

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

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

► **To cite this version:**

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*, 2018, 6 (4), pp.309-313. 10.18178/JOCET.2018.6.4.480 . hal-01876167

**HAL Id: hal-01876167**

**<https://hal-mines-albi.archives-ouvertes.fr/hal-01876167>**

Submitted on 12 Nov 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# 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: CO<sub>2</sub>, H<sub>2</sub>O, and O<sub>2</sub> 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 (H<sub>2</sub> 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 CH<sub>4</sub> than CO<sub>2</sub>, steam addition to biogas reforming medium is recommended to get high methane conversion and to increase the molar ratio of H<sub>2</sub>/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% CO<sub>2</sub> and 50-65% CH<sub>4</sub>), natural gas (roughly 70-95% CH<sub>4</sub>), and flue gas (mainly CO<sub>2</sub>) [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 <sub>4</sub>	vol. %	53-70	35-65	87
CO <sub>2</sub>	vol. %	30-47	15-50	1.2
Other hydrocarbons	vol. %	0	0	12
H <sub>2</sub>	vol. %	0	0-3	-
N <sub>2</sub>	vol. %	0.2	5-40	0.3
O <sub>2</sub>	vol. %	0	0-5	0
H <sub>2</sub> S	ppm	0-10000	0-100	0
NH <sub>3</sub>	ppm	<100	5	0
Total chlorine	mg/Nm <sup>3</sup>	0-5	20-200	0

The authors are with the Université de Toulouse, Mines Albi, UMR CNRS 5302, Centre RAPSODEE, Campus Jarlard, F-81013 Albi cedex 09, France (e-mail: doan.phamminh@mines-albi.fr, thanh\_son.phan@mines-albi.fr, grouset@mines-albi.fr, ange.nzihou@mines-albi.fr).

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 CO<sub>2</sub> in the final products. On the other hand, both CO<sub>2</sub> and CH<sub>4</sub> 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 CH<sub>4</sub> to CO and H<sub>2</sub>. 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 CH<sub>4</sub>.

Reaction	$\Delta_r G$ function (P = 1 bar)	$\Delta_r H_{298}^{\circ}$ (kJ/mol)	Eq.
CH <sub>4</sub> + CO <sub>2</sub> → 2CO + 2H <sub>2</sub>	$\Delta_r G = 61770 - 67.3 * T$	+247	(1)
2CO → C + CO <sub>2</sub>	$\Delta_r G = -39810 + 40.9 * T$	-172	(2)
CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub>	$\Delta_r G = -39802 + 37.673 * T$	-41	(3)
CH <sub>4</sub> → C + 2H <sub>2</sub>	$\Delta_r G = 21960 - 26.5 * T$	+75	(4)
CH <sub>4</sub> + H <sub>2</sub> O → CO + 3H <sub>2</sub>	$\Delta_r G = 210359 - 233.9 * T$	+206	(5)
C + H <sub>2</sub> O → CO + H <sub>2</sub>	$\Delta_r G = 132184 - 138.8 * T$	+131	(6)
2CH <sub>4</sub> + O <sub>2</sub> → 2CO + 4H <sub>2</sub>	$\Delta_r G = -653.9 - 369 * T$	-71	(7)
CH <sub>4</sub> + 2O <sub>2</sub> → CO <sub>2</sub> + 2H <sub>2</sub> O	$\Delta_r G = -803508 + 13 * T - 0.018 * T^2 + 8 * 10^{-6} * T^3$	-802.5	(8)
C + O <sub>2</sub> → CO	$\Delta_r G = -110872 - 89.4 * T$	-110.5	(9)
C + O <sub>2</sub> → CO <sub>2</sub>	$\Delta_r G = -393647 - 2.5 * T$	-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  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{O}_2$ . 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  $\text{H}_2$  and  $\text{CO}$  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  $\text{CH}_4$  and oxidants) is important before any experimental study. In this work, thermodynamic behavior of different initial gas mixtures of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$  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  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$ , as well as the temperature and pressure of the considered system were well-defined. The formation of liquid hydrocarbons was neglected. Only solid carbon ( $\text{C}_s$ ), water, hydrogen and carbon monoxide were considered as products from methane reforming processes.

