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Biomass gasification in supercritical and subcritical water: The effect of the reactor material

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HIGHLIGHTS

- Gasification in subcritical (350 °C) and supercritical (400 °C) water was performed.
- Glucose and beech sawdust at 15 wt.% were gasified without a catalyst.
- Micro-autoclaves made of stainless steel and Inconel® 625 were compared.
- Stainless steel showed higher H_2 productions.
- Inconel® 625 enhances CO methanation.

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ABSTRACT

Batch reactors made of stainless steel and Inconel® 625 were used for the hydrothermal gasification of glucose and beech sawdust under both subcritical (350 °C) and supercritical (400 °C) conditions at a pressure of 30 MPa. These tests were executed over residence times ranging from 60 to 300 min. The amounts of solid, liquid and gas produced and the composition of the resulting gas phase were measured. The results showed that a higher H_2 output was achieved in the stainless steel reactors, while the Inconel® 625 reactors were more effective for the synthesis of CH_4 and light hydrocarbons. A visual observation of the metal surfaces was performed using scanning electron microscopy to explain the persistence of catalytic activity even after an aging treatment and many hours of operation.

1. Introduction

Biomass is among the energy sources that have been most widely considered as possible substitutes for fossil fuels. Compared to fossil resources, biomass is much better distributed throughout the world, and if grown and handled in a sustainable way, it can have a reduced or even no impact on the environment and global warming. Traditional thermo-chemical processes, such as combustion, pyrolysis and gasification, usually require dry feedstock for proper performance. This is an important drawback to the use of biomass because much of the available biomass, especially that resulting from agro-industrial processes, is wet, with moisture contents greater than 80%. To overcome these issues, hydrothermal processes have been proposed. Among these processes, supercritical water gasification (SCWG) has been the focus of significant attention by the scientific community.

SCWG is an innovative technology for converting biomass into valuable combustible gas, possibly with a large content of hydrogen [1]. Such a process is based on the use of water above its critical point ($T > 374.15$ °C; $P > 22.1$ MPa). At these conditions, water exhibits unique properties, behaving in an intermediate manner between a liquid and a gas. As a liquid, it retains a high density, resulting in a high reactivity and solvent power. As a gas, it shows high diffusivity and the ability to mix with most other gases in any proportions. Moreover, in water at the supercritical state, a significant change in the dielectric constant is observed. At such conditions, water behaves like a non-polar solvent, eventually becoming capable of dissolving most organic compounds [2].

SCWG can overcome several problems typically associated with traditional gasification technologies. Wet biomass can be treated directly, without prior drying, paving the way to a feasible energy valorization of many organic wastes and by-products. Moreover, the unique reaction environment drastically reduces the formation of char and tar, which is a crucial issue for the development of biomass gasification technologies [3].

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In the literature, several papers address sub- and supercritical water gasification [4,5], most of which involve tests with different types of biomass in tubular continuous reactors [6–8].

Catalysis is often used in combination with SCWG because the technique's feasibility requires a reduction in the energy demand of the process. A number of papers in the literature deal with this topic; interesting reviews can be found in [9,10]. Some previous research has focused on determining the intrinsic reaction rates while operating the reactor in a non-catalytic environment able to exclude any catalytic wall effects. This approach was introduced by a group from the University of Twente who developed a methodology based on quartz capillaries [11]. Through this technique, glucose and wood were gasified; when the catalyst was inserted in the capillary, the catalytic influence of ruthenium was clearly observed and distinguished from the non-catalyzed behavior [12]. A similar approach was followed by DiLeo and Savage [13]. In their work, the authors performed experiments using quartz batch reactors filled with methanol, with or without a nickel wire. In this way, they concluded that nickel catalyzes H_2 formation and is subject to deactivation with use. In a subsequent work, Resende and Savage performed similar experiments using cellulose and lignin as the feedstock and adding different metals in the form of powders or wires [14]. They confirmed that a catalytic effect took place, and they described differences between the various metals.

All of these studies reproduce the presence of the metal by adding a wire or a powder inside the reactor. Although this approach allows one to clearly understand the influence of a specific metal, it does not reflect the real-world situation in which the metal surface is comprised by the entire inner part of the reactor. Importantly, some authors have reported that the reactor wall effects are non-negligible in methanol SCWG [15,16] and biomass gasification [17]. Moreover, in industrial operations the reactor surface is exposed to the reaction conditions for several hours. It would, therefore, be interesting to observe if the reactor material continues to play a catalytic role even after several runs. Previous studies in the literature do not clarify this aspect in a direct way because they compare data obtained in different reactor types and under different operating conditions [12]. Catalyst deactivation has been shown to occur after a few cycles of several minutes each [13], but the persistence of catalytic activity over a longer time period has not been reported.

