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Doan Pham Minh, Thanh Son Pham, Didier Grouset, Ange Nzihou. Thermodynamic Equilibrium Study of Methane Reforming with Carbon Dioxide, Water and Oxygen. *Journal of Clean Energy Technologies (JOCET)*, 2018, 6 (4), pp.309-313. 10.18178/JOCET.2018.6.4.480 . hal-01876167

HAL Id: hal-01876167

<https://imt-mines-albi.hal.science/hal-01876167>

Submitted on 12 Nov 2018

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Thermodynamic Equilibrium Study of Methane Reforming with Carbon Dioxide, Water and Oxygen

Doan Pham Minh, Thanh Son Phan, Didier Grouset, and Ange Nzihou

Abstract—Waste and biomass valorization can be achieved by biological degradation processes. The resulting biogas can be transformed into liquid fuels or chemicals via reforming processes. This paper aims to study the thermodynamic equilibrium of methane reforming with different oxidants: CO₂, H₂O, and O₂ at atmospheric pressure using FactSage software (6.3. version). The reaction temperature plays crucial role in all cases. High methane conversion together with high selectivity in syngas (H₂ and CO) can be only obtained above 750°C. An excess in oxidants is also required to limit the formation of solid carbon. Taking into account the fact that biogas usually contains more CH₄ than CO₂, steam addition to biogas reforming medium is recommended to get high methane conversion and to increase the molar ratio of H₂/CO, which is favorable for liquid fuels or chemical production via Fisher-Tropsch synthesis, methanol synthesis or hydrogen production.

Index Terms—Biogas, factsage, reforming, thermodynamic equilibrium.

I. INTRODUCTION

Carbon dioxide and methane are the two main gases causing global warming by greenhouse gas effect [1]. They are also the main components of biogas (roughly 35-50% CO₂ and 50-65% CH₄), natural gas (roughly 70-95% CH₄), and flue gas (mainly CO₂) [2], [3]. Biogas is the gaseous product from anaerobic digestion of biomass and organic wastes (digested gas), and also from landfill sites (landfill gas). Table I compares the composition of digested gas, landfill gas with that of a natural gas [4].

TABLE I. COMPOSITION OF DIGESTED GAS, LANDFILL GAS AND A NATURAL GAS [4].

Parameter	Unit	Digested gas	Landfill gas	Natural gas (North sea)
CH ₄	vol. %	53-70	35-65	87
CO ₂	vol. %	30-47	15-50	1.2
Other hydrocarbons	vol. %	0	0	12
H ₂	vol. %	0	0-3	-
N ₂	vol. %	0.2	5-40	0.3
O ₂	vol. %	0	0-5	0
H ₂ S	ppm	0-10000	0-100	0
NH ₃	ppm	<100	5	0
Total chlorine	mg/Nm ³	0-5	20-200	0

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Up-to-date, biogas is mostly used for heat or electricity production. Carbon dioxide and other pollutants are removed to obtain biomethane, which must meet the quality of natural gas before injection into gas grid for further utilization, or burning in gas engine to produce heat or electricity [5], [6]. However, biogas can be also transformed into liquid fuels and chemicals by different reforming processes such as steam reforming, dry reforming and tri-reforming [3], [7], [8]. The main advantage of biogas reforming is the inclusion of CO₂ in the final products. On the other hand, both CO₂ and CH₄ are stable molecules. Thus, the reforming reaction needs a catalyst (i.e. nickel catalysts) and high temperature to reach exploitable chemical kinetic. In addition, different side reactions such as Boudouard reaction, reverse water-gas-shift reaction, methane cracking, and carbon gasification, take place together with the transformation of CH₄ to CO and H₂. Table II summaries these reactions [9]-[11]. Standard enthalpy of reaction ($\Delta_r H_{298}$) was calculated from standard enthalpy of formation [11]. The dependence of Gibbs free energy change per mole of reaction ($\Delta_r G$) on the reaction temperature was previously reported in the literature and some of them were determined from FactSage calculation (details given in the next section).

TABLE II. CHEMICAL REACTIONS FROM DRY REFORMING, STEAM REFORMING AND TRI-REFORMING OF CH₄.