## III. RESULTS

### A. Dry reforming $\text{CH}_4$ with $\text{CO}_2$

Firstly, a mixture containing 1 mole of  $\text{CH}_4$  and 1 mole of  $\text{CO}_2$  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  $\text{CH}_4$  and  $\text{CO}_2$  and the molar ratio of  $\text{H}_2/\text{CO}$  of this system as a function of the temperature. The atmospheric pressure is preferred according to the stoichiometry of the reaction (1) (Table II).

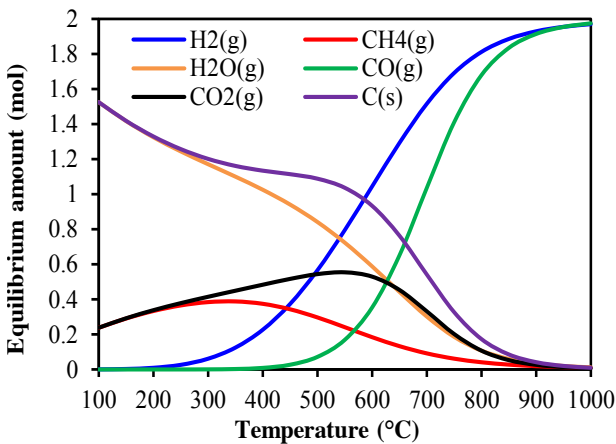


Fig. 1. Thermodynamic equilibrium of the equimolar mixture of  $\text{CH}_4$  and  $\text{CO}_2$ .

Fig. 1 shows that low temperatures particularly favor the formation of solid carbon ( $\text{C}_s$ ) and water as by-products.  $\text{H}_2$  and  $\text{CO}$  are only significantly formed above 250 and 450°C, respectively. Equilibrium amounts of  $\text{CH}_4$  and  $\text{CO}_2$  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  $\text{CH}_4$  and

$\text{CO}_2$  conversion at these temperature as observed in Fig. 2.

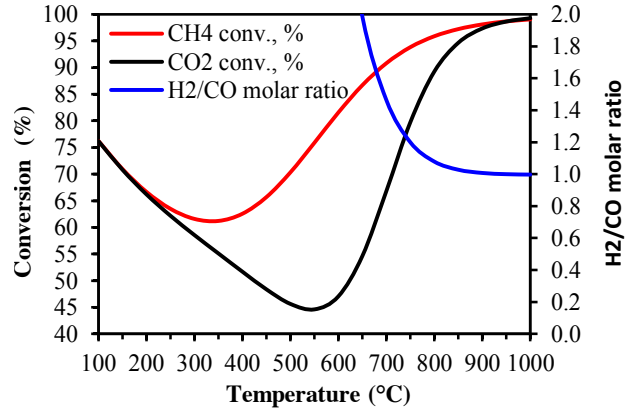


Fig. 2. Conversion of  $\text{CH}_4$  and  $\text{CO}_2$  and molar ratio of  $\text{H}_2/\text{CO}$  of the equimolar mixture of  $\text{CH}_4$  and  $\text{CO}_2$ .

High temperatures ( $> 850^\circ\text{C}$ ) are particularly favorable for  $\text{CH}_4$  and  $\text{CO}_2$  conversion and  $\text{H}_2$  and  $\text{CO}$  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  $\text{CH}_4$  than  $\text{CO}_2$ .  $\text{CH}_4$  content can reach up to 70% while  $\text{CO}_2$  content is lower than 50%. Fig. 2 illustrates the reforming of a mixture of 66.7% of  $\text{CH}_4$  and 33.3% of  $\text{CO}_2$ .

