AIDIC EFCE
ISCRE25 FLORENCE 2018 BRIDGING SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Biogas upgrading based on the Sabatier process with *in situ* water removal – Thermodynamic analysis

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Highlights

- Biogas upgrading based on CO_2 conversion with a water withdrawal approach.
- Membrane reactor improves CH_4 yield only up to a certain water removal fraction.
- Optimum water removal fraction depends on the CH_4/CO_2 feed ratio.

1. Introduction

Depletion of fossil fuel reserves, climate change, fuel prices, as well as political issues have accelerated the development and dissemination of technologies to exploit renewable sources for securing the energy demand in a sustainable way. Among them, biogas was shown to be an interesting option to replace natural gas [1]. However, a considerable fraction of CO_2 is obtained during biogas production, which requires a further separation step for biogas upgrading. Instead of a separation process, an alternative would be converting the CO_2 present in the raw biogas into more CH_4 (Eq. 1 in Table 1) and using renewable-based H_2 (the so-called Power-to-Gas concept). In this regard, the present work studies, from the thermodynamic point of view, the influence of the temperature, pressure, and water removal fraction (*R*) on the methane production for different biogas feed compositions. Water removal fraction might be particularly relevant if the reaction is carried out in a multifunctional reactor that separates the water formed either through a selective membrane or through an appropriate sorbent (in a membrane reactor or in a sorption-enhanced reactor, respectively).

Table 1. Possible reactions occurring during the Sabatier process.

Reaction		$\Delta H_f^{298\,K}$ (kJ mol^{-1})	Equation number
Sabatier	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-165	(1)
Reverse water-gas shift	$H_2 + CO_2 \leftrightarrow CO + H_2O$	41	(2)
CO methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-206	(3)
Carbon formation	$2CO \leftrightarrow C + CO_2$	-172	(4)
	$CH_4 \leftrightarrow 2H_2 + C$	74	(5)
	$CO + H_2 \leftrightarrow H_2O + C$	-131	(6)
	$CO_2 + 2H_2 \leftrightarrow 2H_2O + C$	-90	(7)

2. Methods

The software *Aspen Pus V8.8* was used for the Sabatier process simulations, employing the Gibbs free energy minimization methodology (nonstoichiometric method). For water removal, it was necessary to simulate the H_2O-selective membrane or the H_2O-selective sorbent depending on the R value: a selective membrane is used for $0<R<1$ (which in practice is determined by operating conditions and characteristics of the membrane to be used, namely its permselectivity) and, in contrast, for *R* upper or equal to 0.99, a sorbent is employed (in the sorption-enhanced reactor one is focused in the pre-breakthrough period, during which water is captured in the sorbent and, therefore, its composition is null in the outlet stream). The modular approach used was the same as described in a previous work [2] .

The analysis was performed at temperatures between 200 and 450 ºC, while the total pressure was varied between 1 and 31 atm. H_2 was added to the process according to the stoichiometric H_2/CO_2 ratio of 4. CH_4 and CO_2 contents in biogas typically range between 50-75% and 25-45%, respectively [3]. Therefore, the CH_4/CO_2 ratio in the biogas feed stream was analyzed for 1.11, 1.92 and 2.96 molar ratios, while H_2O and O_2 fractions were kept constant (1.08 and 0.43, respectively); all values are after dilution with H_2.

3. Results and discussion

The influence of pressure and temperature on CH_4 yield, for the different compositions of biogas considered, was firstly assessed considering a traditional methanator (*R*=0). The results obtained (not shown for brevity reasons) evidence that the CH_4 yield decreases with temperature and increases with pressure, in line with the exothermic nature and stoichiometry of the Sabatier reaction. Fig. 1 shows the methane, carbon monoxide and carbon yields variation with the water removal fraction (*R*) and the CH_4/CO_2 ratio at 325 ºC and 1 atm. For a typical biogas stream (CH_4/CO_2 ratio of 1.92) it was found that up to an *R* of 0.2 the thermodynamic equilibrium of Eq.1 was shifted in the direction of the products (methane production) (Fig. 1a) and no carbon formation was achieved (Fig. 1c). On the other hand, the CO production, which remained constant with the increase of *R* (up to 0.2), is explained by the reverse water-gas shift reaction and CO methanation (Fig. 1b). At *R* values higher than 0.2, the removal of water started to shift the thermodynamic equilibrium of reactions (6) and (7) to the right side, implying a decrease in the methane yield (because those reactions imply a consumption of the Sabatier reactants). Also, it is noted a significant increase of coke formation and a decrease of carbon monoxide, which is reactant in reaction (6). It can be observed, by comparing the behavior of different biogas streams, that the optimum *R* value, i.e. which maximizes the CH_4 yield, decreases with an increase of the CH_4/CO_2 ratio. From the optimum *R* value on, the water removal approach does not improve the production of CH_4. This means that the hybrid reactor to consider, namely membrane reactor with a water permselective membrane, should be operated and conditions adapted according to the biogas feed. Moreover, for a CH_4/CO_2 ratio of 2.96 (or higher), it is better to consider a traditional reactor design.

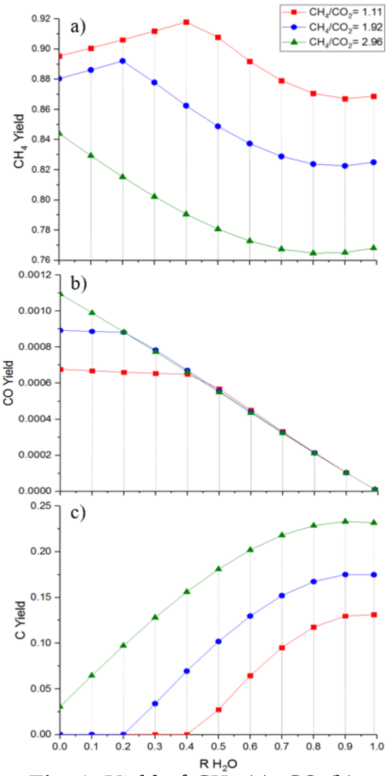

Fig. 1. Yield of CH_4 (a), CO (b) and carbon (c) in the thermodynamic equilibrium at 325 ºC and 1 atm as a function of the water removal fraction and CH_4/CO_2 ratio in the biogas feed.

4. Conclusions

A thermodynamic analysis of biogas upgrading based on CO_2 conversion by the Sabatier reaction and featuring water removal showed that the optimum water removal fraction, which maximizes the methane production, depends on the CH_4/CO_2 ratio in the biogas stream (as well as on the operating temperature and pressure). Except for high CH_4/CO_2 ratios, the water removal approach can be quite advantageous (up to a certain point) not only in terms of methane yield, but also in terms of CO reduction.

Acknowledgments

Ana C. Faria acknowledges LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy, and the project - POCI-01-0145-FEDER-006939 funded by the European Regional Development Fund (ERDF), through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds, through FCT - Fundação para a Ciência e a Tecnologia, for her research grant. The authors also acknowledge NORTE-01-0145-FEDER-000005 – LEPABE-2-ECO-INNOVATION project, supported by the North Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through ERDF. C.V. Miguel is grateful to FCT for his PhD scholarship (SFRH/BD/110580/2015), financed by national funds of the Ministry of Science, Technology and Higher Education and the European Social Fund (ESF) through the Human Capital Operational Programme (POCH).

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Keywords

Methanation; Sabatier reaction; Biogas upgrading; Water removal