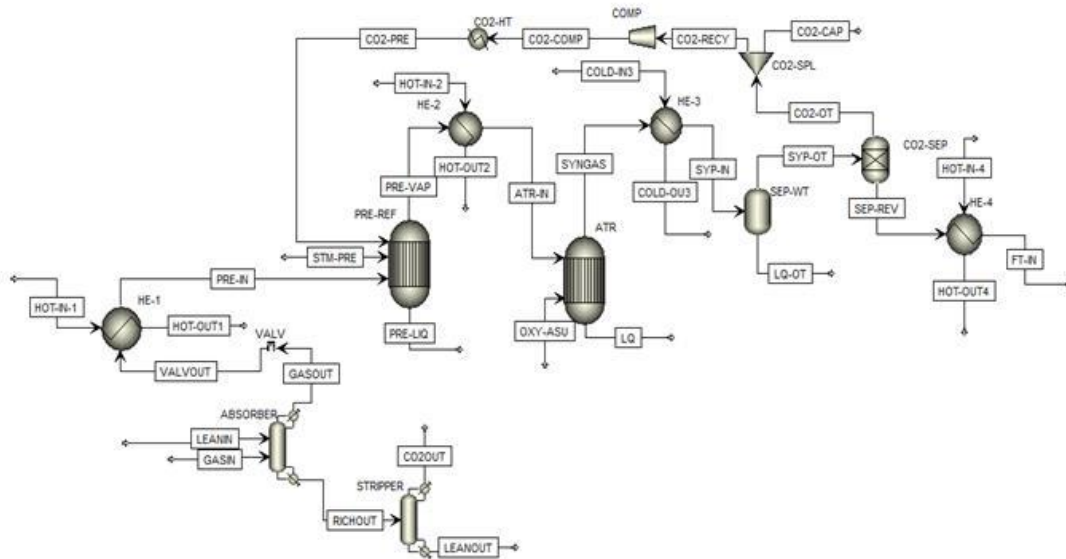


Figure 2. Process flow diagram for ATR

### 3.4.2. Simulation of syngas production by partial oxidation reformer (POX) Technology

The process flow diagram for POX (including the acid gas removal process) is shown in Figure 3.

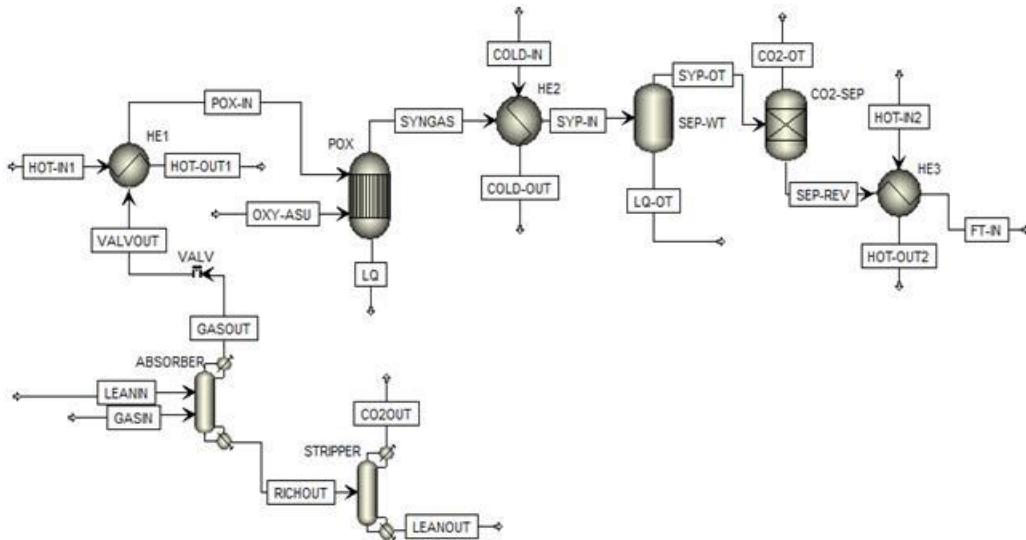


Figure 3. Process flow diagram for POX

### 3.4.2.1. Process description

The partial oxidation reformer is modeled similarly as in the ATR case with the REquil model, which is driven by an equilibrium-based calculation.

