Journal of Environmental Management xxx (2017) 1–8

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Thermodynamic modelling of an onsite methanation reactor for upgrading producer gas from commercial small scale biomass gasifiers

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ARTICLE INFO

Article history:
Received 30 April 2017
Received in revised form
8 June 2017
Accepted 18 June 2017
Available online xxx

Keywords:
Power-to-gas
Wobbe index
Gas reforming
Ammonia
Thermodynamic equilibrium

ABSTRACT

Small scale biomass gasifiers have the advantage of having higher electrical efficiency in comparison to other conventional small scale energy systems. Nonetheless, a major drawback of small scale biomass gasifiers is the relatively poor quality of the producer gas. In addition, several EU Member States are seeking ways to store the excess energy that is produced from renewables like wind power and hydropower. A recent development is the storage of energy by electrolysis of water and the production of hydrogen in a process that is commonly known as “power-to-gas”. The present manuscript proposes an onsite secondary reactor for upgrading producer gas by mixing it with hydrogen in order to initiate methanation reactions. A thermodynamic model has been developed for assessing the potential of the proposed methanation process. The model utilized input parameters from a representative small scale biomass gasifier and molar ratios of hydrogen from 1:0 to 1:4.1. The Villar-Cruise-Smith algorithm was used for minimizing the Gibbs free energy. The model returned the molar fractions of the permanent gases, the heating values and the Wobbe Index. For mixtures of hydrogen and producer gas on a 1:0.9 ratio the increase of the heating value is maximized with an increase of 78%. For ratios higher than 1:3, the Wobbe index increases significantly and surpasses the value of 30 MJ/Nm^3.

1. Introduction

The European Union is committed to a (Low Carbon Economy) model which - through a series of legislative actions - it promotes efficiently and effectively the development of renewable energy technologies (European Commission, 2014). This energy development strategies have boosted the share of renewable energy sources in the energy production mix, particularly in the form of wind and solar power (de Boer et al., 2014). In addition, in areas with special geomorphological characteristics, hydropower can be a major factor in the energy production mix (Autonomous Province of Bolzano, 2016). Nonetheless, the renewable energy production units are generating surplus energy that the existing network is not able to utilize. In some cases this is due to the overgrowth of the renewables (Jentsch et al., 2014) and in other cases because the electricity demand of these networks was already covered by other existing energy facilities, such as thermal energy conversion plants, that cannot be replaced because they ensure the network stability. Therefore several strategies have been proposed and developed for storing the surplus energy, which otherwise would be lost.

A prominent strategy is the concept known as “Power-to-Gas”, where the surplus electricity is used to electrolyze water and produce hydrogen that can be stored and used on demand (Götz et al., 2016). Gahleitner (2013) identified several uses of the stored hydrogen with the main ones being utilization for electricity production with fuel cells, in vehicles, as reactant in the chemical industry and for heat purposes. None of the previously mentioned utilization scenarios has gained more interest than the concept of methanation, which refers to the reaction of hydrogen with carbon oxides for the production of methane. The conversion of hydrogen into methane opens several further utilization possibilities because it can be injected into the natural gas pipelines or used directly in the numerous energy conversion units that operate with natural gas, like gas engines or heating boilers.

In the early 1900s Paul Sabatier discovered that carbon dioxide reacts exothermically with hydrogen for the production of methane and water. This reaction is now commonly known as the Sabatier process (or reaction). Similarly to carbon dioxide, carbon monoxide also reacts exothermically with hydrogen for the production of methane and water (Brooks et al., 2007). Both reactions are

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http://dx.doi.org/10.1016/j.jenvman.2017.06.044
0301-4797/

presented below as Eqs. (1) and (2) respectively.

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O, \quad \Delta H = -165 \text{ kJ/mol} \tag{1}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O, \quad \Delta H = -206 \text{ kJ/mol} \tag{2}$$

Both reactions are reversible and it is generally the case that they propagate faster in relatively low temperatures, in the range of 300–500 °C. The reaction of carbon monoxide is slightly favored if both gases are present. For the purpose of conversion optimization and selectivity it is rather common to use catalysts like nickel, ruthenium and rhodium (Frontera et al., 2017). Methanation of carbon dioxide has very promising potential applications, like carbon capture (Meylan et al., 2017). Nonetheless, carbon dioxide needs preprocessing in order to be separated from the other gases, like nitrogen or steam. For all cases of catalytic co-methanation of carbon dioxide and carbon monoxide the reaction of carbon monoxide is also favored. But the co-methanation of both carbon oxides, instead of one of the two, increase the total methanation rate of the gas mixture. The reason is that carbon monoxide reacts disproportionately and no solid surface carbon is formed by means of solid gas surface reactions (Habazaki et al., 1998). As mentioned before, in most cases carbon dioxide can be found in combined streams with atmospheric nitrogen. In this case, another reaction that becomes relevant for the range of operating conditions that methanation propagates is the Haber process (Eq. (3)), where hydrogen reacts with nitrogen for the production of ammonia.

$$N_2 + 3H_2 \leftrightarrow 2NH_3, \quad \Delta H = -45.8 \text{ kJ/mol} \tag{3}$$