Furthermore, all of the data available in the literature refer only to catalytic effects at supercritical conditions over residence times ranging from a few seconds to 2 h [18–20]. Longer residence times have been documented only at subcritical conditions, in which residence times of up to 10 days were adopted [21], but the evolution of the gaseous products was not investigated. It would be useful to adopt much longer residence times to understand if such catalytic effects only occur in the first minutes of the reaction, or if they also play a role on a longer time-scale.

In this work, batch reactors made of stainless steel and Inconel® 625 were compared to see if catalytic wall effects significantly affect the gasification output. Two substrates were tested: glucose, which has been used in many SCWG studies as a model compound for cellulose, and beech sawdust, a common biomass, which is often produced as a by-product of the furniture industry. Real biomass, such as beech sawdust, comes with ashes and salts, which can have catalytic effects of their own [22]. The combination of such effects with those of the catalytic walls has not been investigated yet. Both sub-critical (350 °C) and supercritical (400 °C) conditions were considered. The tests were conducted at different residence times, ranging from 60 min to 300 min, to evaluate the effect on those reactions and the processes taking place at low rates.

The scientific novelty and advances of this work can be summarized as follows:

- Straight-forward comparison of hydrothermal experimental results obtained in stainless steel and Inconel® 625 reactors;
- Long-term testing with residence times of up to 5 h and with a focus on the reaction kinetics;
- Study of the catalytic activity of the reactor walls even after hundreds of hours of operation;
- Critical comparison of results obtained with a model compound (glucose) and with real biomass (beech sawdust);
- Analysis through scanning electron microscopy (SEM) of the reactor surfaces after hours of exposure to SCWG conditions in the presence of common char- and ash-forming substrates;
- Comparison of the catalytic reactor wall effects between sub- and supercritical conditions.

2. Materials and methods

The work performed in this study involves a number of experimental tests conducted in small batch reactors. These devices were used to perform more than 80 experimental tests, in which solid, liquid and gaseous products were sampled, quantified and analyzed. To observe the behavior of the metallic surfaces, tests were executed in which metallic burrs were added to the reacting mixture and observed using SEM.

2.1. Micro-autoclave preparation and reaction

The tests were executed in small-scale batch reactors, also known as micro-autoclaves. These devices are small metallic vessels with a volume of 5 ml that are able to withstand high pressures. Because of their small volume, the reactors can be heated quickly. The micro-autoclaves consisted of two hollow cylindrical elements to be screwed together. The reaction volume was the internal cavity obtained by screwing together the two parts. Micro-autoclaves have been successfully used in previous studies in the literature [18,19].

Two different micro-autoclaves were used, one made of stainless steel and one made of Inconel® 625. This use of two materials allowed a comparison to be made between the two materials and allowed the significance of wall effects due to the specific materials to be assessed. Stainless steel was chosen because it is one of the most popular manufacturing materials in chemical plants. It is inexpensive, and it can handle the most severe reaction conditions occurring in the present study (400 °C and 30 MPa). The type of stainless steel that was used was 1.4571, the main constituents of which are iron, chromium and nickel in the amounts shown in Table 1. Inconel® 625 is a non-iron alloy made of nickel, chromium and molybdenum (see Table 1 for further details of its composition). Nickel-alloys are generally used in hydrothermal processes because they show great mechanical resistance to harsh reaction conditions, i.e., very high temperature and pressure. Furthermore, they have sufficient chemical resistance to corrosion [23]. However, Inconel® 625 is much more expensive than stainless steel, making its usage particularly burdensome. For each material, two identical micro-autoclaves were adopted to ensure that the results were not affected by any peculiarities of the specific device.

The tests were performed with two substrates: glucose and beech sawdust. Glucose can be considered a model biomass compound because it is the monomer of cellulose, one of the main con-

Table 1
Average composition of the metal alloys used in this study.

	Ni	Cr	Mo	Nb	Mn	Fe	C	Minor
Stainless steel 1.4571	11.5	16.4	2.1	–	1.5	67.8	0.04	0.7
Inconel® 625	61.0	21.5	9.0	3.6	–	2.5	0.06	2.3