Sweet gas is preheated to 455°C, while oxygen from the air separation unit (ASU) is compressed to the pressure of Reformer. Both components are sent to the partial oxidation reformer where an exothermic reaction takes place. The reformer pressure was set to 30 bar, which also corresponds to industrial practice. The POX converts the methane into syngas by reacting with oxygen.

### 3.4.3. Simulation of syngas production by steam-methane reformer (SMR) technology

The process flow diagram for SMR (including the acid gas removal process) is shown in Figure 4.

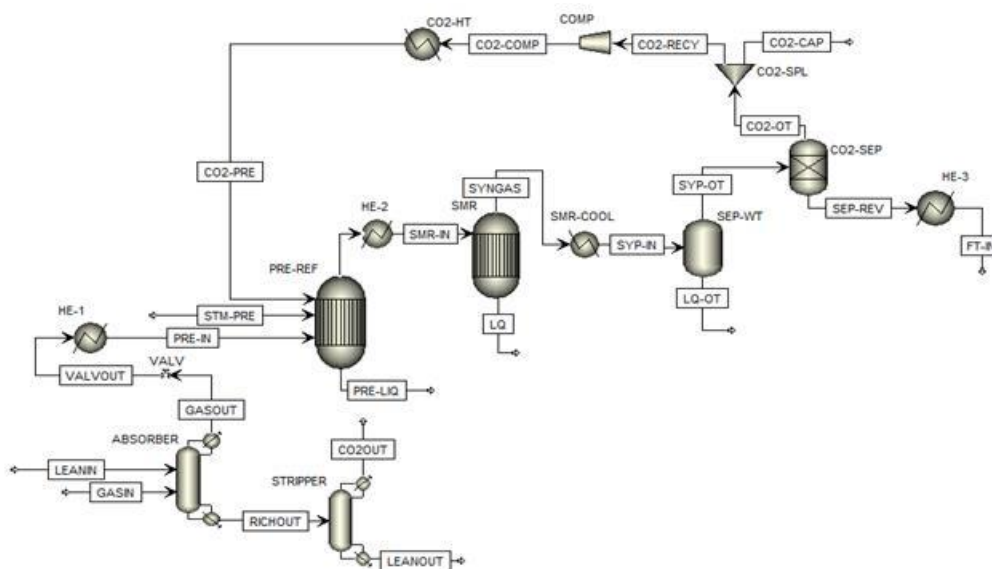


Figure 4. Process flow diagram for SMR

### 3.4.3.1 Process description

The pre-reformer and steam reformer are modeled similarly as in the ATR case except that the reformer operates at a lower pressure 18 bar concerning the other two cases.

## 4. Results and discussion

### 4.1. Key simulation results

The key simulation results are presented in Table 3.

Table 3. The key simulation results of different reforming techniques

| Composition      | ATR Technique       |                 | POX Technique       |                 | SMR Technique       |                 |
|------------------|---------------------|-----------------|---------------------|-----------------|---------------------|-----------------|
|                  | Mole flow (Kmol/hr) | Mole per-cent % | Mole flow (Kmol/hr) | Mole per-cent % | Mole flow (Kmol/hr) | Mole per-cent % |
| H <sub>2</sub>   | 5 032               | 57.2            | 6 058               | 65.66           | 4 932               | 59.7            |
| CO               | 2 516               | 28.6            | 3 131               | 33.93           | 1 670               | 20.2            |
| CH <sub>4</sub>  | 457                 | 5.3             | -                   | -               | 1 429               | 17.3            |
| CO <sub>2</sub>  | 166                 | 1.9             | -                   | -               | 33                  | 0.4             |
| O <sub>2</sub>   | -                   | -               | 1                   | 0.01            | -                   | -               |
| H <sub>2</sub> O | 579                 | 6.6             | 7                   | 0.08            | 164                 | 2               |
| N <sub>2</sub>   | 30                  | 0.4             | 30                  | 0.32            | 30                  | 0.4             |
| Total Flow       | 8 780               | 100             | 9 227               | 100             | 8 258               | 100             |

