CO$_2$ valorization: Production of Synthetic Gasoline and Diesel Fuel from Dry Reforming of Methane
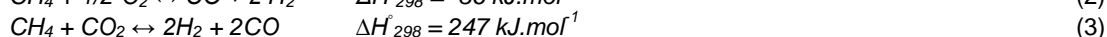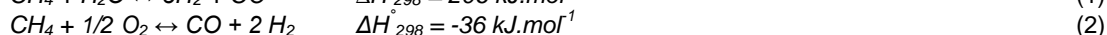
Hanaâ Er-rbib, Chakib Bouallou*, François Werkoff

MINES ParisTech, Centre Energétique et Procédés (CEP)
60 boulevard Saint Michel, 75006 Paris
chakib.bouallou@mines-paristech.fr

The purpose of this study is to illustrate the potential of dry reforming of methane for industrial applications by producing synthetic fuels from the combination of dry and steam reforming of methane. The proposed process includes four main units: production of synthesis gas from the dry and steam reforming of methane, Fischer Tropsch synthesis, hydro-cracking of Fischer Tropsch waxes, product upgrading and hydrogen recovery. Simulation model of this process was carried out with Aspen Plus™ software which allows us to define and analyze the optimum conditions and equipment specifications for each unit. Energy consumption and CO$_2$ balance are also calculated. The main interest of our proposed process is its very favorable carbon balance.

1. Introduction

The dry reforming of methane is a valorisation pathway of CO$_2$ and is an attractive way to generate synthesis gas which is an important step in the Gas To Liquid (GTL) transformation. Currently, GTL products have come into the spotlight for alternative energy carriers as an environmentally benign and highly profitable alternative to petroleum resources. GTL processes are good methods to convert gaseous fuel to the synthetic liquid fuels such as naphtha and diesel. After desulfurization of the natural gas, all GTL processes comprise three main steps: Generation of a synthesis gas (also called syngas) from natural gas can be performed by various methods, such as steam reforming (Eq. 1), partial oxidation (Eq. 2), autothermal reforming (a combination of Eq. 1 and Eq. 2; De Castro et al., 2010) or dry reforming (Eq. 3). The transformation of syngas into liquid hydrocarbons can be performed by Fischer Tropsch (FT) synthesis. This must be followed by cracking waxes; upgrading and separation of higher alcohols and recovery of the remaining hydrogen, in order to obtain sulfur free GTL with very low aromatics.

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \qquad \Delta H^{\circ}_{298} = 206 \ kJ.mol^{-1} \qquad (1)$$
$$CH_4 + 1/2 \ O_2 \leftrightarrow CO + 2 \ H_2 \qquad \Delta H^{\circ}_{298} = -36 \ kJ.mol^{-1} \qquad (2)$$
$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \qquad \Delta H^{\circ}_{298} = 247 \ kJ.mol^{-1} \qquad (3)$$

The FT synthesis requires a H$_2$/CO ratio = 2 (Sie, 1998). Methane steam reforming (SR) requires an additional step to adjust the H$_2$/CO ratio. Partial oxidation (POX) of methane which satisfies the H$_2$/CO ratio of 2 is confronted with difficulties in controlling the process because of the hot spots and explosion danger (Dong Ju et al., 2011). However, the dry reforming of methane (Eq.3) has the advantage of producing a syngas with a H$_2$/CO ratio = 1 which is adjustable by the steam reforming (Eq. 1) in the same reactor. In this work we propose a simulation model of a GTL process which is based on a

combination of dry and steam reforming of methane. Our simulation results will be compared to experimental results reported in the literature, for validating our simulation model.

