



Pure hydrogen from lighter fractions of bio-oil by steam-iron process: Effect of composition of bio-oil, temperature and number of cycles



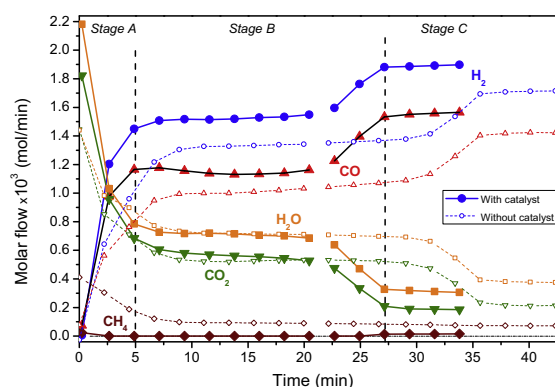
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HIGHLIGHTS

- Synthetic bio-oil produced by mixing model compounds featuring light fractions.
- Design of experiments techniques applied to represent wide range of compositions.
- Iron oxide with additives reduced by vaporized synthetic bio-oils.
- Oxidation of metallic iron releases high purity hydrogen.
- Effect of composition of liquid, reduction temperature and number of cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

High purity hydrogen has been obtained by “steam-iron” process from lighter fractions of synthetic bio-oils of different compositions in a single fixed bed reactor operating cyclically. This process is closely related to chemical looping producing and purifying hydrogen in a single reactor. The feedstock consisted of a blend of four model compounds representing the lighter fractions of a bio-oil. Acetic acid has been chosen as representative of the acidic fraction, hydroxyacetone of the ketonic/aldehydic, methanol of the alcoholic and finally water of the aqueous one. Content of each model compound in the mixture has been fixed by design of experiments techniques according to composition of real bio-oils found in literature. First step involves the reduction of an iron oxide at several temperatures (650–850 °C) by the action of a synthetic bio-oil, which catalytically decomposes into gaseous reductive species (mainly hydrogen and carbon monoxide). Solid carbon was also produced and deposited on the surface of the solid. Once the iron oxide is completely reduced, a second step consists in the oxidation of the metallic iron with steam releasing pure hydrogen. Along this reaction, and due to the low oxidation temperature (550 °C), carbon deposited in the previous step was not appreciably gasified, letting the released hydrogen be virtually free of carbon monoxide ([CO] < 20 ppm). Low proportions of water in the reductive gases have proved to exert a positive effect in the process, diminishing the residual carbon deposited on the solid bed, although decreasing reduction rates. The solid tested along this study, based on an iron oxide with small amounts of alumina and ceria, can produce pure hydrogen following a cyclic process, but exhibits a progressive loss of redox capacity of ca. 3 wt% after each cycle.

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1. Introduction

Hydrogen is becoming a clean and renewable alternative to fossil fuels and consequently its total demand is increasing [1]. One of the severest restrictions that hydrogen must overcome in its race to become an alternative energy vector, is that feedstocks and energy sources needed for its production are generally allocated. Accordingly, a wide variety of possible solutions should be contemplated. One of them, with an extra advantage relying on its renewability, but also with important drawbacks, involves using biomass. Along the last decades, forestry, agricultural wastes and energy crops have been envisaged as an alternative not only for the production of added value products but also as a renewable energy source [2–4]. On the other hand, its treatment is in general still very expensive, and only those processes that justify a trade-off between costs and benefits will gain market quota enough to settle in the middle to long term.

Bio-oil is the liquid coming from the fast pyrolysis of biomass (i.e. woody matter). It is composed of oxygenated hydrocarbons traditionally classified into acidic, ketonic/aldehydic, alcoholic and phenolic fractions [5–7]. The most representative compounds attending to their concentration within these fractions are acetic acid, methanol, hydroxyacetone, and water.

The “steam-iron” process (SIP) [8–12] is based on alternate cycles of reduction and oxidation of an oxygen carrier. It is directly related to other process like Chemical Looping [13–16] for which the “air-reactor” has been replaced by an oxidation reactor (i.e. “steam reactor”), making use of steam instead of air. Iron oxide (Fe_2O_3 – Fe_3O_4) with some other minor species (Al_2O_3 and CeO_2), has accomplished this task in the present study. The reductive agent is flexible and depends on the available feedstock: it could be hydrogen enriched mixtures (e.g. coming from thermocatalytic decomposition of natural gas), biogas (mixtures of methane and carbon dioxide coming from anaerobic digestion of organic wastes), alcohols (e.g. bio-ethanol) or bio-oils. All of them can produce the reduction of the original iron oxide into metallic iron [9,17,18]. The degree of reduction achieved by the solid is one of the adjustable parameters of the process. Some authors recommend complete reduction, but some others advocate that reduction extends only to wustite (FeO) to prevent sinterization of the solid at the expense of reducing the interchangeable amount of oxygen available [19]. Along subsequent oxidation, steam reoxidizes iron (or wustite) to produce hydrogen of high purity and magnetite (Fe_3O_4). This fact represents a significant intensification of the process since hydrogen is produced and purified within the same reactor, decreasing fixed costs of the plant [20].

