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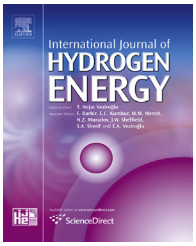

Production of a hydrogen-rich gas from fast pyrolysis bio-oils: Comparison between homogeneous and catalytic steam reforming routes

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ABSTRACT

The aim of the present work is to produce hydrogen from biomass through bio-oil. Two possible upgrading routes are compared: catalytic and non-catalytic steam reforming of bio-oils. The main originality of the paper is to cover all the steps involved in both routes: the fast pyrolysis step to produce the bio-oils, the water extraction for obtaining the bio-oil aqueous fractions and the final steam reforming of the liquids. Two reactors were used in the first pyrolysis step to produce bio-oils from the same wood feedstock: a fluidized bed and a spouted bed. The mass balances and the compositions of both batches of bio-oils and aqueous fractions were in good agreement between both processes. Carboxylic acids, alcohols, aldehydes, ketones, furans, sugars and aromatics were the main compounds detected and quantified. In the steam reforming experiments, catalytic and non-catalytic processes were tested and compared to produce a hydrogen-rich gas from the bio-oils and the aqueous fractions. Moreover, two different catalytic reactors were tested in the catalytic process (a fixed and a fluidized bed). Under the experimental conditions tested, the H_2 yields were as follows: catalytic steam reforming of the aqueous fractions in fixed bed (0.17 g H_2/g organics) > non-catalytic steam reforming of the bio-oils (0.14 g H_2/g organics) > non-catalytic steam reforming of the aqueous fractions (0.13 g H_2/g organics) > catalytic steam reforming of the aqueous fractions in fluidized bed (0.07 g H_2/g organics). These different H_2 yields are a consequence of the different temperatures used in the reforming processes (650 °C and 1400 °C for the catalytic and the non-catalytic, respectively) as well as the high spatial velocity employed in the catalytic tests, which was not sufficiently low to reach equilibrium in the fluidized bed reactor.

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1. Introduction

Nowadays hydrogen is mainly produced from fossil fuels through non-environmentally friendly processes that generate CO_2 and contribute negatively to the greenhouse effect. While a large part of the present production of hydrogen is currently dedicated to producing chemicals, an increase in hydrogen demand is expected over the coming decades for use as a clean fuel in high energetic efficiency systems such as fuel cells. The thermochemical conversion of biomass is a promising route that permits the production of hydrogen from a renewable source. In this context, two possible strategies to produce a hydrogen rich gas are direct conversion of raw biomass and two-step conversion. The latter involves the production of storable intermediates which can be used for further gas production.

Gasification is the most mature process for directly producing a synthesis gas from biomass. This gas is mainly constituted by carbon monoxide and hydrogen. An allothermal entrained flow reactor is often considered as the most promising technology for advanced applications such as hydrogen production, due to the high quality of the produced gas which is both tar and methane free. However, the direct gasification of biomass has several drawbacks when used on a large scale, especially in terms of the organization of feedstock supply together with the fact that lignocellulosic biomass is a resource with variable composition, wide geographical dispersion, and low energy density. All this makes the concept of a possible centralized direct-gasification of biomass strategy unviable.

In these circumstances, the concept of a two-step conversion of biomass is a promising alternative. This consists of preconditioning the biomass in decentralized sites before its transportation to a centralized unit. Fast pyrolysis offers this opportunity as it allows converting the biomass into a liquid combustible product called bio-oil (typically 50–75 wt %) with a much higher volume energy density. The bio-oil can easily be stored and transported from decentralized production sites to a large-scale processing unit and the process is therefore economically sustainable.

The combination of fast pyrolysis followed by the transportation of the bio-oil to large steam reforming units has attracted considerable attention from the research community as one of the promising viable methods for syngas or hydrogen production. After the fast pyrolysis step, two different strategies are possible to upgrade the bio-oil: non-catalytic (homogeneous) steam reforming of bio-oil at high temperature or catalytic steam reforming at medium temperature [1].

Non-catalytic steam reforming of bio-oil can be operated in high temperature reactors. The high temperature entrained-flow reactor has been widely considered for gasification of biomass into a high quality gas, but fewer works have been published on bio-oils. However, bio-oil offers several advantages compared to biomass, in particular in terms of atomization and injection issues. Recently, Chhiti et al. [2] reported experiments of non-catalytic crude bio-oil steam reforming under a non-oxidative atmosphere in a lab-scale High Temperature Entrained Flow Reactor (HT-EFR) over a wide range of temperatures (1000–1400 °C) and determined the composition and the yield of the syngas. They also reported that the thermodynamic equilibrium was reached within several seconds at a temperature of 1400 °C.

The catalytic steam reforming of bio-oil or its fractions was first developed by the National Renewable Energy Laboratory (Colorado USA) in 1994. The use of a catalyst allows carrying out the process at a lower temperature (500–800 °C) than that used in non-catalytic steam reforming. However, the major drawback of this process is that the carbon deposits formed during the reaction can deactivate the catalyst. This has led to a second strategy which involves the separation of the bio-oil into two phases by water addition. The non-soluble fraction consisting of lignin-derived compounds can be used for the production of high value-added chemicals, whereas the aqueous fraction can be processed by catalytic steam reforming in order to produce a hydrogen rich gas [3].

Ni-based catalysts have been widely chosen for this process since they are cost-effective and have high activity and selectivity towards hydrogen. However, they are susceptible to deactivation by carbon deposits on their surface. Remón et al. [4] developed a Ni based catalyst prepared by coprecipitation having the support and the active phase modified with Mg and with Co, respectively. This proved appropriate for the catalytic steam reforming of the aqueous fraction of pyrolysis liquids in fixed bed and fluidized bed reactors. This catalyst showed the lowest coke production among all those tested by Remón et al. and was consequently chosen for the present work.

In the available bibliography there are several studies on the pyrolysis of biomass and the catalytic and non-catalytic steam reforming of bio-oil or its aqueous fractions [1,5–15]. However, since different biomasses, bio-oils and aqueous fractions were used, a comparison of the thermochemical techniques to produce a hydrogen gas from biomass is unreliable. For this reason, in the present work the whole process has been considered and studied, covering all the steps from biomass to the syngas production. As a first step, two sets of bio-oils were produced from the same feedstock (pine sawdust) by using two fast pyrolysis technologies: a fluidized bed and a spouted bed reactor. These pyrolysis experiments were analysed and the bio-oils were characterized in order to obtain information about the chemical composition of these liquids. As a second step, aqueous fractions were prepared from these bio-oils and also characterized. Finally, as a third step, steam reforming experiments were performed to produce hydrogen-rich syngas. On the one hand crude bio-oils and aqueous fractions were used as feedstocks for non-catalytic experiments while, on the other hand, aqueous fractions were used for catalytic experiments in two complementary reactors.

Hence, by covering all the steps involved in both strategies for producing hydrogen from biomass (via bio-oil conversion), this work gives reliable information on the yields and efficiencies obtained with each process in comparable terms.

2. Materials and methods

2.1. *Feedstock characterization*

The biomass used for the production of the bio-oils tested in this work was pine sawdust provided by Kapelbi. It consisted of a mixture of insignis pine from the Basque Country (Spain) and maritime pine from Aquitaine (France). The feedstock