2. Process description

The proposed process includes four steps: 1) the production of synthesis gas from the combination of dry and steam reforming of methane, 2) the Fischer-Tropsch synthesis which produces long-chain hydrocarbons, 3) the upgrading of liquids and the hydrocracking of waxes, 4) an hydrogen recovery.
The Proposed process is shown in Fig. 1, where only the main streams are reported.
Initially the natural gas is preheated and sent to the reforming reactor in which it reacts with steam and CO_2. At the outlet of the reformer, the temperature of the syngas is higher than needed at the inlet of the Fischer-Tropsch reactor. Thus, the synthesis gas is cooled and the remaining water is removed. Synthetic fuels produced by the FT reactor are sent to the separation unit (distillation columns) in order to retrieve the different fractions of diesel, gasoline, LPG (Liquefied petroleum gas) and waxes. The waxes are hydrocracked by using hydrogen that we have separated and purified in the PSA (Pressure Swing Adsorption). Finally, the unreacted gases, especially CH_4 and CO_2 are recycled to the reformer.
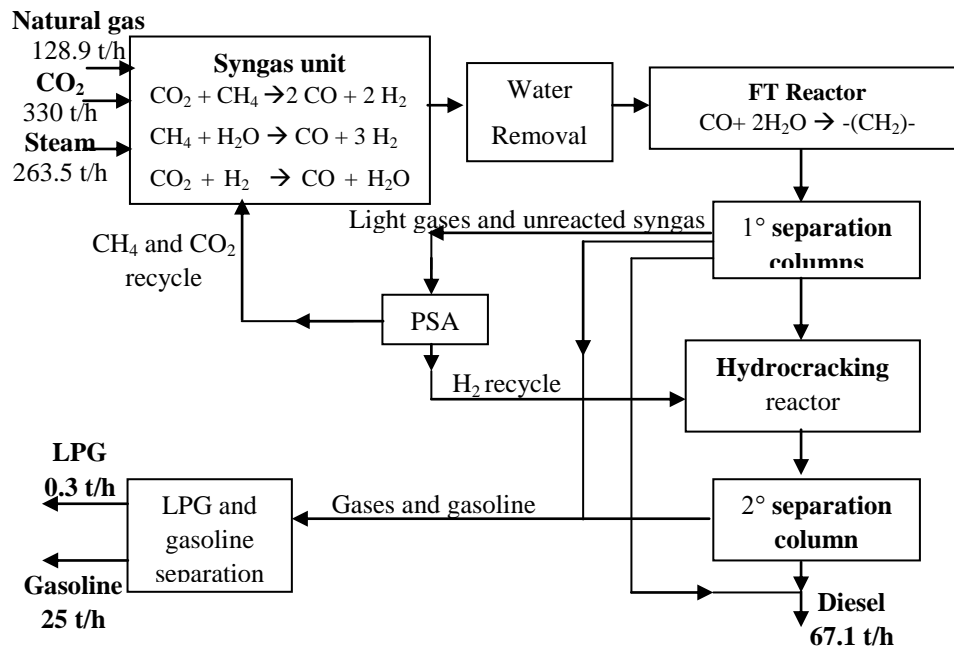

Figure 1: Block flow diagram of GTL process from the combination of dry and steam reforming
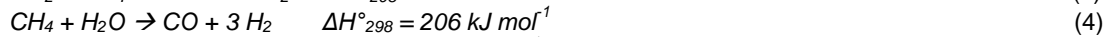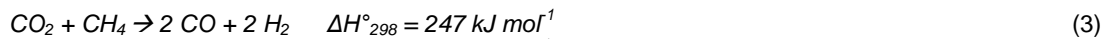
3. Simulation model

3.1 The components and the thermodynamic model

The model simulation was developed using Aspen Plus™. The following compounds have been selected from the Aspen Plus™: oxygen (O_2), nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), water (H_2O), methane (CH_4), ethylene (C_2H_4), ethane (C_2H_6), propylene (C_3H_6), propane (C_3H_8), butene (C_4H_8), butane (C_4H_{10}) and all linear and saturated hydrocarbons C_5H_{11} to $C_{30}H_{62}$, $C_{32}H_{66}$ and $C_{36}H_{74}$. And oxygenated compounds such as methanol (CH_4O), ethanol (C_2H_6O), 1-propanol (C_3H_8O), 1-butanol ($C_4H_{10}O$), 1-pentanol ($C_5H_{12}O$), 1-hexanol ($C_6H_{14}O$) and acetic acid ($C_2H_4O_2$). Linear and saturated hydrocarbons were selected to describe the gasoline, diesel and waxes: C_5 to C_{11}, C_{12} to C_{18} and C_{20} to C_{60}, respectively.