Reaction	$\Delta_r G$ function (P = 1 bar)	$\Delta_r H_{298}^{\circ}$ (kJ/mol)	Eq.
CH ₄ + CO ₂ → 2CO + 2H ₂	$\Delta_r G = 61770 - 67.3 * T$	+247	(1)
2CO → C + CO ₂	$\Delta_r G = -39810 + 40.9 * T$	-172	(2)
CO + H ₂ O → CO ₂ + H ₂	$\Delta_r G = -39802 + 37.673 * T$	-41	(3)
CH ₄ → C + 2H ₂	$\Delta_r G = 21960 - 26.5 * T$	+75	(4)
CH ₄ + H ₂ O → CO + 3H ₂	$\Delta_r G = 210359 - 233.9 * T$	+206	(5)
C + H ₂ O → CO + H ₂	$\Delta_r G = 132184 - 138.8 * T$	+131	(6)
2CH ₄ + O ₂ → 2CO + 4H ₂	$\Delta_r G = -653.9 - 369 * T$	-71	(7)
CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	$\Delta_r G = -803508 + 13 * T - 0.018 * T^2 + 8 * 10^{-6} * T^3$	-802.5	(8)
C + O ₂ → CO	$\Delta_r G = -110872 - 89.4 * T$	-110.5	(9)
C + O ₂ → CO ₂	$\Delta_r G = -393647 - 2.5 * T$	-393.5	(10)

(1) Dry reforming of methane (DRM); (2) Boudouard reaction; (3) Water-gas-shift reaction (WGS); (4) Methane cracking; (5) steam reforming of methane; (6) steam reforming of carbon; (7) partial oxidation of methane; (8) methane combustion; (9) partial oxidation of carbon; (10) carbon combustion. All molecules are under gas state except carbon (C) at solid state.

Table II shows that methane reforming is a complex process implying several chemical equilibriums. Catalytic deactivation is usually reported as the biggest challenge of methane reforming, caused mostly by carbon deposition and catalyst thermal sintering at high temperature [12]-[15]. The determination of operational conditions to limit solid carbon formation and to reduce catalyst thermal sintering is important to deploy biogas reforming at large industrial scale.

This paper is focused on the thermodynamic modelling of

methane reforming with different oxidants including CO_2 , H_2O and O_2 . The influence of different parameters such as the temperature and the molar ratio of oxidants to methane on the conversion of methane and the selectivity in H_2 and CO is investigated. The paper allows selecting the most appropriate conditions for future works on the reforming of a given biogas into synthetic gas.

II. METHODS

The determination of the equilibrium composition of a given system (mixture of CH_4 and oxidants) is important before any experimental study. In this work, thermodynamic behavior of different initial gas mixtures of CH_4 , CO_2 , H_2O , and O_2 was performed using FactSage software (6.3.1 version). The calculation is based on the principle of the Gibbs free energy minimization method. For each calculation, the starting composition of the mixture of CH_4 , CO_2 , H_2O , and O_2 , as well as the temperature and pressure of the considered system were well-defined. The formation of liquid hydrocarbons was neglected. Only solid carbon (C_s), water, hydrogen and carbon monoxide were considered as products from methane reforming processes.

III. RESULTS

A. Dry reforming CH_4 with CO_2

Firstly, a mixture containing 1 mole of CH_4 and 1 mole of CO_2 was considered for FactSage calculation. The pressure was kept constant at 1 bar and the temperature was varied from 100 to 1000°C. Fig. 1 shows the equilibrium while Fig. 2 presents the conversion of CH_4 and CO_2 and the molar ratio of H_2/CO of this system as a function of the temperature. The atmospheric pressure is preferred according to the stoichiometry of the reaction (1) (Table II).

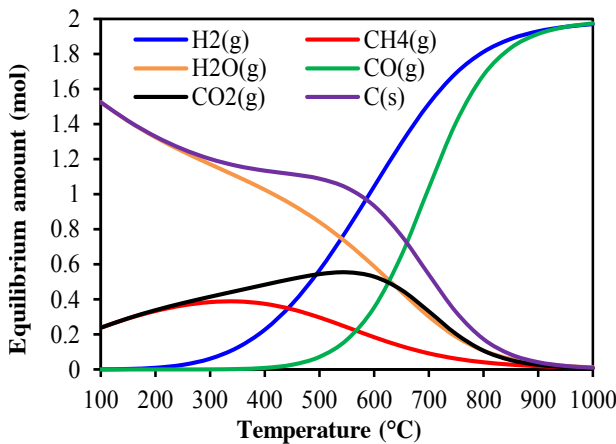


Fig. 1. Thermodynamic equilibrium of the equimolar mixture of CH_4 and CO_2 .

