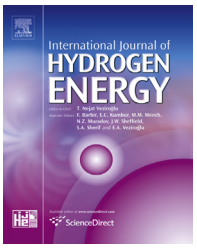
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2015) 1–9

Available online at www.sciencedirect.com

ScienceDirect

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



Thermodynamic comparison between bio-oil and ethanol steam reforming

Carolina Montero [a,*], *Lide Oar-Arteta* [b,1], *Aingeru Remiro* [b,1], *Aitor Arandia* [b,1], *Javier Bilbao* [b,1], *Ana G. Gayubo* [b,1]

[a] *Chemical Engineering Faculty, Central University of Ecuador, Ciudad Universitaria-Ritter s/n y Bolivia, Quito, Ecuador*

[b] *Chemical Engineering Department, University of the Basque Country, P.O. Box 644, 48080, Bilbao, Spain*

ARTICLE INFO

Article history:
Received 16 June 2015
Received in revised form
5 September 2015
Accepted 26 September 2015
Available online xxx

Keywords:
Bio-oil
Ethanol
Hydrogen production
Steam reforming
Thermodynamic

ABSTRACT

The thermodynamic analysis of the steam reforming (under catalytic steam reforming conditions) of a simulated bio-oil (composed of model compounds of components in a real bio-oil) and of ethanol is performed by minimization of Gibb's free energy method with Pro II-Simsci® 8.3 software, and their results are compared. At the equilibrium conditions both oxygenated feeds are completely converted, with H_2, CO_2, CO and CH_4 being the only significant gaseous products. Coke formation is observed below 700 °C for low steam/carbon (S/C) molar ratios (below the stoichiometric value). H_2 yield, which is very similar for both reforming processes (with small differences only for S/C < 2), increases with S/C ratio and goes through a maximum with temperature, being higher than 90% for S/C > 5 and in the 540–640 °C range. Above 600–650 °C (depending on the S/C molar ratio), the energy requirement for steam reforming of ethanol is slightly higher that for bio-oil steam reforming. These results evidence the viability of the joint valorisation of bio-oil and bio-ethanol by means of steam reforming.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Nowadays nearly 90% of the hydrogen is obtained by steam reforming of natural gas or naphtha, but the need to reduce CO_2 emissions has promoted H_2 production from renewable raw materials, such as biomass [1]. These new alternatives for obtaining hydrogen are interesting due to its use as a clean fuel and because it is one of the most important supply in petrochemical, agrochemical, metallurgic, and medicines industries.

Hydrogen can be obtained from biomass directly (gasification, high temperature pyrolysis, catalytic pyrolysis and biological processes) and by routes for obtaining oxygenated hydrocarbons followed by a catalytic reforming process [2]. Bio-ethanol (obtained by biomass fermentation) and bio-oil (a complex mixture of more than 300 oxygenates compounds obtained by flash pyrolysis of biomass), are considered promising biomass derived intermediates for obtaining H_2 by steam reforming [3]. Ethanol is probably the most studied oxygenate for obtaining hydrogen by means of catalytic reforming processes, because it is easy to store, handle and

* *Corresponding author*. Tel.: +593 22544631; fax: +593 22529676.
E-mail address: carodrmontero@gmail.com (C. Montero).
[1] Tel.: +34 946 015361; fax: +34 946 013 500.

http://dx.doi.org/10.1016/j.ijhydene.2015.09.125

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Please cite this article in press as: Montero C, et al., Thermodynamic comparison between bio-oil and ethanol steam reforming, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.09.125

less toxic than other oxygenates [4,5]. Among ethanol reforming processes, the catalytic ethanol steam reforming (ESR) has received a preferential attention, since it allows a direct valorisation of bio-ethanol (~86% H_2O), thus avoiding the cost of its dehydration for use as a fuel [5–9]. Bio-oil is currently receiving increasing attention as a raw material for hydrogen production since it can be obtained in a delocalized way and subsequently transported to a large-scale and centralized catalytic reforming unit especially designed for this purpose [10–13]. Similarly, bio-oil has a great amount of water (~30–40%), which means that steam reforming is also a suitable strategy for bio-oil valorisation. The joint valorisation of a bio-oil/ethanol mixture by steam reforming over a Ni based catalyst has also been recently studied [14], which is considered an interesting route for the development of the bio-refinery concept.

ESR is an endothermic process, whose global reaction has the following stoichiometry:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad (1)$$

Nevertheless, the reaction mechanism is complex and is comprised of numerous individual stages and secondary reactions, such as those in Eqs 2–12, which produce intermediate compounds and sub products, thus reducing H_2 yield and causing catalyst deactivation by coke deposition [4,9].