For the thermodynamic model, the equation of Peng-Robinson with Boston-Mathias alpha function (PR-BM) was applied in the main units (the two reactors, the distillation columns). For water separation, the NRTL model is applied. All the binary interaction parameter values needed for these models were available in Aspen Plus™.

3.2 Syngas production unit

The reforming unit comprises two parts: a pre-reformer and a reformer. In the pre-reformer, higher hydrocarbons contained in the natural gas are completely converted into a mixture of methane, carbon oxides and hydrogen over a nickel catalyst. The reaction temperature is 823 K and the outlet pressure is 5 bar (Kyong-Su et al., 2010). In the reformer, the temperature of the reaction varies in a temperature range: [973, 1273] K and a pressure range: [1-5] bar. The reactions involved are:

$$CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2 \qquad \Delta H°_{298} = 247\ kJ\ mol^{-1} \qquad (3)$$
$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \qquad \Delta H°_{298} = 206\ kJ\ mol^{-1} \qquad (4)$$
$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H°_{298} = 41\ kJ\ mol^{-1} \qquad (5)$$

For our simulation, we assumed that the reforming unit is fed by 128.9 t/h of natural gas with 94.9% of methane and 330 t/h of CO_2 and 263.5 t/h of H_2O.

3.3 The Fischer Tropsch unit

The synthesis gas produced by the reformer is cooled. Then, water is removed in a flash column. After, the catalytic reaction for the production of long-chain hydrocarbons is carried out in the FT re
actor. The catalyst that we have retained is Cobalt. Thus; the Fischer Tropsch synthesis requires a H2/CO ratio between 1.9 and 2.1 (Sudiro et al., 2009). Note that the FT reactor can work at a relatively low temperature, in order to maximize the production of diesel and waxes: this process is known as low temperature FischerTropsch (LTFT) (see Figure 2).
The FT synthesis was modeled by a Rstoic reactor at 513 K and 20 bar. The conversion of synthesis gas was estimated at 87% (Sudiro et al., 2009). The selectivity values were taken from Sudiro et al. (2009) (see Figure 2).
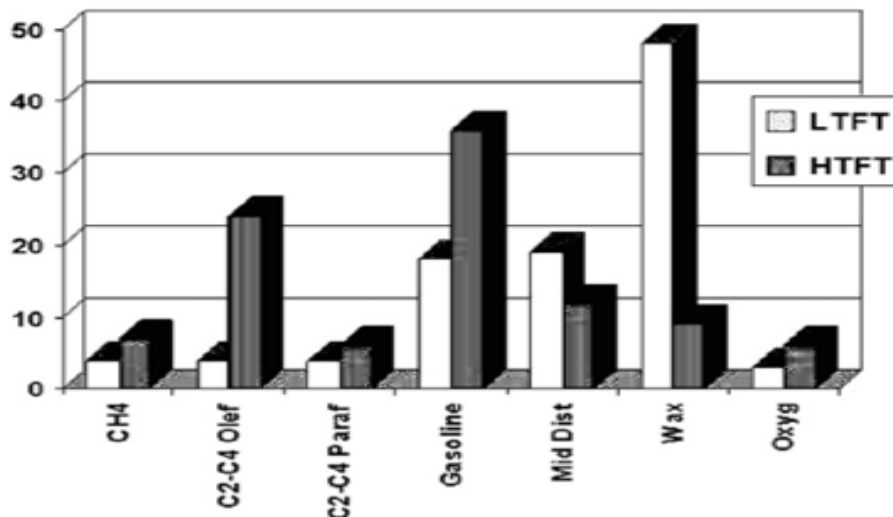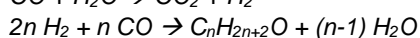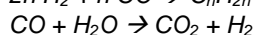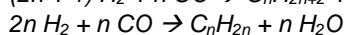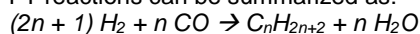