Fig. 1 shows that low temperatures particularly favor the formation of solid carbon (C_s) and water as by-products. H_2 and CO are only significantly formed above 250 and 450°C, respectively. Equilibrium amounts of CH_4 and CO_2 reach a maximum around 350 and 550°C, respectively, because of the exo-thermicity of the water-gas-shift (WGS) and Boudouard reactions. This leads to a minimum of CH_4 and

CO_2 conversion at these temperature as observed in Fig. 2.

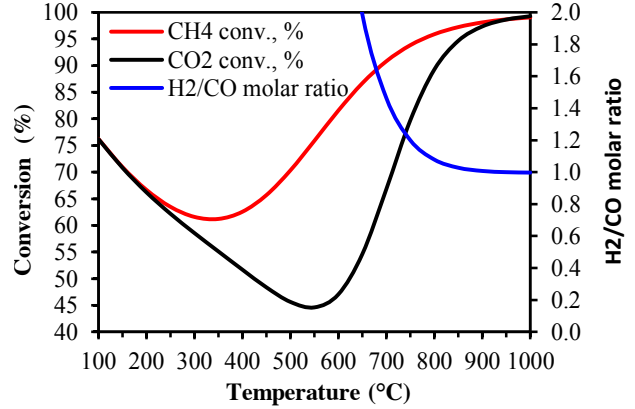


Fig. 2. Conversion of CH_4 and CO_2 and molar ratio of H_2/CO of the equimolar mixture of CH_4 and CO_2 .

High temperatures ($> 850^\circ\text{C}$) are particularly favorable for CH_4 and CO_2 conversion and H_2 and CO production. They also allow reducing considerably by-products content.

These results match well with the experimental data reported in the literature [16].

As shown in Table 1, biogas usually contains more CH_4 than CO_2 . CH_4 content can reach up to 70% while CO_2 content is lower than 50%. Fig. 2 illustrates the reforming of a mixture of 66.7% of CH_4 and 33.3% of CO_2 .

Increasing the CH_4 content to 66.7% mostly leads to higher H_2 production at high temperatures. High temperatures, above 850°C , allow a complete transformation of this gas mixture. However, C_s was omnipresent in the temperature range investigated, due to the methane cracking reaction. This must be a drawback of this system. Thus, adding other oxidants such as CO_2 , H_2O or O_2 to biogas reforming medium is strongly recommended to limit C_s formation.

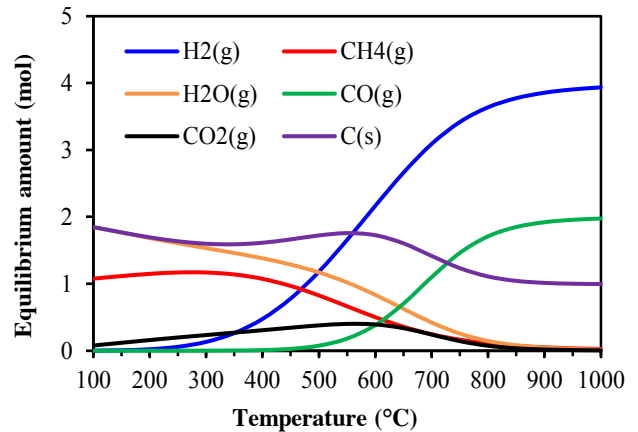


Fig. 3. Thermodynamic equilibrium of the mixture containing 2 moles of CH_4 and 1 mole of CO_2 .

B. Dual Reforming of CH_4 with CO_2 and H_2O

As shown above, H_2O addition to biogas reforming medium appears as a solution to limit C_s formation. Fig. 4 shows the results obtained with a mixture of 50% CH_4 , 25% H_2O , and 25% CO_2 (molar %). This corresponds to an equimolar mixture for the dual dry and steam reforming of methane according to Eqs. (1) and (5). As expected, the formation of C_s and H_2O as by-products is favorable at low

temperature. Increasing the temperature leads to the decrease of C_s and H_2O amounts and to the increase of CO and H_2 amounts.

