H_2 production by sorption enhanced steam reforming of biomass-derived bio-oil

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M.V. Gil[1], G. Esteban-Díez[1,2], C. Pevida[2], F. Rubiera[2], D. Chen[1]

[1]Norwegian University of Science and Technology, Sem Sælands vei 4, 7491 Trondheim, Norway
[2]Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

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Hydrogen is recognized as a clean transportation fuel and energy carrier and it will play an important role in the future global economy. Moreover, hydrogen is an important raw material for industrial uses in the chemical and petroleum companies [1]. Most hydrogen is currently produced from fossil fuels, mainly by means of the steam methane reforming (SMR) of natural gas. So, there is a great interest on the development of technologies to produce hydrogen based on the utilization of renewable energy sources, since it means no net production of atmospheric CO_2.

The sorption enhanced steam reforming (SESR) process is purposed in the present work as an emerging alternative technology for hydrogen production, which may be used for the manufacture of ammonia fertilizers via the Haber process, for methanol synthesis and for conversion of heavy petroleum sources to lighter fractions via hydrocracking. This technology consists on the integration of reforming reaction (H_2 production) and separation (CO_2 sorption) in a single unit operation. The reactor contains the catalyst needed for the reforming process together with a CO_2 sorbent for the in situ removal of carbon dioxide from the gaseous phase. Thus, the steam reforming, WGS and CO_2 capture reactions are conducted simultaneously in one single reactor. Since the CO_2 is in situ removed, the H_2 production is promoted due to the displacement of the reforming and WGS reaction equilibriums towards higher hydrogen production.

The full environmental benefits of using hydrogen as an energy carrier can only be achieved if the hydrogen is produced from renewable sources, such as biomass [2]. The coupling of biomass conversion technologies with CO_2 capture and storage technologies offers the potential to achieve an effective reduction in CO_2 from the atmosphere [3]. One of the most promising methods for using biomass to produce H_2 is via the fast pyrolysis of biomass, method that produces bio-oil, which can be catalytically reformed for hydrogen production. Bio-oil is a complex mixture of low and high molecular weight oxygenated compounds, which can be classified into a carbohydrate-derived solution and a lignin-derived fraction.

In the present work, hydrogen production by sorption enhanced steam reforming (SESR) of the bio-oil obtained from the fast pyrolysis of biomass was thermodynamic and experimentally studied through the mixture of three main model compounds in a fixed bed reactor. The oxygenated model compounds of the components present in the bio-oils produced by the fast pyrolysis of biomass selected in the present work were: acetic acid (AcH) as an model compound of organic acids, acetone (AcCO) as a model compound of carbonyl-containing constituents (mainly aldehydes and ketones) and phenol (PhOH) as a model compound of phenolic constituents.

The reactions for the conversion of acetic acid, acetone and phenol to hydrogen are shown in Eqs. 1-3, respectively, which are a combination of steam reforming (SR) and water gas shift (WGS) (Eq. 4) reactions:

$$C_2H_4O_2 + 2H_2O \rightarrow 4H_2 + 2CO_2 \quad (1)$$
$$C_3H_6O + 5H_2O \rightarrow 8H_2 + 3CO_2 \quad (2)$$
$$C_6H_6O + 11H_2O \rightarrow 14H_2 + 6CO_2 \quad (3)$$
$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (4)$$

The SESR process involves the shift of the equilibrium of the reversible reforming and WGS reactions based on the Le Chatelier's principle to enhance hydrogen production through in situ CO_2 removal from the reaction zone in order to obtain a high hydrogen conversion in a single step. When a CaO-based sorbent is used in the proposed SESR process, it will be incorporated into the catalyst bed to in situ remove the CO_2 from the gaseous phase, as shown in Eq. (5):

$$CaO_{(s)} + CO_2 \leftrightarrow CaCO_{3(s)} \quad (5)$$

Hence, the overall reactions for the sorption enhanced steam reforming (SESR) process of acetic acid, acetone and phenol are shown in Eqs. 6-8, respectively.

$$C_2H_4O_2 + 2H_2O + 2CaO_{(s)} \rightarrow 4H_2 + 2CaCO_{3(s)} \quad (6)$$

$$C_3H_6O + 5H_2O + 3CaO_{(s)} \rightarrow 8H_2 + 3CaCO_{3(s)} \quad (7)$$

$$C_6H_6O + 11H_2O + 6CaO_{(s)} \rightarrow 14H_2 + 6CaCO_{3(s)} \quad (8)$$

The complete conversion of acetic acid and acetone by SESR produces 4, 8 and 14 mol of hydrogen, respectively, per mole of model compound.

In the SESR process the catalytic reforming reaction and the CO_2 removal by sorption are carried out simultaneously in a single reactor. The effect of the weight hourly space velocity (WHSV) during the SESR of the blends of model compounds was investigated under atmospheric pressure over a Pd/Ni-Co hydrotalcite-like material (HT) catalyst and using dolomite as CO_2 sorbent. The weight hourly space velocity (WHSV) is defined as the ratio of the mass flow rate of the inlet acetic acid to the mass of catalyst ($g_{acetic\ acid}\ g_{catalyst}^{-1}\ h^{-1}$).

A fixed bed reactor was used for the experiments. It consists of a downdraft fixed bed stainless steel reactor, where the gases are delivered by Bronkhorst® mass flow controllers and the reaction temperature is controlled by a type K thermocouple inserted into the catalyst/sorbent bed. The effluent gas from the reactor is directed into a thermoelectric cooler, where steam excess, unreacted materials and all other liquids that may have been formed are condensed. The composition of the dried gas is analyzed using an on-line dual channel Agilent® 3000 Micro GC, equipped with both Molsieve and Plot U columns and a TCD detector. The species detected were H_2, CH_4, CO, and CO_2. The product distribution was calculated on the basis of the dry composition of the gas effluent. The flow rates of the species generated during the experiment were calculated by means of a nitrogen balance, since the amount of nitrogen fed in and the composition of the nitrogen evolved are known. Moreover, the H_2 yield and H_2 selectivity were calculated.

It was found that lower WHSV values favoured the H_2 yield, H_2 selectivity and H_2 concentration, while decreased the CH_4 concentration. The results of the present work showed that the SESR process can be successfully employed for the production of H_2 with high yield and purity from bio-oil. Therefore, the steam reforming with in situ CO_2 capture process is presented as a promising technology for hydrogen production from biomass-derived compounds.

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