Figure 2: Values of selectivity for FT synthesis at low and high temperature for the catalyst "Cobalt" (Sudiro et al., 2009)

FT reactions can be summarized as:
$$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$$
$$2n\ H_2 + n\ CO \rightarrow C_nH_{2n} + n\ H_2O$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$2n\ H_2 + n\ CO \rightarrow C_nH_{2n+2}O + (n-1)\ H_2O$$

Overall, 42 reactions were considered, taking into account the selectivity for each product at low temperatures. These reactions generated paraffins, olefins and some oxygenated compounds as well as WGS reaction (Water Gas Shift) (Sudiro et al., 2009).

3.4 The hydro-cracking of waxes and the separation of FT products

The FT products are cooled and separated from water and oxygen compounds before the separation of heavy and light products into a distillation column. The light products are composed of gasoline, LPG and light gases. The heavy products are composed of diesel and waxes. Waxes are finally converted into high quality diesel in the hydrocracking unit, which was modeled using a RYield reactor. Product yields and operating conditions are taken from the work of Bezergianni et al., (2009). The hydrogen consumed in this section is 0.65 % of the heavy feed (Sudiro et al., 2009).

The first column is a direct steam stripping tower with a lateral stripper to recover the diesel fraction. Gases and gasoline are withdrawn from the top, while the residue, with the waxes, is sent to the hydrocracking reactor. The reactor outlet is sent to a second column, very similar to the first one, the bottom of which is recycled to the reactor, while the distillate, together with the other top product, is sent to two columns in series, where LPG and gasoline are recovered. Finally, the light gases (CO_2, CO, H_2 and CH_4) are sent to the recovery unit of hydrogen.

3.5 Hydrogen recovery

Hydrocracking requires hydrogen as a reactant. For this reason, we added a hydrogen recovery unit in order to recycle unreacted hydrogen to the hydrocracking unit. This step is performed by a PSA, which is a technology for separating and purifying a gas mixture. The PSA is designed to recover 90 % of H_2 with a purity of 99.95 %. This block is fed by light gases (hydrogen, CO_2, CH_4, CO and some traces of hydrocarbons).

3.6 Recycling of light gases and unreacted syngas

After the recovery of hydrogen, the gas leaving the PSA block contains several compounds that have not reacted or that were produced during the process such as CO_2, CO, CH_4, H_2 and traces of hydrocarbons. This gas mixture is recycled to the reformer. This recycling allows, on the one hand, reducing the amount of the inlet methane and on the other hand to increase the energy efficiency of the process. Indeed, according to the results of the simulation, without recycling efficiency is 52% but with recycling it becomes 62 %.
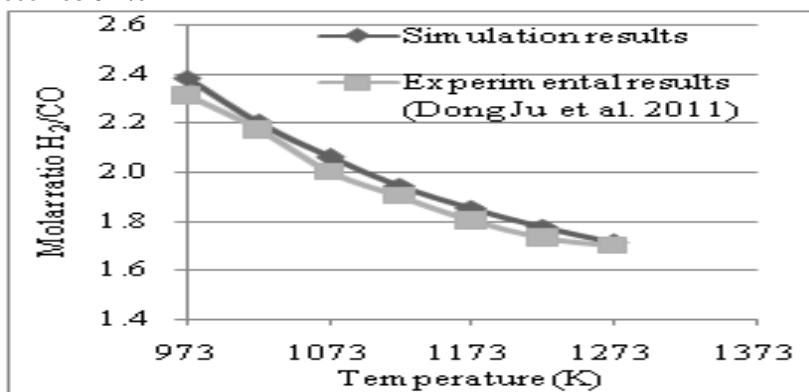

Figure 3: the effect of temperature on the H2/CO ratio; Feed molar ratio of CH4:H2O:CO2 = 1.0:2.0:1.0 and P = 1 bar)

4. Results

Depending on the operating conditions: temperature, pressure and $CH_4/H_2O/CO_2$ ratios, the H_2/CO ratio changes and thus influences the performance of the FT reaction.