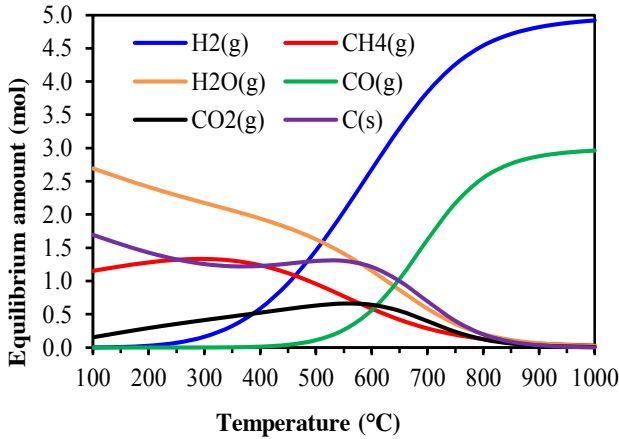


Fig. 4. Thermodynamic equilibrium of the mixture containing 2 moles of CH_4 , 1 mole of H_2O and 1 mole of CO_2 .

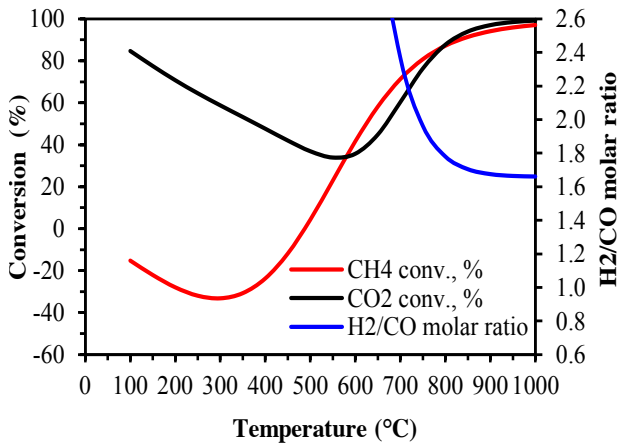


Fig. 5. Conversion of CH_4 and CO_2 and molar ratio of H_2/CO of the mixture containing 2 moles of CH_4 , 1 mole of H_2O and 1 mole of CO_2 .

Above $850^\circ C$, H_2 and CO are the main products of the reaction. Comparing to DRM which has the molar ratio of H_2/CO close to 1, dual reforming of methane with CO_2 and H_2O allows obtaining molar ratio of H_2/CO close to 1.7 (Fig. 5) which is more favorable downstream utilization of syngas such as Fisher-Tropsch synthesis, methanol synthesis or hydrogen production via WGS process.

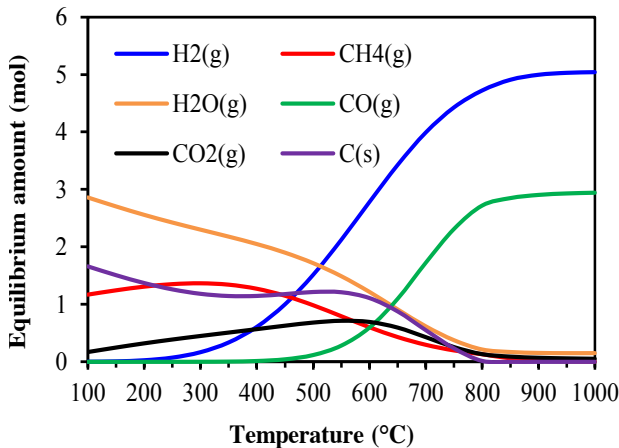


Fig. 6. Thermodynamic equilibrium of the mixture containing 2 moles of CH_4 , 1.2 mole of H_2O and 1 mole of CO_2 .

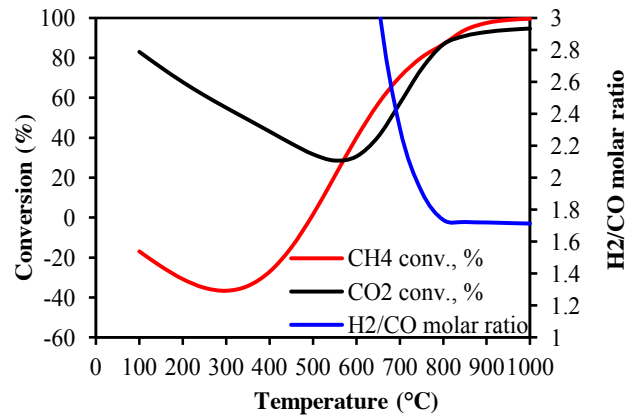


Fig. 7. Conversion of CH_4 and CO_2 and molar ratio of H_2/CO of the mixture containing 2 moles of CH_4 , 1.2 mole of H_2O and 1 mole of CO_2 .

