

H₂ production via sorption enhanced steam reforming of biomass-derived phenol in fluidized bed reactor

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Hydrogen is considered as one of the clean energy carriers with more potential for the near future. The demand for H₂ is expected to increase exponentially, both for conventional industrial uses and for clean energy generation, particularly in fuel cell applications [1]. However, hydrogen is still predominantly produced from fossil fuels by steam methane reforming (SMR) of natural gas or via partial oxidation of heavy oil fractions, which generate CO₂ as a byproduct. The increasing concentration of greenhouse gases in the atmosphere and the worldwide recognition of their effect on Climate Change have increased the concern on the control of the CO₂ emissions from the energy generation industry, since CO₂ is the greenhouse gas with the largest contribution to climate change.

In this scenario, several strategies for CO₂ reduction are under study and the sorption enhanced steam reforming (SESR) process is becoming an important topic since it integrates hydrogen production and CO₂ separation. During the SESR process, carbon dioxide is captured by a sorbent within the reactor itself. Following Le Chatelier's principle, CO₂ removal shifts the reversible reforming and water gas shift (WGS) reactions to the product side beyond their conventional thermodynamic limits, increasing the production of hydrogen.

Captured CO₂ is converted to a solid carbonate when a CaO-based sorbent is used; this sorbent can be regenerated to release a relatively pure CO₂ suitable for storage. The SESR process can be carried out at lower reaction temperatures than conventional reforming processes, which would reduce catalyst coking and sintering, as well as investment and operation costs. However, it requires of very active and stable reforming catalysts. In addition, heat released by the exothermic carbonation reaction supplies most of the heat required by the endothermic reforming reactions. Nevertheless, energy will be required to regenerate the sorbent by the energy-intensive calcination reaction.

The full environmental benefit of hydrogen as energy carrier can only be reached if it is produced from renewable sources, such as biomass [2]. Biomass offers the best route for accelerating the introduction of green hydrogen as a major fuel in the future, since biomass does not contribute to a net increase in atmospheric CO₂. Furthermore, the coupling of biomass conversion technologies with CO₂ capture and storage technologies offers the potential to achieve an effective reduction in CO₂ from the atmosphere [3].

H₂ can be produced from biomass through routes with intermediate steps of production of oxygenates, which are subsequently reformed. Fast pyrolysis is an attractive method to produce pyrolysis oil (bio-oil) from different types of biomass, which will be later treated by catalytic reforming to obtain hydrogen. Bio-oil is a complex mixture of a large number of compounds including acids, aldehydes, alcohols, ketones, phenols and sugars.

Acetic acid, acetone and phenol are used as model compounds of bio-oil produced by fast pyrolysis of biomass as they are frequently found in bio-oil composition; they are good representatives of acids, ketones and aromatics. Several works on hydrogen production by conventional steam reforming of bio-oil compounds have been reported in the literature [4-6], but the sorption enhanced concept has not been extensively studied. Furthermore, although the SESR process significantly enhances the hydrogen production in relation to the conventional steam reforming, the operation variables need to be evaluated and optimized for each of the biomass-derived compounds in order to maximize the H₂ production for each particular case. Phenol has been chosen in the present work since it is one of the most scarcely studied bio-oil model compounds.

The objective of the present study was to investigate the effect of the reforming reaction temperature on the H₂ production by sorption enhanced steam reforming of phenol over a Pd/Ni-Co hydrotalcite-derived catalyst and using dolomite as CO₂ sorbent in a bench-scale fluidized bed reactor. Experiments were carried out between 525 and 725 °C, using a low weight hourly space velocity (WHSV) of 0.3667 h⁻¹. Owing to the low solubility of phenol in water, a high steam-to-carbon ratio of 11 was chosen to ensure complete solubilisation. Possible interactions with other bio-oil compounds, such as acetic acid and acetone, were also studied in order to approach the simulation of the whole bio-oil behavior. H₂ yield, H₂ selectivity and H₂ purity, as well as CH₄, CO and CO₂ concentrations in the effluent gas were assessed. Thermodynamic equilibrium analysis of the process was carried out in order to assess the theoretical feasibility of the process at the studied reaction conditions and to compare the equilibrium values with the experimental results.

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