Figure 3 shows the comparison of the simulation results from this work with experimental results carried out by Dong Ju et al. (2011) for the steam and dry reforming of methane, showing the effect of

temperature on the H_2/CO ratio. It was found that the H_2/CO mole ratio showed similar trends with the experimental results. Note that the H_2/CO ratio of synthesis gas decreases as the temperature increases.

The interesting range of H_2/CO ratio is [1.9 - 2.1] as the catalyst used is cobalt. Figure 4 shows the flow rate of synthetic fuels produced for different values of H_2/CO.

As can be seen from Figure 4, the maximum production is reached at **H_2/CO ratio = 2.05**.

The effect of pressure and CH_4/H_2O/CO_2 ratio is illustrated in Figures 5 and 6 respectively. The pressure has no influence on the performance of the reformer, up to 5bar. By cons, beyond 5 bar the risk of catalyst deactivation becomes more important.

The simulation results show also that increasing the fraction of steam; the H_2/CO ratio increases (see Fig. 6). Therefore, the optimal conditions for this H_2/CO ratio are: T = 1093K, P = 5 bar and CH_4/H_2O/CO_2 1/1.95/1.

5. Energy consumption and CO_2 balance of the proposed process

The GTL process produces 67.1 t / h of diesel, 25 t / h of gasoline and 0.3 t / h of LPG.

The process provided a thermal energy of 2.6 MJ/kg of fuel produced and consumed electrical energy of 1.9 MJ/kg of fuel produced. The distillation requires high pressure steam (553-573 K). The total steam required for this process is about 290.1 t/h (263.5 t/h by reformer and 26.6 t/h by distillation). Steam at medium pressure (10 bar) obtained in the cooling of FT reactor can be sent to steam turbines to produce electricity.
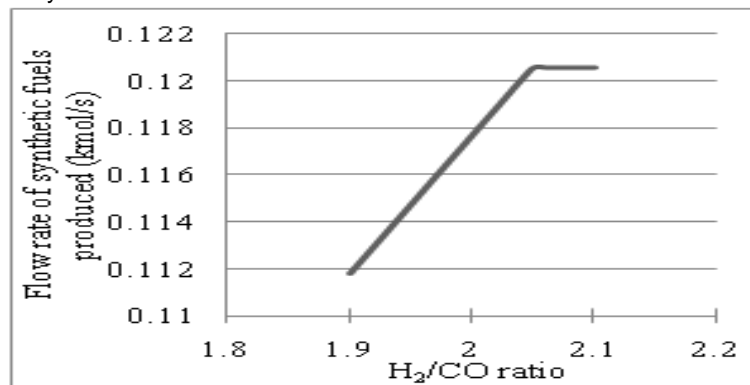