Iron oxide and metallic iron can act both as catalyst for the decomposition of organic molecules like methane and methanol, or as reactive materials. Their catalytic role is reserved however for temperatures above 800 °C [21,22]. Since optimal temperature for reduction of these oxides is close to 700 °C, the presence of an additional catalyst might be necessary to decompose reactants at a significant rate. On the other side, nickel is a catalytically active species traditionally involved in methane steam reforming (MSR) [23–27]. In this reaction, nickel acts as a catalytically active site fixing the carbon atom of the methane molecule, and forcing it to decompose into carbon and hydrogen. This leads to a progressive deactivation of the catalyst by coking. Deactivation can be softened by using NiAl_2O_4 with some excess of nickel oxide above its stoichiometric composition to favour the formation of NiO well dispersed along the solid [28] and consequently allowing Ni^0 (catalytically active species) to emerge upon prior or “*in situ*” reduction.

Prior to the work described in this paper, it was tested the methane dry reforming of biogas ($\text{CH}_4 + \text{CO}_2$ mixtures) (MDR)

using a mechanical solid mixture consisting of doped iron oxide (85 wt%) and a catalyst (15 wt%) [29]. In turn, the catalyst was composed of 10 wt% NiO in excess above the stoichiometric NiAl_2O_4 . Similar results have been obtained using bio-oil and nickel as catalytically active species in the work carried out by Wang et al. [30]. An advantage of this catalyst is that its activation is produced *in situ*, and consequently, a previous reduction with extra hydrogen that would lower the total hydrogen yield of the process is not required. Also the work of Zeng et al. [31] is worth mentioning. In this case, authors use iron oxide for processing non-aqueous fractions of bio-oil.

The aim of this research is studying the technical feasibility of using lighter fractions of bio-oils as an alternative source for hydrogen supply. To do that, and according to the particularities of the process (i.e. alternate redox cycles), the conceptualization of the process requires using a set of unsynchronized fixed beds operating in parallel in order to keep a continuous production of hydrogen, as it has been suggested by Sanz et al. [20]. Other approximations to the conceptualization of the process can be found in the works performed by Bleeker et al. [32] and Plou et al. [33]; in this last case, only for modelling Gibbs reactors and the overall kinetics of the process.

The operating conditions were chosen according to the aim of producing pure hydrogen in the most efficient achievable way. Thus, reduction step was carried out at several temperatures in order to determine the optimal point of lower carbon formation (lower temperature), and lower sinterization and loss of reactivity (higher temperature) due to a decreasing surface area [34]. Upon reduction, iron was re-oxidized with steam to release pure hydrogen. Temperatures required to carry out this step should be low to avoid gasification of the eventual carbon deposited in the previous reduction, but at the same time, high enough to proceed at a reasonable reaction rate. An appropriate temperature for this purpose was established in 550 °C [35], based on an appreciable rate at moderate costs associated to steam production.

2. Materials and methods

2.1. Solids

The solid used as reactant was a mechanical mixture of three components: doped iron oxide based on hematite (Fe_2O_3), reforming catalyst and inert silica. The first one, which was the most abundant, acted as oxygen carrier reacting with the reductive gas stream. Dopants were ceria (CeO_2) and alumina (Al_2O_3) and their proportions were optimized in a previous work [36] accounting for only 2 wt% of the sample (1.75 and 0.25 wt% respectively). Alumina confers structural and mechanical resistance for avoiding loss of reactivity along cycles. Ceria is able to increase the reaction rate in those reactions for which oxygen migration is required [37]. It was synthesized in our lab by the gel-citrates method. More details about this method can be found in previous works [29,38–40]. Other synthesis methods (e.g. combustion, co-precipitation or urea based methods) were tested with worse results than the one employed in this work [41].

Catalyst consisted in a nickel aluminate (NiAl_2O_4) with excess of nickel to favour the appearance of NiO. The optimal excess of nickel, as well as the ratio between oxygen carrier and catalyst, was determined in a previous work [29]. The synthesis method for the catalyst consisted in a co-precipitation method at increasing pH. The precipitating agent was ammonia, following the work of Al-Ubaid and Wolf [42]. Both solids were mixed up with silica to avoid hot spots along the bed of solids. Particle diameter ranged from 160 to 200 μm .

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