

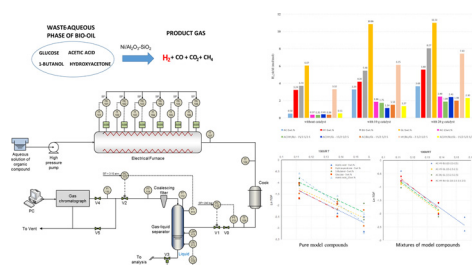
# Hydrogen production from supercritical water reforming of acetic acid, acetol, 1-butanol and glucose over Ni-based catalyst

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Supercritical water reforming (SCWR) of four main constituents of bio-oil aqueous phase (acetic acid, acetol, 1-butanol and glucose) to produce hydrogen was studied in a tubular fixed-bed reactor using commercial Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalyst. The process was carried out under different operating conditions at 240 bar (500–800 °C, 5.0–22.5 wt.% of organic compounds and values of weight-hourly space velocity (WSHV) of 2.5–22.5 g<sub>org-comp</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). The data were reported as reaction rates, expressed as turnover frequencies (TOF), and the Arrhenius parameters (pre-exponential factor and apparent activation energy) were obtained. The process performance was compared to that without using any catalyst and that regarding equilibrium condition. Hydrogen yields were very close to those values predicted by equilibrium within the operating window tested in this study.

## 1. Introduction

The rising problems of global warming and fossil fuels depletion have led to innovative technologies for producing clean energy. Bio-oil from biomass fast pyrolysis is a complex mixture of oxygenated hydrocarbons (acetic acid, methanol, aldehydes, ketones, cyclopentenones, furans, alkyl-phenols, alkyl-methoxy-phenols, anhydrosugars, and oligomeric sugars derived from biopolymer structures), which may contain 15–30 wt.% water [1]. As a previous step for upgrading, bio-oil can be fractionated into two phases by adding water. The oil phase is rich in organic compounds and it could be further upgraded to biofuels

by a hydrothermal process. The aqueous phase has 70–80 wt.% water [2,3] with low-molecular-weight organic compounds, such as alcohols, ketones, aldehydes, and carboxylic acids.

The water-rich phase is less valuable and its valorization has been sought during the last years. Due to the relative low content of the organic compounds, the cost of extraction techniques is too high. In fact, if large amounts of bio-oil aqueous phase were produced this stream might be considered as waste. However, it may be valorized by a suitable process. As a valorization alternative, hydrogen production via catalytic reforming has been explored [4–6], but this type of process is energy-intensive due to the large amount of water that must be

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evaporated.

Supercritical water reforming (SCWR) is an emerging thermo-chemical process that can convert wet biomass and organic wastes into syngas and hydrogen without vaporizing water. This way, SCWR reduces the energy requirement with respect to other reforming processes, thus overcoming the energy barrier. SCWR involves reactions of organic compounds in water medium at supercritical state, which is highly beneficial for reaction rates [7–9]. Indeed, SCW is more and more used. Recently, the upgrading of bio-oils by the reforming in supercritical water to produce gaseous and liquid biofuels has been studied [10,11].

Additionally, we have verified that SCWR of glycerol can be successfully performed with and without catalyst, and in such a way that an energy self-sufficient process with no external fuel can be performed [12–14]. Recently, we have studied the SCWR of four model compounds (acetic acid, acetol (hydroxyacetone), 1-butanol and glucose) in the absence of a catalyst. These compounds are representative of the main oxygenate organics present in the aqueous fraction of bio-oil [15]. Although high conversions were obtained, gas yields were far from equilibrium. We hypothesized that a kinetic limitation occurred during the gasification of liquids and the subsequent methane reforming under supercritical conditions. Therefore, the use of a catalyst would allow higher gas yields, especially, an increase in the hydrogen production.

The main aim and novelty of the present study is the assessment of the hydrogen production from SCWR of the above-mentioned four organic constituents of the bio-oil aqueous fraction over a Ni-based commercial catalyst. The reaction rate of the SCWR of those compounds to hydrogen expressed as turnover frequency (*TOF*), which is based on the number of active sites, is another objective. The kinetics results are described as rate equations and the Arrhenius parameters (normalized pre-exponential factor and apparent activation energy) are obtained. This quantitative measurement of catalyst activity is very important to compare the results with those expected from the likely rate-determining step and with others obtained in similar studies. The paper also provides the effect of temperature (500–800 °C), feed concentration (2.5–22.5 wt.%), and weight-hourly space velocity (2.5–22.5  $\text{g}_{\text{org-comp}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$ ) on the hydrogen production. In addition, the experimental results are compared with those obtained without adding a catalyst and with simulation results obtained using a non-stoichiometric approach by Aspen Plus (assuming equilibrium), as well as with other findings from previous studies. The use of a catalyst allows the increase in the reaction rate and the decrease in the reforming temperature, thus reducing the energy requirement.