The syngas ratio is adjusted to 2 which a low ( $H_2O/CH_4$ ) ratio and ( $O_2/CH_4$ ) ratio of 0.53 is adapted for the base case of ATR. The molar ratio of ( $O_2/CH_4$ ) ratio is adapted to 0.66, and the syngas ratio is 1.93 for the base case of POX. The molar ratio of ( $H_2O/CH_4$ ) is 0.68, and the syngas ratio is 2.93 for the base case of SMR so the treated gas must be taken for  $H_2$  removal to adjust the  $H_2$ : CO ratio to 2; 31% of the  $H_2$  contained in the syngas is removed, along with traces of water,  $CO_2$ , and  $CH_4$ . The adjusted syngas is heated to  $227^\circ C$  and fed to the FT reactor.

#### 4.2. Effect of parameters on syngas ratio

##### 4.2.1. Effect of temperature on syngas ratio

It can be seen that a reduction of the  $H_2/CO$  ratios with increasing temperatures reaching a favorable value of 2 for ATR, as expected, the conversion of the reactants also increased with temperature, with syngas ratio reaching a value of 2.91 for SMR as the temperature reaches 1300 K. Hence, the temperature is an important parameter in determining the  $H_2/CO$  ratio of the product gas.

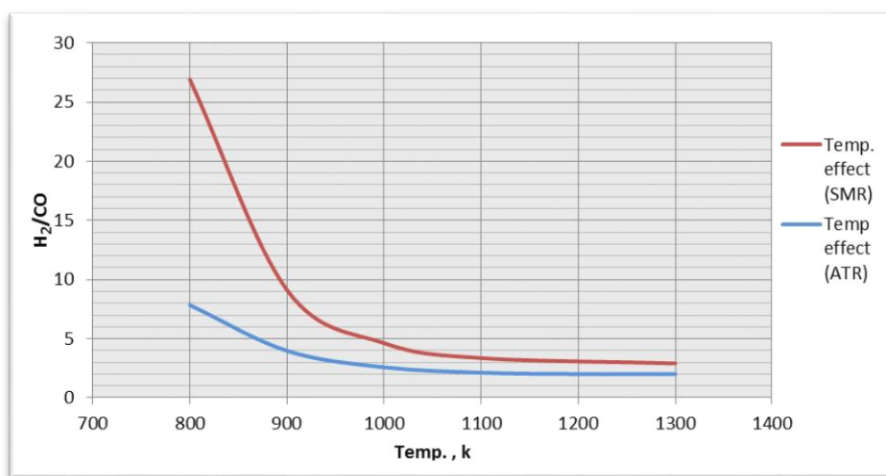


Figure 5. Effect of temperature on syngas ratio

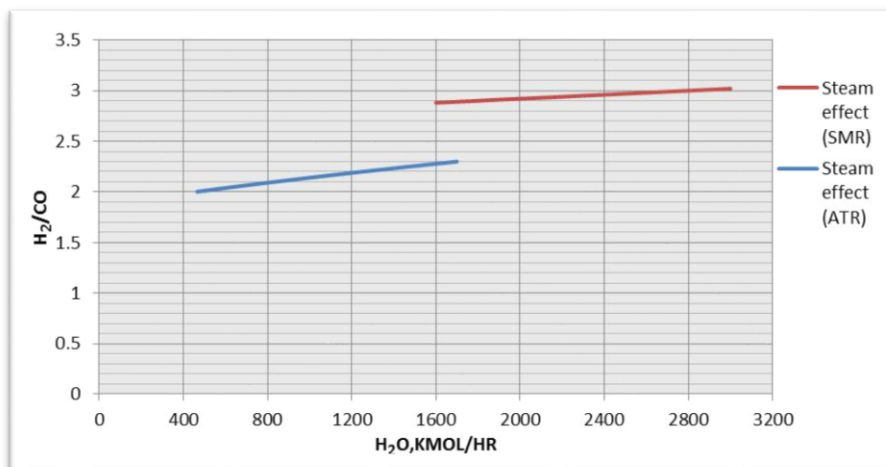


Figure 6. Effect of steam on syngas ratio

#### 4.2.2. Effect of steam on syngas ratio

It can be seen that increasing of the H<sub>2</sub>/CO ratios with increasing steam. The suitable syngas ratio is 2.91 at a steam value of 1890 kmol/hr which represent H<sub>2</sub>O/CH<sub>4</sub> of 0.68 for SMR technique. Hence, the steam is an important parameter in determining the H<sub>2</sub>/CO ratio of the product gas.