Increasing the  $\text{CH}_4$  content to 66.7% mostly leads to higher  $\text{H}_2$  production at high temperatures. High temperatures, above  $850^\circ\text{C}$ , allow a complete transformation of this gas mixture. However,  $\text{C}_s$  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  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  or  $\text{O}_2$  to biogas reforming medium is strongly recommended to limit  $\text{C}_s$  formation.

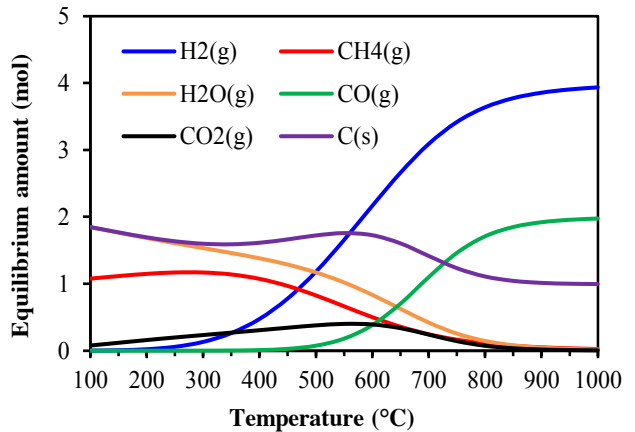


Fig. 3. Thermodynamic equilibrium of the mixture containing 2 moles of  $\text{CH}_4$  and 1 mole of  $\text{CO}_2$ .

### B. Dual Reforming of $\text{CH}_4$ with $\text{CO}_2$ and $\text{H}_2\text{O}$

As shown above,  $\text{H}_2\text{O}$  addition to biogas reforming medium appears as a solution to limit  $\text{C}_s$  formation. Fig. 4 shows the results obtained with a mixture of 50%  $\text{CH}_4$ , 25%  $\text{H}_2\text{O}$ , and 25%  $\text{CO}_2$  (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  $\text{C}_s$  and  $\text{H}_2\text{O}$  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.

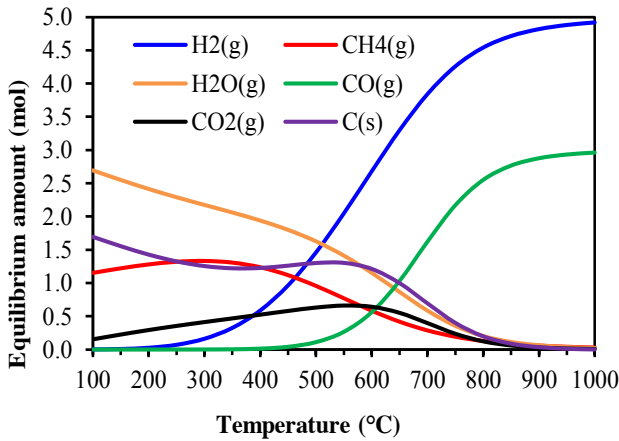


Fig. 4. Thermodynamic equilibrium of the mixture containing 2 moles of  $CH_4$ , 1 mole of  $H_2O$  and 1 mole of  $CO_2$ .

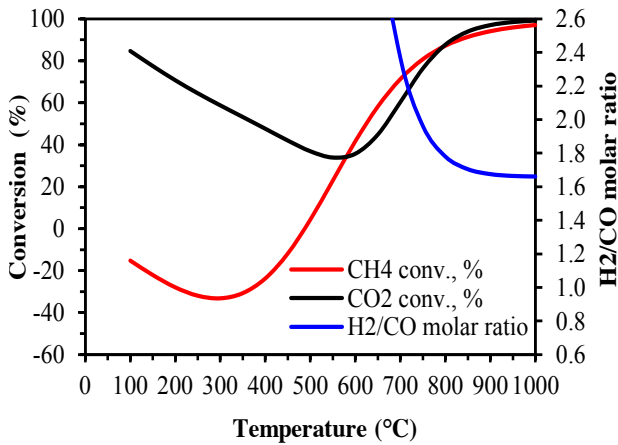


Fig. 5. Conversion of  $CH_4$  and  $CO_2$  and molar ratio of  $H_2/CO$  of the mixture containing 2 moles of  $CH_4$ , 1 mole of  $H_2O$  and 1 mole of  $CO_2$ .