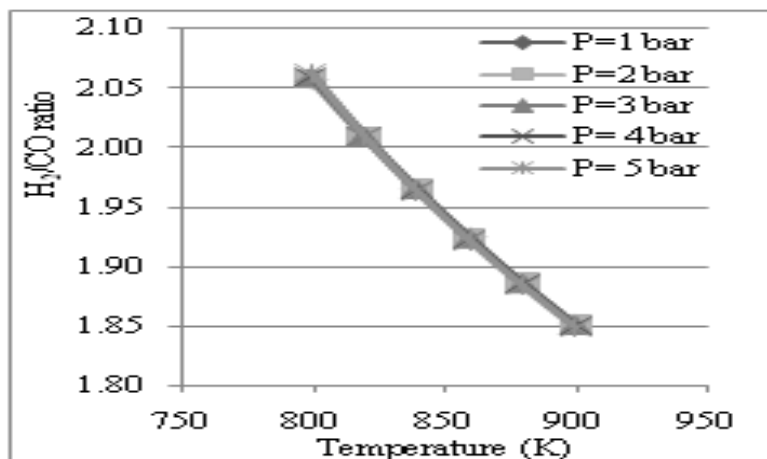**Figure 4: The effect of the inlet H_2/CO ratio on the flow rate of fuels produced**
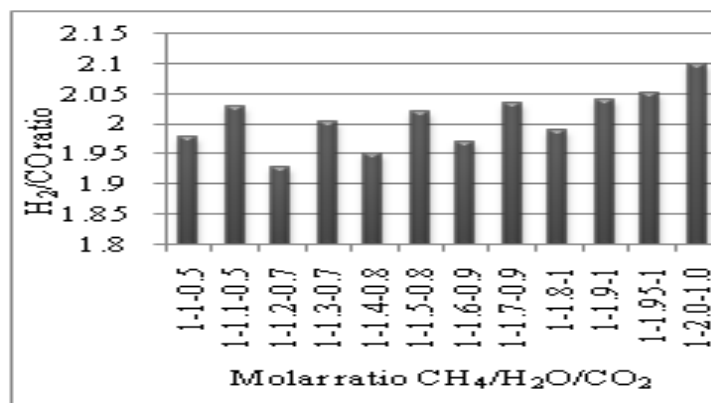

Figure 5: The effect of pressure on the H2/CO molar ratio

Figure 6: The effect of molar ratio $CH_4/H_2O/CO_2$ on the H_2/CO molar ratio

Another interesting result of the simulations performed is related to CO_2 emissions, which are reduced thanks to the use of dry reforming. The proposed process emits 90 t/h of CO_2 and consumes 330 t/h of CO_2. Table 1 summarizes and compares the total CO_2 emitted per tons of liquid fuel in the proposed process and GTL process which syngas is produced from autothermal reforming. It is clear that CO_2 emissions with the proposed method are reduced and even more the process consumes CO_2.

Table 1: CO_2 production comparison in the proposed process and GTL process which syngas is produced from autothermal reforming

	GTL process (Sudiro et al., 2009)	Proposed process
CO_2 balance (t of CO_2/t of liquid fuels produced)	0.63	-2.6

6. Conclusion

In this study, we propose a simulation model of GTL process by coupling dry and steam reforming of methane. This process could produce synthetic fuels composed of 72% of diesel, 26% of gasoline and 2 % of LPG. Simulation results show that this process allows CO_2 mitigation by consuming 330 t/h of CO_2 for producing 93 t/h of synthetic fuel. Apart from any economic consideration, this process looks a particularly attractive alternative for reducing oil dependence in the transport sector while promoting the CO_2 mitigation. In a long-term perspective we expect that the simulation model developed in this work serve as a design basis for pilot-scale GTL process.

References

Bezergianni S., Kalogianni A., 2009, Hydrocracking of used cooking oil for biofuels production, Bioresour. Technol., 100, 3927-3932.

De Castro J., Rivera-Tinoco R., Bouallou C., 2010, Hydrogen production from natural gas: Auto-Thermal Reforming and CO 2 capture, Chem. Eng. Trans., 21, 163-168.

Dong Ju, M., Yun Ju, L., Suk-In, H., 2011, Studies on the steam and CO_2 reforming of methane for GTL-FPSO applications, Catal. Today, 174, 31-36.

Kyong-Su H., Jong Wook B., Kang-Jae, W., Ki-Won, J., 2010, Efficient utilization of greenhouse gas in a Gas-to-Liquid Process combined with carbon dioxide reforming of methane, Environ. Sci. Technol., 44, 1412-1417.

Sie D.T., 1998, Process development and scale up: IV case history of development of a Fischer Tropsch synthesis process, Rev., Chem. Eng., 14, 109-150.

Sudiro M., Bertucco A., 2009, Production of synthetic gasoline and gasoil fuel by alternative processes using natural gas and coal: Process simulation and optimization, Energy, 34, 2206-2214.