#### 4.2.3. Effect of oxygen on syngas ratio

It can be seen that increasing of the H<sub>2</sub>/CO ratios with increasing oxygen values up to a certain value of oxygen which over this value a syngas ratio still constant for POX Technique. Hence, the oxygen value is an important parameter in determining the H<sub>2</sub>/CO ratio of the product gas.

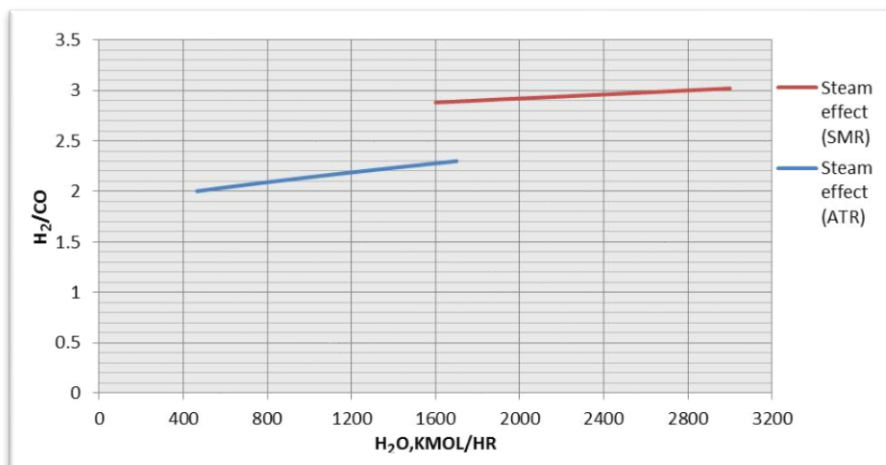


Figure 7. Effect of oxygen on syngas ratio

#### 4.3. Comparison and analysis of three syngas production techniques

The choice of reforming technology is determined by balancing between the characteristics of each one. The product syngas composition from each reforming technologies can be manipulated by altering various process conditions and/or by means of additional process steps as shown in Table 4.

Table 4. Simulation parameters for each syngas configuration

| Simulation parameter      | ATR  | POX  | SMR  |
|---------------------------|------|------|------|
| Operation conditions      |      |      |      |
| Operating pressure [bar]  | 30   | 30   | 18   |
| Operating Temperature [K] | 1300 | 1300 | 1300 |
| Steam to carbon ratio     | 0.17 | -    | 0.68 |
| Oxygen to carbon ratio    | 0.53 | 0.57 | -    |
| Results                   |      |      |      |
| Syngas ratio              | 2    | 1.93 | 2.91 |

