



Optimization for biogas to chemicals via tri-reforming. Analysis of Fischer-Tropsch fuels from biogas

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ABSTRACT

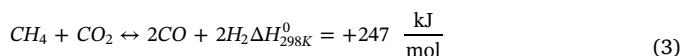
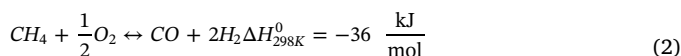
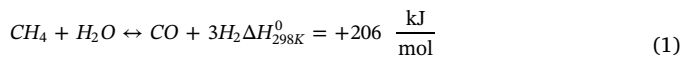
This paper presents an optimization approach for the production of syngas from biogas via tri-reforming. The optimization, formulated as a NLP problem, is performed for three syngas ratios according to the desired product: methanol, ethanol or Fischer-Tropsch (FT) fuels. As a result, the optimal operating conditions and biogas composition are defined. For the production of ethanol, a biogas composed by a $\text{CH}_4:\text{CO}_2$ ratio of 0.52:0.48 is desired, requiring 0.035 mol of O_2 per mol of Biogas in the reformer. For the production of methanol and FT, biogas with the largest content of methane is suggested to be reformed with 0.275 mol O_2 /mol biogas. The largest $\text{H}_2:\text{CO}$ ratio required for methanol is achieved by feeding steam in a WGS reactor after the reformer. The syngas optimization study is completed by evaluating tri-reforming for the production of FT fuels from biogas via high and low temperature FT synthesis. The production cost for a plant fed with 12 MMm³/y of biogas results in \$3/gal for biodiesel via HTFT and \$1.7/gal via LTFT.

1. Introduction

Developed societies generate large volumes of organic wastes such as sludge from water treatment, urban and forest residues or manure [1]. Most of these organic wastes require treatment before disposal. Anaerobic digestion represents a technology that allows not only processing and stabilizing the waste, but also generates additional value in the form of biogas and digestate, as part of the circular economy initiative [2–4]. For decades, these products were the only ones obtained, being the biogas applied for the production of power [5,6] and/or as a source of methane for natural gas networks [5,7,8]. However, biogas is an interesting source of carbon not only because of the methane, but also due to its CO_2 content. Initially, biogas was upgraded transforming the methane into syngas and hydrogen via steam reforming (SR) [9–12] and auto-thermal reforming (ATR) [13,14]. However, the inherent CO_2 within the biogas can be also used to produce syngas via dry reforming (DR) [15]. Hernandez and Martin evaluated the possibility of using biogas for the production of methanol via combined SR and DR [15]. Dry reforming does not only upgrade the biogas [16], but it also reduces CO_2 emissions of the process [15]. The syngas produced from the reformer was also evaluated by Hernandez et al. [17] for the production of other chemicals such as DME, ethanol or F-T fuels. However, the study was conceived as a product design problem for the selection of waste type and the evaluation focused on determining the $\text{H}_2:\text{CO}$ ratio

required, and no process design beyond syngas production was performed for each of the chemicals produced except for methanol. The production process of methanol defined by Hernandez and Martin [15] was thermodynamically evaluated by Vita et al. [18] proposing upgrades such as the use of tri-reforming (TR) and providing a range of profitability for the process. This process has also been recently optimized by Oliveira dos Santos et al. [19] for different biogas sources.

TR is a technology that combines three methane reforming processes [20]: SR (Eq. (1)), partial oxidation (POX) (Eq. (2)) and DR (Eq. (3)). The synergetic combination of these three technologies has the merit of the economic advantage of SR [21,22], the high energy efficiency of the exothermal POX [23,24], and the environmental advantage of carbon dioxide reforming [9,10,25–27].



Kinetic models have been proposed and optimized for the TR of methane [28–30], natural gas [31,32] and biogas [33]. The integration of tri-reforming in process optimization and design has only been recently addressed by Balasubramanian et al. [34]. They performed an

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Nomenclature

C_i	cost of the material/product i .
C_p	specific heat capacity at constant pressure (J/mol K)
$fc(i,j,k)$	molar flow rate of component i , from unit j to k (mol/s)
$frac_i$	mass fraction corresponding to the group of components defined in i .
F	global molar flow rate (mol/s).
ΔH_{298K}^0	reaction enthalpy at 298 K
Hf_i	enthalpy of formation of component i (J/mol)
J	set of components
k_p	equilibrium constant defined as ration between vapour pressures.
K_c	polytropic constant for compressors.
LHV_i	low heating value of component i (J/kg)
m_i	mass flow rate of component i (kg/s)
mol_i	mol of component i .