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.

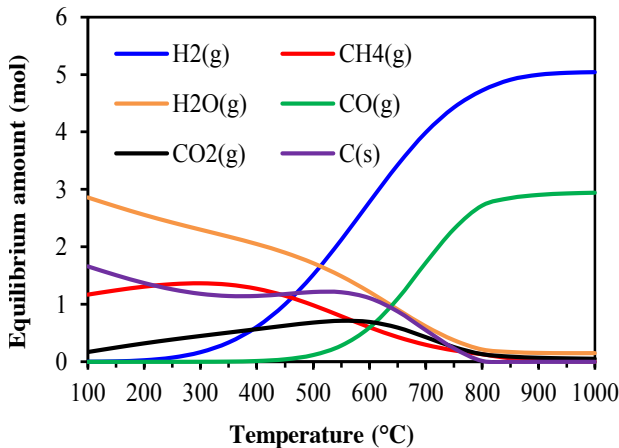


Fig. 6. Thermodynamic equilibrium of the mixture containing 2 moles of  $CH_4$ , 1.2 mole of  $H_2O$  and 1 mole of  $CO_2$ .

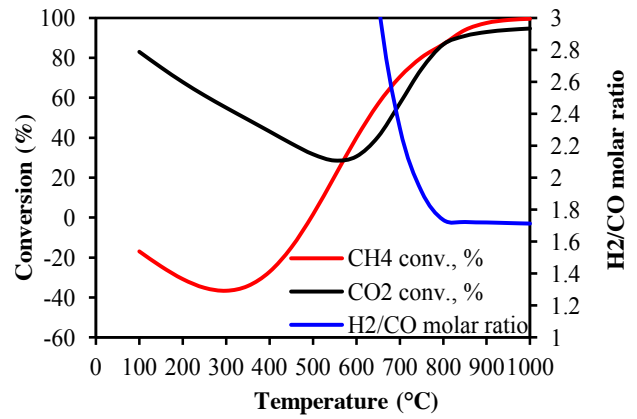


Fig. 7. Conversion of  $CH_4$  and  $CO_2$  and molar ratio of  $H_2/CO$  of the mixture containing 2 moles of  $CH_4$ , 1.2 mole of  $H_2O$  and 1 mole of  $CO_2$ .

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  $T > 850^\circ C$  ( $< 3\%$ ).

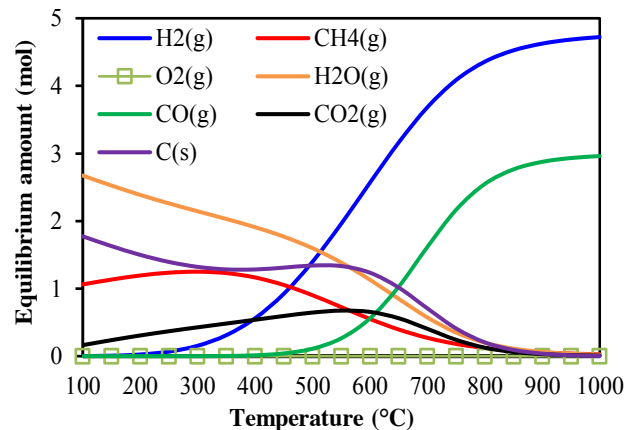


Fig. 8. Thermodynamic equilibrium of the mixture containing 2 moles of  $CH_4$ , 0.8 mole of  $H_2O$ , 1 mole of  $CO_2$  and 0.1 mole of  $O_2$ .

