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Hydrogen production via catalytic steam reforming of the aqueous fraction of bio-oil using nickel-based coprecipitated catalysts

F. Bimbela, M. Oliva, J. Ruiz, L. García*, J. Arauzo

Thermochemical Processes Group (GPT), Aragon Institute for Engineering Research (I3A), Universidad de Zaragoza, c/ Mariano Esquillor s/n, Zaragoza ES50018, Spain

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ABSTRACT

Hydrogen production was studied in the catalytic steam reforming of a synthetic and a real aqueous fraction of bio-oil. Ni/Al coprecipitated catalysts with varying nickel content (23, 28 and 33 relative atomic %) were prepared by an increasing pH technique and tested during 2 h under different experimental conditions in a small bench scale fixed bed setup. The 28% Ni catalyst yielded a more stable performance over time (steam-to-carbon molar ratio, S/C = 5.58) at 650 °C and a catalyst weight/organic flow rate (W/m_{org}) ratio of 1.7 g catalyst min/g organic. Using the synthetic aqueous fraction as feed, almost complete overall carbon conversion to gas and hydrogen yields close to equilibrium could be obtained with the 28% Ni catalyst throughout. Up to 63% of overall carbon conversion to gas and an overall hydrogen yield of 0.09 g/g organic could be achieved when using the real aqueous fraction of bio-oil, but the catalyst performance showed a decay with time after 20 min of reaction due to severe coke deposition. Increasing the W/m_{org} ratio up to 5 g catalyst min/g organic yielded a more stable catalyst performance throughout, but overall carbon conversion to gas did not surpass 83% and the overall hydrogen yield was only ca. 77% of the thermodynamic equilibrium. Increasing reaction temperatures (600–800 °C) up to 750 °C enhanced the overall carbon conversion to gas and the overall yield to hydrogen. However, at 800 °C the catalyst performance was slightly worse, as a result of an increase in thermal cracking reactions leading to an increased formation of carbon deposits.

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1. Introduction

Hydrogen may become the energy carrier that could replace fossil fuels in the future, or it may simply continue to be an important commodity widely used in industry, particularly in oil refinery processes or in the production of ammonia for the manufacture of fertilizers. It is, however, a fact that current

hydrogen production is substantial, between 38 and 53 million metric tonnes worldwide as of 2010 [1,2]. According to the US DoE, around 95% of the current US hydrogen production, which constitutes about half of world's hydrogen supply, comes from steam reforming of natural gas or other fossil fuel-based technologies [3,4], and the figures are not much different in the rest of the world [5]. Circa 80–92% of current

* Corresponding author. Tel.: +34 976 76 2194; fax: +34 976 76 2043.
E-mail address: luciag@unizar.es (L. García).

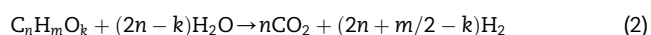
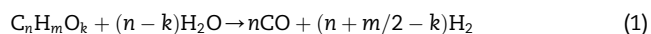
global hydrogen production is destined for its use as a chemical in industry [1], but the prospects of using hydrogen in fuel cells for mobile and portable applications are promising and this ratio may vary in the near future, involving a substantial increase in hydrogen needs and demand. Therefore, it remains necessary to seek alternative, sustainable and environmentally-friendly means of producing hydrogen.

In this context, hydrogen production from biomass poses one of the main alternatives along with other renewable sources, namely combining solar energy with water hydrolysis. Among these renewable energies, the use of biomass plays an important role because of its potential and availability, not only as an energy source but also as a source of raw materials. Biomass-derived renewable energy sources have the added benefit of no net increase in CO₂ emissions.

A review of processes and materials for efficient hydrogen production from biomass has recently been published [6]. The usual method for using energy resources and materials contained in biomass comprises thermal processes or biological transformation. Among the thermal processes, flash pyrolysis has become an alternative to obtain a liquid known as bio-oil through a rapid heating of biomass, giving yields of transformation of biomass into bio-oil of about 75–80% [7]. This fluid is a complex mixture of different compounds comprising acids, alcohols, aldehydes, sugars, phenolic compounds, etc. Its composition varies depending on the source of biomass used and on the pyrolysis reactor [8].