## 2. Methodology

### 2.1. Experimental section

The experiments were carried out with acetic acid (> 99.7% purity), hydroxyacetone (> 95.0% purity), 1-butanol (> 99.4% purity) and glucose (> 99.5% purity), as well as with deionized water. A commercial Ni-based catalyst supported on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  with 66 wt.% Ni (Sigma-Aldrich 208779) was used. Table 1 shows the main characteristics of fresh Ni catalyst and Ni catalyst exposed to SCW (without reforming).

Metal content was measured by inductively coupled plasma atomic emission spectroscopy (Horiba Jobin Yvon Ultima 2). The BET surface area along with the areas and volumes of micropores and mesopores were obtained by means of physisorption using nitrogen as an adsorptive agent (Micromeritics ASAP 2420 System). Structural information on an atomic scale of both crystalline and non-crystalline (amorphous) materials was acquired using XRD (Bruker D8 Advance A25 equipment). X-ray Photoelectron Spectroscopy (XPS) was used to distinguish the different oxidation states of catalyst (ESCA Phoibos HSA3500 150 MCD-9).

Regarding the analysis of liquid samples, the total organic carbon

**Table 1**

Main characteristics of fresh Ni catalyst and Ni catalyst exposed to SCW (but without reforming).

Catalyst	BET surface area ( $\text{m}^2/\text{g}$ )	Crystal structure		Specific pore volume ( $\text{mL/g}$ )	Average pore diameter (nm)
		Amorphous	Crystalline		
Ni as provided	166.2	50.0%	50.0%	0.27	6.02
Ni exposed to SCW (600 °C)	118.8	35.2%	64.8%	0.31	10.05
Ni exposed to SCW (800 °C)	98.5	33.7%	66.3%	0.26	9.57

(TOC) was obtained by an analyzer Shimadzu TOC-VCSH with an auto sampler ASI-V. Concentrations of acetic acid and acetol were measured by a mass spectrometer with quadrupole analyzer Agilent 5977A and using a gas chromatograph/mass spectrometer (Agilent 7890B) for polar capillary columns (Sapiens-5MS (30 m–0.25 mm–0.25  $\mu\text{m}$ ), Teknokroma). Heating ramps at temperatures from 60 to 300 °C for 24 min were performed in the analysis method. The glucose was measured in the same equipment but using a non-polar column (19091 S-433U HP-5MS UI (30 m–0.25 mm–0.25  $\mu\text{m}$ )), where glucose had to be previously derivatized with MBTFA and a spectral deconvolution program was applied. The analysis method was performed at temperatures from 80 to 280 °C using heating ramps for 37.5 min and the mass range ( $m/z$ ) was between 30 and 475.

A diagram of the experimental plant is illustrated in Fig. 1. The aqueous solution of model compounds was pumped and heated to the operating temperature by an electrical tubular furnace housing the reactor (2.0 m length; 7.92 mm ID). The product gas leaving the reformer was cooled down to 40 °C and the condensate (mostly water) was expanded through a back-pressure valve. Next, the condensate was separated from the gas in a knockout drum. The mass flow-rate of the gas stream was measured and a sample of this stream was continuously analyzed by a gas chromatograph (Agilent 7890A). The tests were conducted for 3–6 h. The two catalyst loads were 10 and 20 g, which occupied about 200 and 400 mm inside reactor arranged at 700 and 500 mm from the reactor outlet, respectively. Catalyst was capped with pieces of glass fiber, and it was not reduced before testing. The material of reactor (made of Inconel 625, with a high content in nickel) did not exhibit catalytic activity, because the reactor was sufficiently aged after having been operating for more than 2000 h in previous tests.

All the experiments were conducted at 240 bar. The furnace temperature varied between 500 and 800 °C, and the weight-hourly space velocity (WHSV), defined as the mass flow-rate of organic model compound ('omc') divided by the mass of catalyst ('cat'), ranged from 2.5 to 22.5  $\text{g}_{\text{omc}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$  by changing the feed concentration, pumping a feed flow-rate of 1.0 L/h. The feeding mixtures compositions contained acetol, 1-butanol and/or glucose (from 2.5 to 5.0 wt.%), as well as acetic acid (from 5.0 to 15.0 wt.%). The most concentrated mixture of model compounds was 22.5 wt.%, which is a representative value of bio-oil aqueous fraction.

The hydrogen yield was computed as follows:

$$\eta_{\text{H}_2} = \frac{N_{\text{H}_2}}{\sum_i N_{i,\text{feed}}} \quad (1)$$

where  $N$  denotes the number of moles of the compound referred in the subscript. Likewise, the organic compound conversion is the result obtained by dividing the difference between moles of organic compound fed to the reactor and those present in the liquid by the moles of organic compound fed to the reactor. Equally, the carbon-to-gas (-liquid or -solid) efficiency is obtained by dividing the moles of gas (liquid or solid) carbon by the carbon moles fed to the reactor.

Carbon balance was calculated from the carbon content in the feed,

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