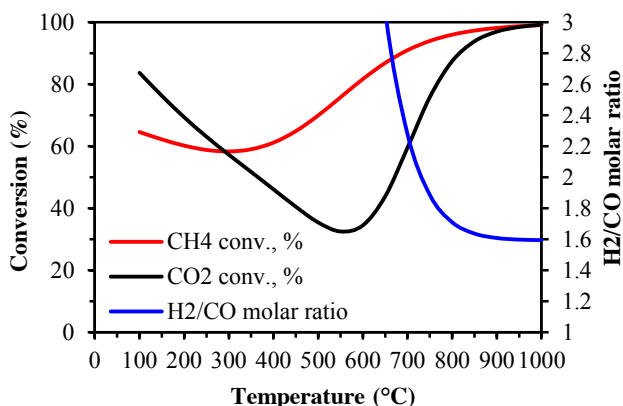


Fig. 9. Conversion of  $\text{CH}_4$  and  $\text{CO}_2$  and molar ratio of  $\text{H}_2/\text{CO}$  of the mixture containing 2 moles of  $\text{CH}_4$ , 0.8 mole of  $\text{H}_2\text{O}$ , 1 mole of  $\text{CO}_2$  and 0.1 mole of  $\text{O}_2$ .

Tri-reforming of  $\text{CH}_4$  with a mixture containing slightly more oxidants than  $\text{CH}_4$  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  $800^\circ\text{C}$  and above,  $\text{C}_s$  is practically negligible which suggests that catalytic deactivation caused by carbon deposition can be considerably reduced. With this mixture, both  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are slightly in excess when  $\text{CH}_4$  is completely consumed around  $900^\circ\text{C}$  (Figs. 10 and 11). The excess of oxidants allows limit or avoid the formation of  $\text{C}_s$ .

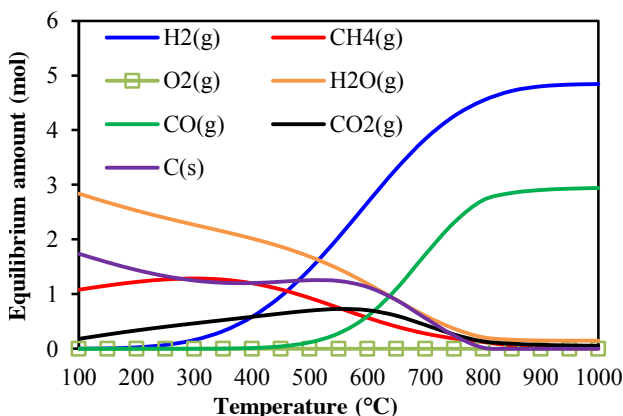


Fig. 10. Thermodynamic equilibrium of the mixture containing 2 moles of  $\text{CH}_4$ , 1 mole of  $\text{H}_2\text{O}$ , 1 mole of  $\text{CO}_2$  and 0.1 mole of  $\text{O}_2$ .

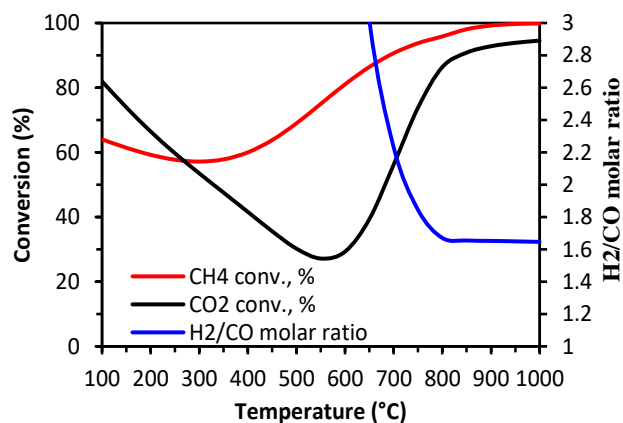


Fig. 11. Conversion of  $\text{CH}_4$  and  $\text{CO}_2$  and molar ratio of  $\text{H}_2/\text{CO}$  of the mixture containing 2 moles of  $\text{CH}_4$ , 1 mole of  $\text{H}_2\text{O}$ , 1 mole of  $\text{CO}_2$  and 0.1 mole of  $\text{O}_2$ .

