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# Hydrogen from ethanol by steam iron process in fixed bed reactor

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## ABSTRACT

This research is devoted to the use of ethanol (i.e. bio-ethanol) in the combined production and purification of hydrogen by redox processes. The process has been studied in a single lab scale fixed bed reactor. Iron oxides, apart from their remarked redox behavior, exert an important catalytic role allowing the complete decomposition of ethanol at temperatures in the range from 625 to 750 °C. The resulting gas stream (mainly H<sub>2</sub> and CO) reduces the solid to metallic iron. During a subsequent oxidation with steam, the solid can be regenerated to magnetite producing high purity hydrogen (suitable to be used in PEM fuel cells). Even though small amounts of coke are deposited during the reduction step, this is barely gasified by steam during the oxidation step (detection of CO<sub>x</sub> in concentrations lower than 1 ppm). Influence of parameters like temperature, ethanol partial pressure and alternate cycles' effect has been studied in order to maximize the production of pure hydrogen.

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## 1. Introduction

The present study is focused in the joint production and purification of hydrogen from renewable ethanol. Ethanol is a great option which can be converted into hydrogen due to its relative low-toxicity (lesser than that of methanol), easy-generation from renewable sources, and low production costs [1].

Nowadays, most ethanol is produced by fermentation processes using raw materials like sugar cane, cereal grain and other materials with high starch content [2]. This way, biomass has produced up to 85.2 million cubic meters per year of bio-ethanol in 2012 all over the world [3], being currently the most used biofuel in transportation [4]. To refer to this

commodity the term “bio-ethanol” has been adopted not only to specify its biological origin but also or primarily as a marketing resource. During the last decade, ethanol has attracted considerable attention given that its research has achieved interesting improvements through the so called sustainable 2nd generation bio-fuels (ethanol obtained from lignocellulosic materials) [5]. This research has been the consequence of trying to avoid the drawbacks derived from the use of agro-food assets in the production of fuels, and to confer added value to crops and lands of low productivity [6].

The main process to produce hydrogen from ethanol involves steam reforming [7]. Nevertheless, an original method has been proposed in the near past that consists in its thermal catalytic decomposition [1]. This method takes advantage not only of the hydrogen production itself, but also of the

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coproduction of carbon nanostructured materials (carbon nanofibers – CNF and nanotubes – CNT). Although, it has been studied by several research groups [1,8], the drawback of low hydrogen purity by significant presence of CO and CO<sub>2</sub> still remains.

The goal sought in this work tries to cope with this problem through the simultaneous production and purification of hydrogen from ethanol by the steam iron process (SIP) [9,10], in a fixed bed reactor. This process is based on alternate cycles of solid reduction and oxidation. During reduction steps, a highly reductive stream (ethanol) reacts with iron oxides to produce a reduced form of the solid and variable compositions of the exhaust gases. On a later step, the previously reduced iron is re-oxidized with steam to form magnetite and a high purity hydrogen stream [4]. This process is closely related also to the chemical looping reduction, a variant of the chemical looping combustion using steam to re-oxidized the solid and releasing hydrogen [11].

### 1.1. Reaction network

Based on literature [1,8,12], the reactions that probably better describe the process of ethanol decomposition along the experiments are the following:

*Thermal decomposition:*



*Ethanol dehydration:*



Besides, these products could generate the following reactions:



The sum of reactions (r.1) plus (r.3), and (r.2) plus (r.4), would conform the *ethanol decomposition* reactions (r.5) and (r.6):



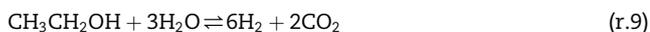
On the other hand ethylene from (r.2) could be *hydrogenated* as shown in (r.7):



Methanol could come from the *carbonylation* of ethanol to ethyl formate, followed by *catalytic hydrogenolysis* of the ethyl formate to methanol and ethanol [12] resulting in:



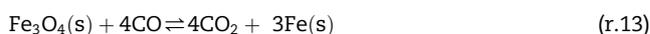
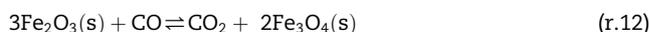
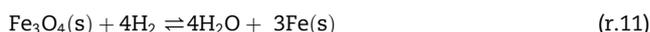
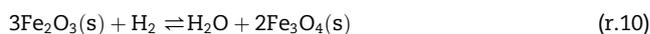
The presence of CO<sub>2</sub> could result also from *steam reforming* of ethanol if water can be present in the reacting atmosphere:



Ethanol decomposition, as described by (r.1), (r.5) and (r.6) generates a gas stream rich in hydrogen and carbon monoxide with a considerable reductive potential that could allow

the reduction of the solid starting from hematite up to metallic iron. This would constitute the first step of the above mentioned SIP.

At the experimental conditions used throughout this work (600–750 °C and 1 bar), iron oxide reduction by hydrogen exhibits two stages [9,13]: The first one consists in the reduction from hematite (Fe<sub>2</sub>O<sub>3</sub>) to magnetite (Fe<sub>3</sub>O<sub>4</sub>) (r.10). The second is the reduction from magnetite to metallic iron (r.11). Similar behavior can be attained when CO is the reducer gas (r.12) and (r.13). Although reduction of intermediate wustite was expected at temperature higher than 570 °C [14] according to thermodynamic solid phase diagrams [15], it was not empirically evidenced.



During the second step of steam iron process, the reduced iron is oxidized by steam producing pure hydrogen. The former solid is regenerated only to intermediate magnetite due to thermodynamic restrictions at experimental temperatures and partial pressures (reverse of r.11, now on labeled as r.11\*).

It is important to note that also reactions between gaseous reactants and products can take place within the reactor. These could produce reactions such as *methanation* (r.14), *Water Gas Shift* (r.15) or *Boudouard* reaction (r.16).



Finally, deposited coke during the reduction step could be gasified during the subsequent oxidation step, as shown in (r.17).



## 2. Experimental

### 2.1. Experimental setup

The experimental system consisted of a cylindrical fixed bed reactor made out of quartz ( $\varnothing_i = 13$  mm,  $L = 420$  mm). The solid bed is constituted by 2.125 g: 75%w “triple” oxide (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>). Its length is roughly 2 cm. The usage of an additivated solid (cerium and aluminum oxides),  $\varnothing_{\text{particle}} = 160\text{--}200$  μm, has been proposed in order to improve the stability to sintering of the solid [16]. The other 25%w is SiO<sub>2</sub> of same diameter acting as inert. Silica is added to avoid agglomeration of the reacting solid upon reoxidation and to decrease preferential pathways of the gas stream in its cross-sectional distribution. No temperature profiles greater than

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