It should be denoted that the conversion rate of the Haber process is relatively low for the operating conditions of methanation but it still provides measurable products. But the optimization of ammonia production via catalysis is -in this case-a relatively difficult task because carbon monoxide and carbon dioxide act as poising agents of the catalysts that increase ammonia production (Khorsand et al., 2007). Catalysts like nickel or rhodium, that enhance the methanation of carbon oxides, is questionable if they can be used for gas mixtures that contain several other gases without being poisoned or deactivated. Some major causes for deactivation of the catalysts are the chemisorption of sulfur, potential deposition of solid carbon on the surface of the catalyst and destruction due to thermal stressor or thermal sintering (Rönsch et al., 2015). Therefore, the use of catalysts can be economically unsustainable for upgrading complicated gas mixtures. Another efficient method for methanation is the application of biological processes. Guneratnam et al. (2017) used thermophillic bacteria, i.e. Methanothermobacter species, which proved to be very resilient and upgraded successfully the quality of biogas. Kirchbacher et al. (2017) combined catalytic/membrane based methanation with a two-step fermentation process and managed to reach methane concentrations of up to 96%.

Except from the previously described pathway of “Power-to-gas”, a more conventional way to produce renewable gaseous fuels has been gasification of biomass which is gaining a lot of momentum in several European countries. Between 10 and 14% of the energy production worldwide is from biomass utilization (McKendry, 2002). The projections for the potential contribution of biomass in the European energy production mix are even more promising if the agricultural waste are taken into consideration. The projection by Ericsson and Nilsson (2006) that by the year 2020 approximately 0.8 EJ y^{-1} of agricultural waste will be produced in the EU is a reliable number that is well within the range set by other studies, as reported by Prando et al. (2014). Except from the promising potential, biomass is a CO_2 neutral resource (McKendry, 2002).

Among the different conventional small scale conversion technologies for biomass-to-energy, gasification has the advantage of having higher electrical production efficiency (Dong et al., 2009). Gasification can primarily be defined as a thermal process which by means of endothermic reforming reactions permutes a feedstock into mainly gaseous products (Vakalis et al., 2013). Patuzzi et al. (2016), reported the impressive growth of small scale gasifiers in the area of South Tyrol, Italy. Similarly, the German Biomass Research Center monitored and analyzed the status of biomass gasifiers in Germany (Zeymer et al., 2012). Both these reports concluded that the vast majority of these facilities have been downdraft fixed bed small scale gasifiers. These gasifiers use air in sub-stoichiometric quantities as gasifying medium and the final product is defined as producer gas. It consists from fluctuating compositions of carbon monoxide, carbon dioxide, hydrogen and small quantities of methane (Gikas, 2016). Due to the use of air as gasifying medium, the final product has significantly high compositions of nitrogen in the range of 50%. The significant joint composition of inert gases in the producer gases, i.e. nitrogen and carbon monoxide, is the main reason for their poor quality and the low heating values of producer gases. On one hand, the novel small scale biomass gasifiers have significantly better performance than older facilities and Vakalis and Baratieri (2015) identified that the main drivers of optimization have been the integration of automation control systems, the modular form of the facilities and the integration of newly-developed patents. On the other hand, even after these enhancements the quality of the producer gases is still very poor in comparison to other gaseous fuels. In addition, it is evident from the literature that gasification produces different species from anaerobic digestion which produces gaseous fuels with higher methane yields (Gikas, 2014).

The main aim of this manuscript is to assess the potential upgrading of producer gas from fixed bed small scale gasifier by means of methanation reactions. Thus, in the framework of this work a secondary onsite reactor is introduced. The scope of this reactor is to accommodate the reaction of producer gas with hydrogen for non-catalytic partial methanation and partial ammonia production. The expected result is the reduction of the inert gases concentration and the improvement of the overall gas quality. The carbon oxides will be converted to methane and a fraction of the nitrogen will be converted to ammonia and removed via condensation. The secondary reactor is projected to be downstream of the gasifier. In order to identify optimal operating parameters of this reactor a thermodynamic model has been developed. All the relevant details and the operating principles are described in the section “Materials and Methods”.

Previous studies have analyzed the potential reaction of syngas from gasification and hydrogen for the production of synthetic natural gas. Van der Meijden et al. (2010) compared the production of synthetic natural gas from three wood gasifiers. The authors analyzed large scale gasifiers which used carbon dioxide and oxygen as gasifying mediums. Gassner and Maréchal (2009) presented theoretical mathematical process models for production of synthetic natural gas from different large scale gasification technologies. Duret et al. (2005) proposed a design for producing synthetic natural gas from the product of a circulating fluidized bed which uses steam as a gasification agent. The common denominator of these studies is the utilization of larger scale gasifiers as base for the analysis. These gasifiers use (theoretically or in reality, depending the study) steam, oxygen and carbon dioxide as gasifying agents. It should be denoted that the product for large scale and non-air blown gasifiers is usually defined as syngas and consists primarily from carbon monoxide and hydrogen. Although the quality is not equivalent to natural gas, it is good enough that can be used for efficient energy production or as material in the chemical industry.

Please cite this article in press as: Vakalis, S., et al., Thermodynamic modelling of an onsite methanation reactor for upgrading producer gas from commercial small scale biomass gasifiers, Journal of Environmental Management (2017), http://dx.doi.org/10.1016/j.jenvman.2017.06.044