Dehydration $C_2H_5OH \leftrightarrow C_2H_4 + H_2O$ (2)

Ethylene steam reforming $C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$ (3)

Dehydrogenation $C_2H_5OH \leftrightarrow C_2H_4O + H_2$ (4)

Acetaldehyde decomposition $C_2H_4O \rightarrow CH_4 + CO$ (5)

Ethanol decomposition $C_2H_5OH \rightarrow CO + CH_4 + H_2$ (6)

Water Gas Shift reaction (WGS) $CO + H_2O \leftrightarrow H_2 + CO_2$ (7)

CO methanation $CO + 3H_2 \leftrightarrow CH_4 + H_2O$ (8)

Methane steam reforming $CH_4 + H_2O \leftrightarrow CO + 3H_2$ (9)

Boudouard reaction $2CO \leftrightarrow CO_2 + C$ (10)

Methane decomposition $CH_4 \rightarrow 2H_2 + C$ (11)

Coke gasification $C + H_2O \rightarrow CO + H_2$ (12)

The steam reforming of oxygenates in bio-oil (BSR) (whose overall chemical formula is $C_nH_mO_k$) takes place through the formation of $CO + H_2$,

$$C_nH_mO_k + (n-k)H_2O \rightarrow nCO + (n + m/2 - k)H_2 \quad (13)$$

followed by the water gas shift (WGS) reaction, Eq. (7), with the overall reaction being as follows:

$$C_nH_mO_k + (2n-k)H_2O \rightarrow nCO_2 + (2n + m/2 - k)H_2 \quad (14)$$

As a result, the maximum stoichiometric hydrogen yield by bio-oil steam reforming is (2n + m/2-k) $mol_{H2}/mol_{oxygenate}$, although the H_2 yield is lower than this maximum depending on the operating conditions, mostly because of the equilibrium of the WGS reaction, Eq. (7), and other secondary reactions such as methanation, Eq. (8), methane steam reforming, Eq. (9), and coke formation by Boudouard reaction, Eq. (10), by cracking of oxygenates in bio-oil, Eq. (15), and by cracking reactions of hydrocarbons, Eq. (16).

$$C_nH_mO_k \rightarrow C_xH_yO_z + \text{gas}(H_2,\ CO_2,\ CO,\ CH_4,\ CH_x) + C \quad (15)$$

$$CH_x \rightarrow \text{coke precursors (olefins + aromatics)} \rightarrow \frac{x}{2}H_2 + C \quad (16)$$

In order to identify the most favourable operating conditions that maximize H_2 yield in both ESR and BSR, the thermodynamic study of both processes is an important tool. The thermodynamics of ESR has been widely studied [15–21], as well as of other ethanol reforming process such as partial-oxidation, oxidative steam reforming and autothermal reforming [20–23]. Nevertheless, there is more scarce information concerning the thermodynamics of bio-oil reforming processes, due to the complex nature of this feed. This last topic has been previously approached in literature with bio-oil selected oxygenated compounds, such as acetic acid [24–27], acetone [24,25], hydroxyacetone (acetol) [28,29], ethylene glycol [24–26], isopropyl alcohol, lactic acid and phenol [30], as well as with a mixture of three model oxygenates (acetic acid, ethylene glycol and acetone) [24,25]. Although the same reaction products are obtained in the thermodynamic equilibrium of the steam reforming of different oxygenated compounds (H_2, CO, CO_2, CH_4 and coke), the results in the literature show that the maximum H_2 yield and the operating conditions corresponding to that maximum depend on the nature and composition of the oxygenated feed. Thus, according to Aktas et al. [30], the temperature/steam-to-fuel ratio combinations that favoured desired syngas features (such as molar H_2/CO ratio around 2 with minimal presence of CO_2 and CH_4) were (1200 K, 4), (1200 K, 5) and (1000 K, 9) for steam reforming of isopropyl alcohol, lactic acid and phenol, respectively. Similarly, the thermodynamic study of sorption enhanced steam reforming of alcohols performed by Lima da Silva and Müller [31] reports that, in order to maximize H_2 formation with minimum CO content, the optimum steam-to-fuel ratio increases as the number of carbon atoms in the alcohol is increased (being 4:1, 6:1, 9:1 and 12:1 for methanol, ethanol, glycerol and n-butanol, respectively).

The afore mentioned thermodynamic studies are the basis for choosing the reforming conditions maximizing the production of H_2, and minimizing the formation of by-products (CO and CH_4), which are the precursors for coke formation, and therefore responsible for catalyst deactivation. In this work, a thermodynamic analysis of the steam reforming of a simulated crude bio-oil is performed with the aim of determining the operating conditions (temperature and S/C molar ratio) allowing the maximum H_2 yield and minimum yield of by-products (CO, CH_4) and coke. This simulated bio-oil is composed of model compounds representative of the main families of components in bio-oil (acids, esters, ketones, aldehydes, ethers, alcohols, phenols). Moreover, the results corresponding to ethanol steam reforming are also presented in order to compare the operating conditions required for

Please cite this article in press as: Montero C, et al., Thermodynamic comparison between bio-oil and ethanol steam reforming, International Journal of Hydrogen Energy (2015), http://dx.doi.org/10.1016/j.ijhydene.2015.09.125

Download English Version:

https://daneshyari.com/en/article/7713111

Download Persian Version:

https://daneshyari.com/article/7713111

Daneshyari.com