From the Fig. 10,  $\text{C}_s$  can be practically avoided at  $800^\circ\text{C}$

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,  $\text{C}_s$  formation can be avoided at  $750^\circ\text{C}$  and above. On the other hand, there is large excess of  $\text{CO}_2$  ( $\approx 35\%$ ) and  $\text{H}_2\text{O}$  ( $\approx 38\%$ ) which must burden the energy balance of the global reforming process. In fact, unreacted  $\text{CO}_2$  and  $\text{H}_2\text{O}$  leave the reactor at high temperature and can cause the loss of non-negligible energy amount.

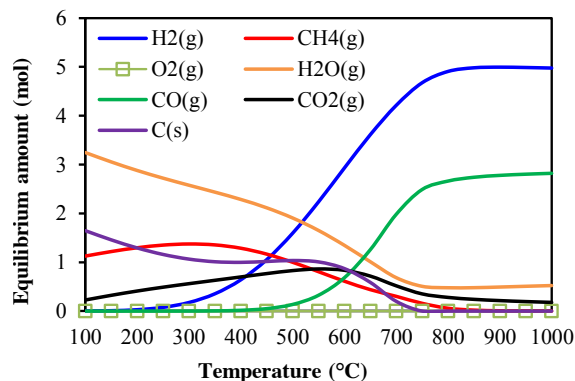


Fig. 12. Thermodynamic equilibrium of the mixture containing 2 moles of  $\text{CH}_4$ , 1.5 mole of  $\text{H}_2\text{O}$ , 1 mole of  $\text{CO}_2$  and 0.1 mole of  $\text{O}_2$ .

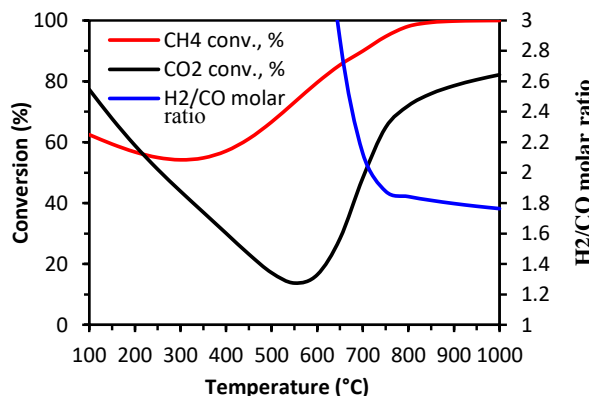


Fig. 13. Conversion of  $\text{CH}_4$  and  $\text{CO}_2$  and molar ratio of  $\text{H}_2/\text{CO}$  of the mixture containing 2 moles of  $\text{CH}_4$ , 1.5 mole of  $\text{H}_2\text{O}$ , 1 mole of  $\text{CO}_2$  and 0.1 mole of  $\text{O}_2$ .

#### D. Discussion

As previously mentioned, both  $\text{CH}_4$  and  $\text{CO}_2$  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  $\text{CH}_4$  than  $\text{CO}_2$ , is not desired because  $\text{CH}_4$  cracking reaction largely takes place and leads to carbon deposition. Addition of  $\text{CO}_2$ , for example from carbon capture and utilization (CCU) process, can be a good solution. However, the molar ratio of  $\text{H}_2/\text{CO}$  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  $\text{H}_2/\text{CO}$  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 H<sub>2</sub>O with CH<sub>4</sub> leads to higher H<sub>2</sub>/CO molar ratio compared to that from the reaction of CO<sub>2</sub> with CH<sub>4</sub> (3/1 versus 1/1), biogas steam reforming produces more H<sub>2</sub> 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% CH<sub>4</sub>, 25% CO<sub>2</sub> and 25% H<sub>2</sub>O (molar %), the molar ratio of H<sub>2</sub>/CO can reach nearly 1.7 at high CH<sub>4</sub> conversion (Fig. 5).