Fig. 6 shows the results obtained with a mixture of 47.6% CH_4 , 23.8% CO_2 and 28.6% H_2O (molar %). This mixture is slightly deficit in CH_4 , considering the dual dry and steam methane reforming (Eqs. (1) and (5)). Under these conditions, H_2O is omnipresent up to $1000^\circ C$. Thus, C_s is completely removed above $800^\circ C$. This suggests that catalyst deactivation by coke deposition can be limited or even avoided. In parallel, the molar ratio of H_2/CO reaches more than 1.7 above $800^\circ C$ which is favorable for liquid fuels or chemicals synthesis (Fig. 7). At $1000^\circ C$, CH_4 is totally converted while CO_2 is still present which also allows gasifying traces of C_s , together with H_2O .

C. Tri-Reforming of Methane

Landfill gas contains some amounts of oxygen, which can raise up to 5 vol.% as shown in Table I. Tri-reforming of methane corresponds to the process implying together CO_2 , H_2O and O_2 as oxidants. Fig. 8 and 9 show the results obtained with a mixture of 51.3% CH_4 , 25.6% CO_2 , 20.5% H_2O and 2.6% O_2 at atmospheric pressure. This mixture corresponds to a stoichiometric reaction of CH_4 with the three oxidants, according to Eqs. (1), (5) and (7).

Oxygen is completely consumed regardless of the reaction temperature. Above $800^\circ C$, CH_4 and CO_2 consumption reaches high values ($> 90\%$), while H_2 and CO are also highly privileged as the main products. Both CH_4 and CO_2 can be nearly completely converted into H_2 and CO at $1000^\circ C$ for this mixture. C_s is considerably reduced at $T > 850^\circ C$ ($< 3\%$).

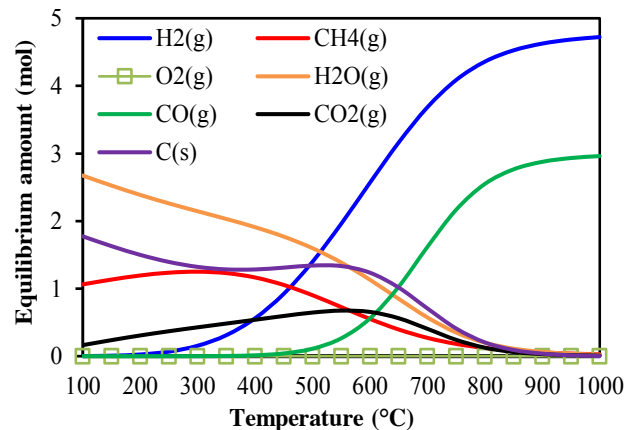


Fig. 8. Thermodynamic equilibrium of the mixture containing 2 moles of CH_4 , 0.8 mole of H_2O , 1 mole of CO_2 and 0.1 mole of O_2 .

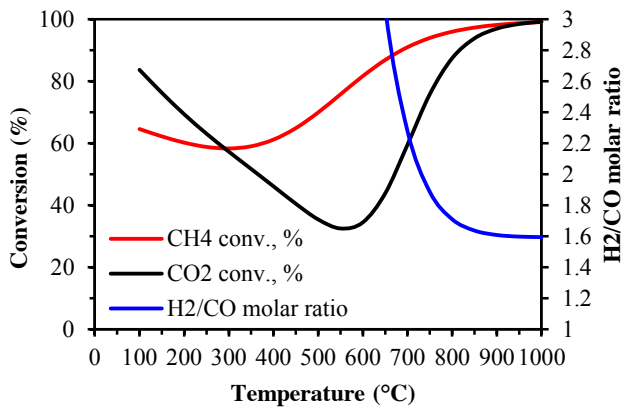


Fig. 9. Conversion of CH_4 and CO_2 and molar ratio of H_2/CO of the mixture containing 2 moles of CH_4 , 0.8 mole of H_2O , 1 mole of CO_2 and 0.1 mole of O_2 .

