



Catalytic steam reforming of butanol in a fluidized bed and comparison with other oxygenated compounds



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ABSTRACT

Fluidized bed steam reforming of butanol was studied at 650 °C, atmospheric pressure and a steam to carbon (S/C) molar ratio of 14.7. The influence of the space velocity (G_{C1} HSV) was tested with different catalysts. The use of a Ni/Al catalyst with 28.5 wt.% Ni content gave almost equilibrium conditions at a G_{C1} HSV of around 11000 h⁻¹. At higher G_{C1} HSV values, carbon conversion to gas and gas yields diverged from equilibrium values. The catalyst composition was also analysed using several Ni/Al research catalysts modified with Ca or Mg, studying their effect on the nickel reducibility and activity. A comparative study of steam reforming of oxygenated compounds (butanol, ethanol, acetol and acetic acid) was also carried out. The steam reforming of alcohols showed high stability over time in comparison to the other compounds. The characterization of used catalysts by FESEM and TPO showed a greater proportion of refractory carbon when using acetic acid and acetol in comparison to the alcohol steam reforming which, in addition, presented less carbon content on the catalyst surface.

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1. Introduction

Biomass derived from forest or agricultural residues, energy crops or organic waste streams could partly replace fossil fuels as part of a biorefinery strategy. Such biomass has the potential to be processed for synthesis gas production in order to generate chemicals or fuel. In this context, catalytic steam reforming of pyrolysis liquids can be a viable process for the production of valuable gases. The aqueous fraction of pyrolysis oil is obtained after a simple water extraction (weight ratio 2:1, water: pyrolysis oil) and the catalytic steam reforming of this fraction produces a hydrogen rich syngas.

The aqueous fraction of the pyrolysis liquid consists of a complex mixture of a large number of organic compounds which includes different functional groups: acids, ketones, aldehydes, alcohols, sugars, phenols and more complex carbohydrate materials emulsified with water [1].

Model compounds have been widely used in order to simplify the process and gain further insights into bio-oil and the steam reforming of its water-soluble fraction. Acetic acid has been widely employed [2–12]. Other model compounds such as hydroxyacetaldehyde, m-cresol, dibenzyl ether and sugars were studied by Wang et al. [2] and Markevich et al. [3]. Wang et al. also worked with phenol, syringol, ADP, levoglucosan, cellulose, xylan, and lignin [13]. Rioche et al. used phenol, acetone and ethanol [4]. Recently, m-cresol has been attracting

more attention because it can easily lead to carbon deposition [14]. In a previous work, acetic acid and acetol were studied in a quartz fluidized bed reactor with the purpose of studying their influence on the performance of various research catalysts [15].

The catalytic steam reforming of butanol was studied in the present work. Oasmaa and Meier [1] determined that butanol is present within the alcohol fraction of bio-oil. Moreover, interest in n-butanol is likely to increase as it can be produced by biological processes [16] and it has been proposed as an alternative to conventional gasoline and diesel fuels [17]. Butanol offers advantages such as a lower vapour pressure than ethanol or gasoline, a higher energy content than ethanol and a higher hydrogen content than ethanol or methanol. Therefore, butanol has also been suggested as a source for generating hydrogen for fuel cell applications.

In spite of the potential use of butanol, there are few studies in the literature reporting on its thermochemical processing. For instance, there are considerably fewer experimental works on butanol steam reforming as a single compound or within a mixture of oxygenated hydrocarbons as compared to ethanol or methanol [18–21]. These few reports on butanol are mainly focused on thermodynamic processes such as butanol dry reforming [22], steam reforming [17,23–25], partial oxidation [26] and alternative technologies such as aqueous phase reforming [27]. The majority of the previously cited experimental works were performed in a catalytic fixed bed configuration. The use of a fluidized bed reactor has some advantages related to its processing capacity and the catalyst stability which are relevant at an industrial scale. Therefore, the study of catalytic steam reforming of butanol in a fluidized bed has been considered of interest.

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Coprecipitated Ni/Al catalysts have been used in fluidized beds for steam gasification of biomass [28] and catalytic steam reforming of the aqueous fraction of bio-oil [29]. The catalysts to be used in the fluidized bed must have an appropriate mechanical strength. Magrini-Bair et al. developed impregnated Ni catalysts for conditioning syngas from biomass gasification using attrition-resistant supports [30]. Previous works demonstrated the positive effect of Ca and Mg for increasing the attrition resistance of coprecipitated Ni/Al catalysts [15].

The present work deals with experiments in a fluidized bed reactor using Ni/Al research catalysts modified with Ca or Mg, in order to contribute to the knowledge of the catalytic steam reforming of butanol. The influence of the catalyst weight/butanol flow rate ratio (W/m_{butanol}) and catalyst composition were studied. Moreover, catalytic steam reforming experiments of other oxygenated compounds such as ethanol, acetic acid and acetol were performed to show their influence on catalyst reforming activity and stability.

2. Experimental

2.1. Experimental system

Fig. 1 shows a schematic of the experimental setup where the experiments were carried out. This is a bench-scale installation with a tubular 1 in. (2.54 cm) quartz fluidized bed reactor. The aqueous solutions of the organic compounds were fed into the reactor bed by being sprayed through a quartz coaxial injection nozzle. The liquid was delivered by an HPLC pump at a flow rate of around 0.78–0.79 mL/min. The product gas composition was measured by an Agilent P200 Micro GC gas chromatograph equipped with thermal conductivity (TCD) detectors measuring the concentrations of CO_2 , CO, CH_4 , C_2 (C_2H_4 and C_2H_6), N_2 and H_2 . A CO/CO_2 IR analyzer was used to give a rapid value of the content of these gases in order to check if the installation was performing adequately. A more detailed description of the setup and the experimental procedure can be found in previous works [12,15,29].