Tri-reforming of CH<sub>4</sub> 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 CO<sub>2</sub> and H<sub>2</sub>O. Using high molar ratio of (H<sub>2</sub>O + CO<sub>2</sub> + O<sub>2</sub>)/CH<sub>4</sub> can decrease the temperature limit where C<sub>s</sub> is limited or avoided. Lowering the reaction temperature of CH<sub>4</sub> 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 CO<sub>2</sub> and H<sub>2</sub>O (> 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 CH<sub>4</sub> with CO<sub>2</sub>, 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.

#### REFERENCES

- [1] G. P. Robertson, E. A. Paul, and R. R. Harwood, "Greenhouse gases in intensive agriculture: Contributions of individual gases to the radiative forcing of the atmosphere," *Science*, vol. 289, pp. 1922-1925, September 2000.
- [2] M. Balat and H. Balat, "Biogas as a renewable energy source—A review," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 31, pp. 1280–1293, May 2009.
- [3] Y. T. Shah, "Chemical energy from natural and synthetic gas," CRC Press, 2017.
- [4] M. Persson, O. Jönsson, and A. Wellinger, "Biogas upgrading to vehicle fuel standards and grid injection," *In IEA Bioenergy Task*, vol. 37, 2006.
- [5] A. Petersson and A. Wellinger, "Biogas upgrading technologies – developments and innovations," *In IEA Bioenergy, Task 37 - Energy from biogas and landfill gas*, 2009.
- [6] A. Wellinger, J. Murphy, and D. Baxter, *The Biogas Handbook-Science, Production and Applications*, Woodhead Publishing, 2013.
- [7] T. N. Wedraogo, "Valorisation du biogaz par purification et par reformage," PhD thesis, Université de Lorraine (France), 2014.
- [8] C. Song and W. Pan, "Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H<sub>2</sub>/CO ratios," *Catal. Today*, vol. 98, pp. 463-484, December 2004.
- [9] B. Rêgo de Vasconcelos, "Phosphates-based catalysts for synthetic gas (syngas) production using CO<sub>2</sub> and CH<sub>4</sub>," PhD thesis, Université de Toulouse III (France), 2016.
- [10] S. Wang and G. Q. Lu, "Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: state of the art," *Energy Fuels*, vol. 10, pp. 896-904, July 1996.
- [11] D. R. Lide, *Handbook of Chemistry and Physics*, 84<sup>th</sup> Ed., CRC Press, 2003-2004.
- [12] Y. T. Shah, *Chemical Energy from Natural Gas and Synthetic Gas*, CRC Press, 2017, ch. 6, pp. 357-434.
- [13] T. S. Phan, A. R. Sane, B. Rêgo de Vasconcelos, A. Nzihou, P. Sharrock, D. Grouset, and D. Pham Minh, "Hydroxyapatite supported bimetallic cobalt and nickel catalysts for syngas production from dry reforming of methane," *Appl. Catal. B: Env.*, vol. 224, pp. 310–321, May 2018.
- [14] N. A. K. Aramouni, J. G. Touma, B. A. Tarboush, J. Zeaiter, M. N. Ahmad, "Catalyst design for dry reforming of methane: Analysis review," *Renew. Sust. Ener. Rev.*, [Online]. Nov. 2017. Available: <http://www.sciencedirect.com/science/article/pii/S1364032117313278>
- [15] G. Nahara, D. Mote, and V. Dupont, "Hydrogen production from reforming of biogas: Review of technological advances and an Indian perspective," *Renew. Sust. Ener. Rev.*, vol. 76, pp. 1032–1052, September 2017.
- [16] Y. Wang, L. Yao, S. Wang, D. Mao, and C. Hu, "Low-temperature catalytic CO<sub>2</sub> dry reforming of methane on Ni-based catalysts: A review," *Fuel Proc. Technol.*, vol. 169, pp. 199-206, January 2018.
- [17] G. Jiménez-García and R. Maya-Yescas, "Differences between Fisher–Tropsch synthesis of either gasoline or diesel based on changes of entropy and free energy," *Fuel*, vol. 149, pp. 184-190, June 2015.