Tri-reforming of CH_4 with a mixture containing slightly more oxidants than CH_4 is illustrated in Figs. 10 and 11. The molar ratio of $(\text{H}_2\text{O} + \text{CO}_2 + \text{O}_2)/\text{CH}_4$ of this mixture is equal to 2.1/2. Oxygen can be completely consumed within the temperature range studied. At 800°C and above, C_s is practically negligible which suggests that catalytic deactivation caused by carbon deposition can be considerably reduced. With this mixture, both CO_2 and H_2O are slightly in excess when CH_4 is completely consumed around 900°C (Figs. 10 and 11). The excess of oxidants allows limit or avoid the formation of C_s .

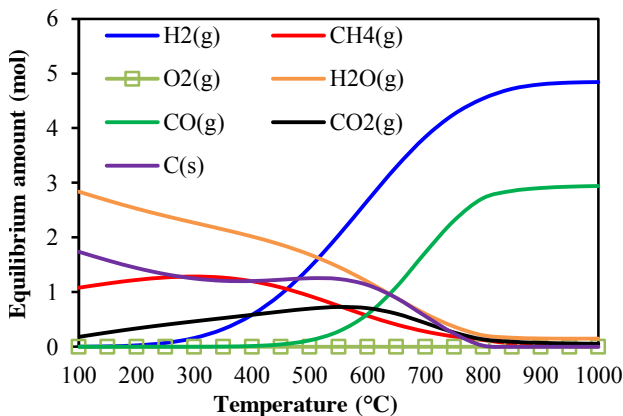


Fig. 10. Thermodynamic equilibrium of the mixture containing 2 moles of CH_4 , 1 mole of H_2O , 1 mole of CO_2 and 0.1 mole of O_2 .

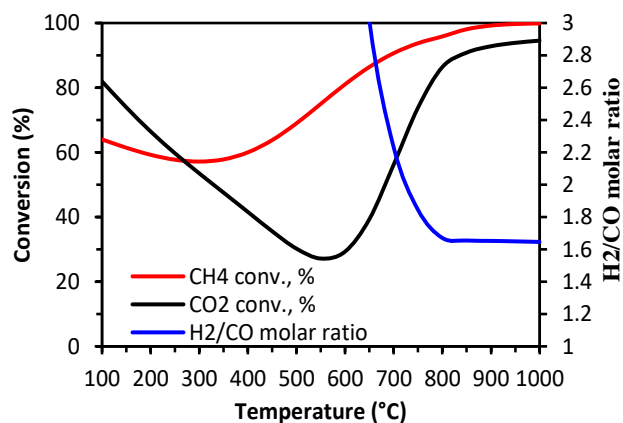


Fig. 11. Conversion of CH_4 and CO_2 and molar ratio of H_2/CO of the mixture containing 2 moles of CH_4 , 1 mole of H_2O , 1 mole of CO_2 and 0.1 mole of O_2 .

From the Fig. 10, C_s can be practically avoided at 800°C

and above, when using a mixture slightly-surplus in oxidants. But this temperature limit seems to be still high and can cause the catalytic deactivation by the sintering of active phase or catalyst support. Figs. 12 and 13 report the results obtained with a mixture having large excess of oxidants. Its molar ratio of $(\text{H}_2\text{O} + \text{CO}_2 + \text{O}_2)/\text{CH}_4$ is equal to 2.6/2. With this mixture, C_s formation can be avoided at 750°C and above. On the other hand, there is large excess of CO_2 ($\approx 35\%$) and H_2O ($\approx 38\%$) which must burden the energy balance of the global reforming process. In fact, unreacted CO_2 and H_2O leave the reactor at high temperature and can cause the loss of non-negligible energy amount.

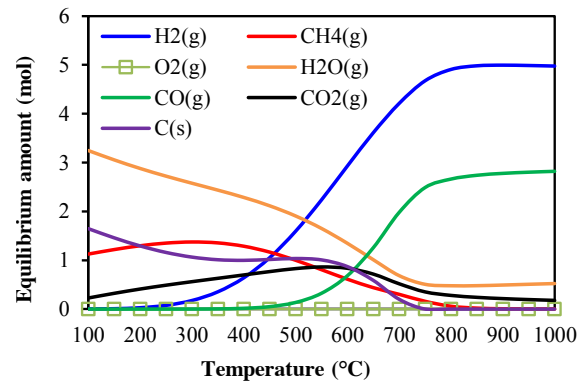


Fig. 12. Thermodynamic equilibrium of the mixture containing 2 moles of CH_4 , 1.5 mole of H_2O , 1 mole of CO_2 and 0.1 mole of O_2 .