From Table 4, SMR Technique is not ideally suited to GTL plants. This is due to the fact that FT. Synthesis requires an H<sub>2</sub>/CO ratio of about 2, which is lower than that obtainable with SMR which has a value of 2.91. For a complete reaction of conversion of methane to syngas, it is needed to a large amount of steam, and the reaction is endothermic. POX Technique has a syngas ratio slightly lower than that is required for FT synthesis which has a value of 1.93. ATR Technique has a syngas ratio value of 2 which is typically suited to FT synthesis



#### 4.4. The additional study focused on ATR and POX Techniques

The most favorable syngas ratio for the cobalt-based catalyst is a value of 2. The additional study focused on ATR Technique is executed and also focused on POX which has a value of syngas ratio closed to the desired value.

##### 4.4.1. Greenhouse gas emissions

Table 5. The CO<sub>2</sub> emissions of feed and product streams

| Stream Type   | ATR Technique |                            | POX Technique |                            |
|---------------|---------------|----------------------------|---------------|----------------------------|
|               | flow(kg/sec)  | CO <sub>2</sub> e (kg/sec) | flow(kg/sec)  | CO <sub>2</sub> e (kg/sec) |
| Total feed    | 18 0193.1     | 309                        | 126 145.8     | 309                        |
| Total product | 18 0193.1     | 53.4                       | 126 145.8     | 0.56                       |

##### 4.4.2. Process heat duty

There is a majority of heat was produced which may be used for power cogeneration. Also, when a simulation model completed the F-T reactor produces a higher amount of heat. The process net heat that is excess in ATR Technique = 1.26E+08 Btu/hr and in POX = 1.56 E+08 Btu/hr.

Table 6. Heat duty for each unit

| ATR Technique |                  | POX Technique |                  |
|---------------|------------------|---------------|------------------|
| Units         | Enthalpy (kJ/hr) | Units         | Enthalpy (kJ/hr) |
| Heat 1        | 6.36E+07         | Heat 1        | 6.36E+07         |
| Heat 2        | 4.39E+07         | Heat 2        | 5.371 E+07       |
| Heat 3        | 5.07E+07         | Cool 1        | -2.822E+08       |
| Heat 4        | 3.61E+04         | -             | -                |
| Cool 1        | -2.91E+08        | -             | -                |

##### 4.4.3. Heating and cooling utilities

As thermal pinch analysis is conducted to determine the potential heat that could be exchanged among the hot and cold streams. The grand composite curves for ATR and POX are shown in Figure 8, 9.

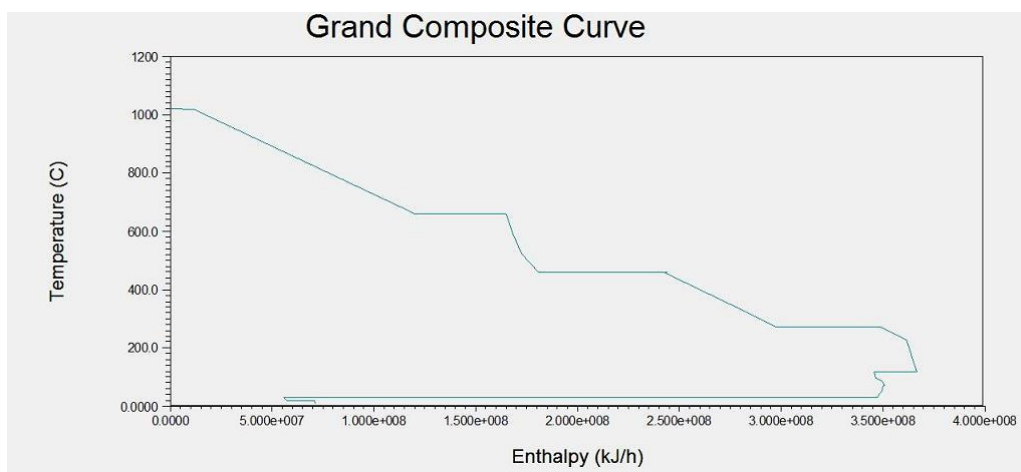


Figure 8. The grand composite curve of ATR

From ATR diagram it indicates that after heat integration, the minimum cooling utility is 68.1million Btu/hr and the minimum heating utility is zero. From POX diagram the minimum cooling utility is zero, and the minimum heating utility is 1.49 million Btu/hr. The savings for heating and cooling utilities resulting from heat integration are listed in Table 7.