MW_i	molar mass of component i (kg/kmol)
nc	number of carbon atoms in the formula of a component.
nh	number of hydrogen atoms in the formula of a component.
P_i	partial pressure of component i (bar)
Q	heat flux (J/s)
S_i	selectivity to component i
T	temperature (K)
w_i	mass fraction of component i
W	electricity (W)
y_i	molar fraction of component i
X_i	conversion of component i
Z	profit (\$/mol of biogas)
α	chain growth from Anderson-Schulz-Flory distribution
η_c	compressor efficiency
$\$i$	price of component i

MINLP optimization selecting the optimal reformer, including tri-reforming, for different H_2 :CO syngas ratios and using natural gas as raw material [34]. However, to the best of authors' knowledge the only study concerning the optimization of biogas TR does not consider the cleaning of the biogas or the tune-up of the syngas produced, the optimization was performed to the kinetics of the reformer alone [33]. No optimization studies have been performed integrating the biogas TR in process design and complete process design of fuels production is not available either. Thus, in this work we propose a parametric optimization approach evaluating different O_2 :Biogas ratios. The optimization is first applied for the production of syngas with different H_2 :CO ratios depending on the syngas application: for the production of methanol, DME, ethanol or F-T. The study allows identifying the optimal type of reformer, the optimal biogas composition and if an external supply of CO_2 , steam or oxygen are required.

The manuscript is completed with a second study. A novel integrated process is designed for the production of FT-fuels from biogas as raw material. The integration of tri-reforming has been performed for the production of different chemicals such as methanol, using natural gas [35] and biogas [18,19] as raw material, DME, using natural gas as raw material [36], or fuel for SOFC [37]. Meanwhile for the production of FT fuels via tri-reforming, processes have also been recently presented using natural gas [38] or biomass as raw material [39]. However, no process has been developed for biogas to FT fuels via tri-reforming. To the best of authors' knowledge, the only two studies concerning biogas to FT fuels uses auto-thermal reforming for the processing of biogas [40,41] or natural gas [42]. Therefore, a new process for the production of FT-fuels from biogas is also presented in this work, including the evaluation of two modes of operation, high and low temperature Fischer – Tropsch (HTFT & LTFT). For the first time, the biogas is not only used for the direct production of FT-fuels, but it is also considered in the operation of complementary units such as the burner, where it is used as fuel, or the hydro-treatment unit, where the hydrogen used to enhance the yield from the wax obtained at low temperature FT (LTFT) is obtained from biogas reforming.

The rest of the paper is structured as follows. In Section 2, the modelling issues for the process optimization of biogas to syngas via tri-reforming are described. In Section 3, the modelling issues for the process design of syngas to Fischer-Tropsch fuels are defined. In Section 4, the results are presented. Finally, remarks and conclusions are drawn in Section 5.

2. Modelling issues. Biogas to syngas

The process section of syngas production from biogas is presented in Fig. 1. The biogas generated from anaerobic digestion consists mainly of methane and CO_2 , apart from other species in small quantities such as nitrogen, H_2S , steam or NH_3 . These components of the biogas together with the rest of the components of the tri-reforming system belong to the set $J = \{CH_4, CO_2, N_2, H_2S, H_2O, NH_3, H_2, CO, O_2\}$. Before processing the biogas, some of its components need to be removed since they can reduce the catalyst efficiency. Thus, a clean-up stage is initially introduced in the process in order to prepare the biogas to be fed to the reformer. After the reforming stage, it may be necessary to clean and tune-up the H_2 :CO ratio of the syngas. A cleaning process to remove the unreacted and impurities is suggested. It is followed by a hydrogen tuned-up section consisting of a PSA membrane unit for H_2 recovery, a by-pass and a water gas shift (WGS) reactor. Finally, a CO_2 removal section composed by a PSA membrane and a by-pass is considered.

2.1. Biogas cleaning section

Biogas is a complex mixture of gases with a wide range of components and different compositions that are dependent on the biogas source [5,6,43,44]. In this work biogas production is not addressed, but the optimal composition will also be computed. For simplification, in the present work the ranges of composition provided in Table 1 are taken [44]. These ranges are general enough to consider different biogas sources such as sludge, pig or cattle manure as well as their blend to obtain intermediate mixtures. In the same way, if external

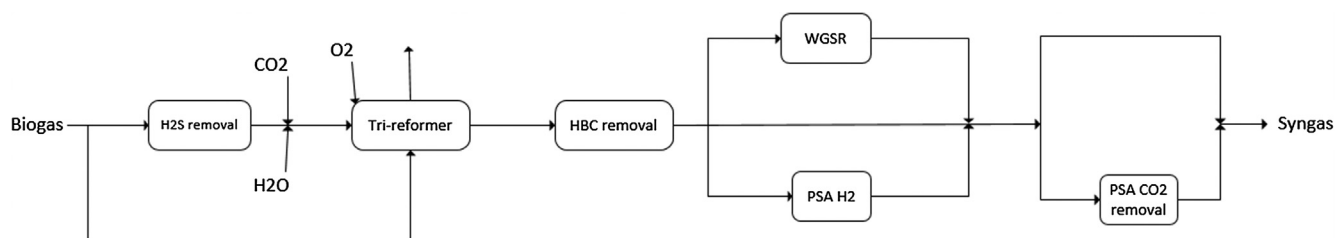


Fig. 1. Syngas processing.

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