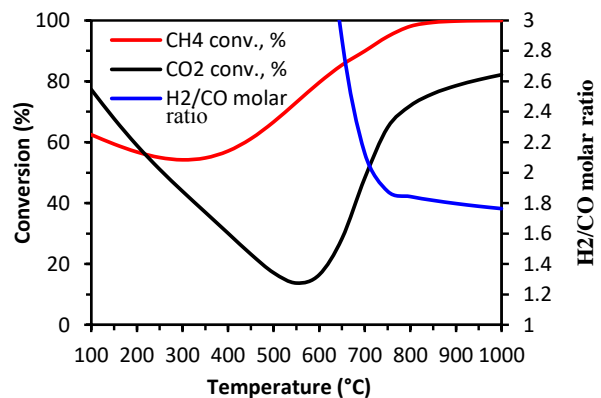


Fig. 13. Conversion of CH_4 and CO_2 and molar ratio of H_2/CO of the mixture containing 2 moles of CH_4 , 1.5 mole of H_2O , 1 mole of CO_2 and 0.1 mole of O_2 .

D. Discussion

As previously mentioned, both CH_4 and CO_2 molecules are chemically stable. Thus the conversion of these substrates needs high temperatures to be thermodynamically favored. A catalyst is also mandatory to get exploitable chemical kinetic of reforming reactions. The dry reforming of biogas, which contains more CH_4 than CO_2 , is not desired because CH_4 cracking reaction largely takes place and leads to carbon deposition. Addition of CO_2 , for example from carbon capture and utilization (CCU) process, can be a good solution. However, the molar ratio of H_2/CO does not exceed 1/1 and can be an inconvenience for the downstream utilization of this syngas, mostly for chemical synthesis processes such as Fisher-Tropsch or methanol synthesis. An additional WGS step is needed to increase this molar ratio of H_2/CO to above 2, which is required for chemical synthesis processes [17].

Biogas reforming with water vapor (steam reforming) is an

alternative to dry reforming process. Because the reaction of H₂O with CH₄ leads to higher H₂/CO molar ratio compared to that from the reaction of CO₂ with CH₄ (3/1 versus 1/1), biogas steam reforming produces more H₂ than CO. The resulting syngas is thus more adapted to chemical synthesis processes for liquid fuels or chemicals production. In the case of the mixture containing 50% CH₄, 25% CO₂ and 25% H₂O (molar %), the molar ratio of H₂/CO can reach nearly 1.7 at high CH₄ conversion (Fig. 5).

Tri-reforming of CH₄ answers to the case of landfill gas, which usually contains some amounts of oxygen. From the thermodynamic point of view, oxygen appears as the most active oxidant and must be consumed on the first place, before CO₂ and H₂O. Using high molar ratio of (H₂O + CO₂ + O₂)/CH₄ can decrease the temperature limit where C_s is limited or avoided. Lowering the reaction temperature of CH₄ reforming is important in order to limit the catalyst deactivation by thermal sintering. However, large excess of oxidants must be accompanied by heat recovery from downstream products, as well as the recycling of unreacted CO₂ and H₂O (> 35% in Fig. 12) in order to improve mass and energy balance of the global process.

IV. CONCLUSION

This work addresses a short study on the thermodynamic equilibrium of methane reforming processes. Different combinations are considered including: dry reforming of CH₄ with CO₂, dual dry and steam reforming, and tri-reforming. In all cases, high temperature of at least 750°C is required to reach high methane conversion and to limit the formation of solid carbon. Also, reaction mixture containing more oxidants than methane is recommended to limit, even avoid the formation of solid carbon.

The next study can be focused on an experimental study of methane reforming under the most favorable conditions of dual dry and steam reforming, or tri-reforming, and on the mass and energy balance of the global process.

ACKNOWLEDGMENT

The authors gratefully thank ADEME (VABHYOGAZ 3 project) for financial support of this work.

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