Bio-oil can be more easily transported than the original biomass, which is an advantage since the energy density of the transported material is significantly increased. On the other hand, it is a thermally unstable material which tends to polymerize when heated [9]. By water addition bio-oil can be separated into two fractions: an organic fraction and an aqueous fraction [10]. The first, which contains poorly soluble compounds from the decomposition of lignin, has been addressed as a source of chemicals with high added value, while the latter, with high water content, has been typically employed for the production of certain chemicals including smoky flavours, levoglucosan and glycolaldehyde [11]. An additional way to valorize the aqueous fraction of bio-oil is through hydrogen production by means of a catalytic steam reforming process, similar to natural gas or naphtha reforming [12] proceeding through the following reactions [13]:

Steam reforming of oxygenates:



Water gas shift (WGS) reaction:



The process yields a hydrogen-rich syngas which, conveniently conditioned, can serve for the production of high-purity hydrogen.

Given the thermal instability of bio-oil, which undergoes thermal decomposition processes and polymerization and thus creates severe clogging problems upon being fed into reactors, a number of studies published in the literature have used model compounds of bio-oil to study the catalytic steam

reforming process [6]. In previous works by our research group, acetic acid [14–17], acetol [17–20] and butanol [17,19] were selected as model compounds representing the major functional groups present in the aqueous fraction of bio-oil.

The configurations of reactors used for the catalytic reforming of the aqueous fraction of bio-oil and model compounds have been multiple, predominantly fixed-bed and fluidized bed reactors.

Regarding the development of suitable catalysts for the process, two main approaches can be found in the literature: supported noble metal catalysts and Ni-based catalysts, both commercial and laboratory prepared. Some authors have studied supported noble metal catalysts such as Pt, Ru and Pd, in the catalytic steam reforming of bio-oil or model compounds of it [21–27]. On the other hand, Ni-based catalysts have shown appropriate activity and selectivity towards hydrogen production at a much lower cost [10,12–20,28–30].

The catalysts for this process must present a high degree of activity for reforming, a high selectivity towards hydrogen production, a decrease in the formation of by-products such as CH₄ and C₂, and they must also be resistant to deactivation by coke formation on the catalyst surface. Deactivation by coking is the main issue for Ni-based catalysts which are more susceptible to carbon formation than noble metal-based catalysts [28].

The S/C ratio is a relevant process parameter. A high S/C ratio can help increasing the yield to H₂, as a consequence of modifying the WGS equilibrium reaction. Besides, the excess of steam has been proven to be beneficial for gasifying some of the carbonaceous deposits on the catalyst surface, hence enhancing the carbon conversion to gas and partially alleviating the deactivation of the catalyst [10,17,29]. On the other hand, using a very high S/C ratio is not appropriate in terms of the energy efficiency of the process. The amount of energy required to evaporate and heat the water up to the reaction temperature may compromise the viability of the process. Thus, an adequate S/C ratio must be selected, typically in the range between 5 and 7 [12].

The present work is a continuation of our previous works [14,17,19], aiming to increase insights into the behaviour of the catalytic reforming of the aqueous fraction of bio-oil, both synthetic and also real fractions derived from pine wood, and working with a research Ni/Al catalyst prepared by coprecipitation. The aim is to study the influence of the following variables: reforming temperature, weight of catalyst/organic flow rate ratio and Ni content of the catalyst, in order to analyse their influence on the yield and selectivity to hydrogen, conversion of the aqueous fraction, activity and catalyst deactivation.

2. Materials and methods

2.1. Experimental system

The experimental system is based on a small bench scale catalytic test rig consisting of a fixed bed placed inside a tubular reactor, made of quartz in order to avoid any catalytic wall effects, with a high-performance liquid chromatography (HPLC) pump to feed the reactants at a specified rate, a

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