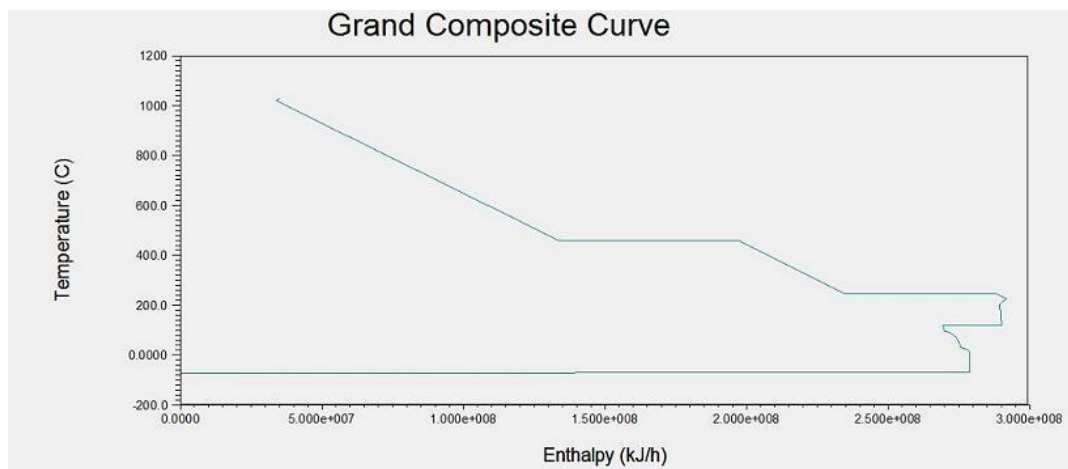


Figure 9. The grand composite curve of POX

Table 7. Heating and cooling utility savings

|                    | ATR technique            |                           | POX technique            |                           |
|--------------------|--------------------------|---------------------------|--------------------------|---------------------------|
|                    | Hot utilities<br>(kJ/hr) | Cold utilities<br>(kJ/hr) | Hot utilities<br>(kJ/hr) | Cold utilities<br>(kJ/hr) |
| Before integration | 8.68E+07                 | 3.13E+07                  | 5.12E+07                 | 10.31E+06                 |
| After integration  | 0                        | 7.18E+07                  | 1.57E+06                 | 0                         |
| Savings (\$/yr)    | 2,957,764                | 1,043,276                 | 6,761,871                | 127,238                   |

## 5. Conclusion

A gas to liquid process (GTL) based on different reforming techniques has been simulated and optimized by Aspen Plus. The parameter study conducted through the use of case studies was found to give the best one. The Results of The different reforming techniques are conducted and compared, and the following is concluded:

- The results for the SMR base case GTL process indicate that technologies for monetizing stranded natural gas via the SMR route would be intrinsically disadvantaged by the net requirement for Syngas ratio and the reaction is strongly endothermic.
- POX Technique has the largest amount of syngas, a small content of CO<sub>2</sub> emissions and a large amount of saving heat as compared with ATR Technique but syngas ratio is slightly smaller than the desired value.
- ATR Technique needs to amounts of both steam and oxygen while POX needs to only oxygen and total amounts ATR need are more than required for POX Technique.
- The choice between ATR and POX Techniques is based on availability and flexibility and POX is the best reforming one and it has to be expanded.

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