The majority of the experiments were carried out using a 6.54 wt.% butanol aqueous solution due to its low solubility in water (below 7.7 g of butanol per 100 g of water), corresponding to a steam to carbon (S/C) molar ratio of 14.7. The experiments were performed at 650 °C, atmospheric pressure and fluidization conditions of u/u_{mf} of 10, defined as the ratio between the superficial gas velocity and the theoretically calculated velocity for minimum fluidization. The catalyst weight/

butanol mass flow rate ratio (W/m_{butanol}) ranged from 0 to around $8 \text{ g}_{\text{catalyst}} \cdot \text{min}/\text{g}_{\text{butanol}}$, corresponding to $G_{\text{C}_1}\text{HSV}$ values of ∞ to around 8500 h^{-1} , respectively. This space velocity has been previously defined [2].

For the comparative study of oxygenated compounds (butanol, ethanol, acetic acid and acetol) the same rig was used and similar operating conditions were employed to carry out all the experiments. These conditions were 650 °C, S/C of 7.64, $G_{\text{C}_1}\text{HSV}$ around 30000 h^{-1} and u/u_{mf} of 6. Two pumps were employed to feed butanol with a S/C ratio of 7.64, one for water and the other for butanol.

The mass balance closure of every experiment is called the recovery and indicates its accuracy. Values of 1 within a 5% error were accepted (recovery between 0.95 and 1.05). The butanol used in the whole study was 1-butanol.

2.2. Catalyst preparation

Three research catalysts were prepared by coprecipitation and one by impregnation. The main characteristics of these catalysts are shown in Table 1.

A Ni–Al catalyst with 28.5 wt.% nickel content was synthesised by a coprecipitation method at a rising pH and was further modified by adding Mg or Ca as promoters in order to prepare other catalysts. The catalysts thus prepared are referred to as follows: NiAl (Ni–Al catalyst), NiAlCa0.12 (Ni–Al catalyst modified with calcium with a 0.12 Ca/Al molar ratio) and NiAlMg0.26 (Ni–Al catalyst modified with magnesium with a 0.26 Mg/Al molar ratio). These modified catalysts showed good resistance to attrition combined with good performance in the catalytic steam reforming of acetic acid as a model compound [15]. They were also tested during the steam reforming of the aqueous fraction of pyrolysis oil [29]. The catalyst preparation has been previously reported in these cited works [15,29].

In addition, an impregnated catalyst (named ImpNiAlCa_{0.03}) was also prepared by a method similar to that described by Lu et al. [31]. First of all, the support was prepared by coprecipitation of the Ca and Al nitrates by adding an ammonium hydroxide solution until reaching a final pH of 7.9. The colloid was then dried at 100 °C and calcined up to 900 °C for 3 h. The calcined support thus obtained was impregnated by incipient wetness impregnation in a $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, dried at 100 °C and finally calcined up to 750 °C for 3 h in order to obtain the final calcined precursor of the catalyst.

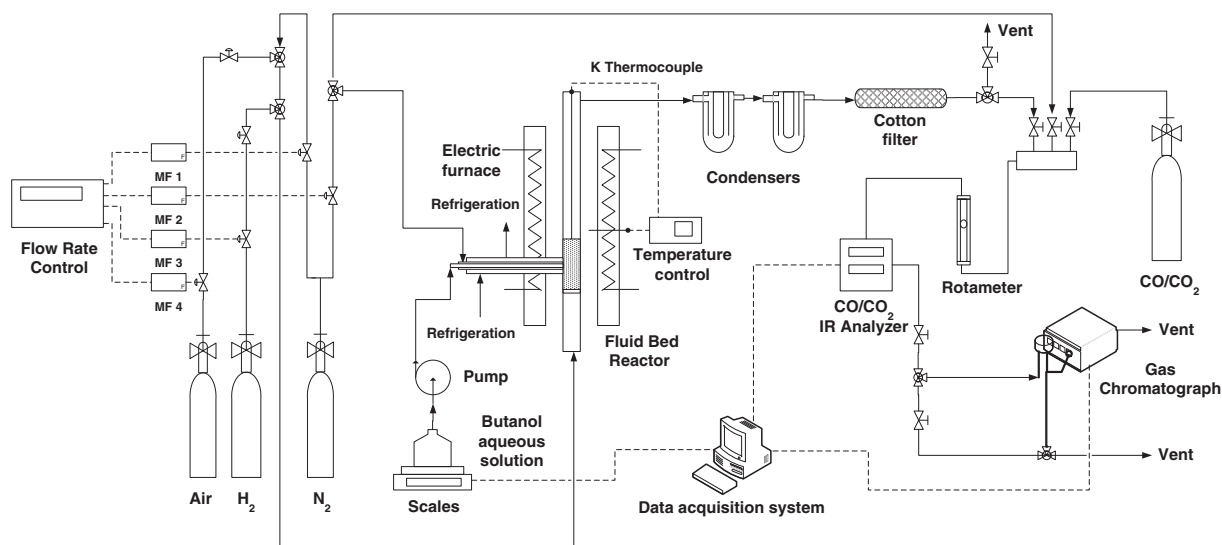


Fig. 1. Schematic of the fluidized bed steam reforming experimental setup.

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