



Semi-continuous biomass gasification with water under sub critical conditions



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HIGHLIGHTS

- Results of the gasification process with water in near critical point.
- Sodium oxide effect was evaluated in order to establish its effect on the products.
- Hydrothermal process of biomass and wastes.
- Possible to obtain a liquid phase that includes some precursor of different products.

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ABSTRACT

The paper reports on gasification of almond shells with water at high pressure (above critical value) and temperature. The experimental set up was a semi-continuous reactor, an innovative configuration allowing to continuously remove the gas product from the reaction vessel. The adoption of pressure conditions well above water critical value (30 MPa) and relatively low temperature (300 °C) confirmed suitable reaction pathways for biomass conversion with high efficiency leading to a liquid phase rich of some interesting compounds (HMF, furfural). In order to increase the process performances, sodium hydroxide was added as promoter of the gasification reactions. According to an already proposed reaction scheme, results confirmed a positive impact of the additional compound to the liquid yield and quality, while the gaseous phase was enriched in carbon dioxide.

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1. Introduction

Gasification using water in supercritical conditions is a promising technique for solving some of the critical points related to processing of biomasses at high level of humidity such as food processing waste, algae or sludge without any pre-drying [1].

In particular, the amount of the food processing waste is very large in Europe and is an increasing problem. Food waste is mainly composed of an organic material with high moisture content. The total amount of food waste and by-products produced in the European Union has been estimated at approximately 222 million tons per year [2].

In addition, the high pressure of obtained syngas allows an energy recovery via expansion but the gas is also suitable as natural gas substitute directly available for transportation and civil and industrial usage. In this concern, gas purification steps (mainly CO₂ capture) are favoured at high pressure. Also the liquid phase

contains some important chemicals intermediate that can positively impact the process economy, after proper separation and purification and Fig. 1 summarises some of the final applications for products of biomasses gasification with water in supercritical conditions.

Hydrothermal processes in super- or near super-critical conditions of water, exhibited different advantages with respect to traditional biomass gasification [3–5].

- Its physical state makes water a proper reactant of the process, able to solubilise organic compounds and reduce the tars formation. This reduces solids elimination costs with respect to traditional processes. In addition, humid biomasses do not need preliminary drying saves energy and preserves some of the energy of raw materials.
- Raw materials contain lignocellulosic fraction, fatty acids and proteins that can be transformed in commercially valuable compounds such as methane, hydrogen, bio crude oil, and biogas. In addition some relevant intermediates such as furfurals, aldehydes and organic acids can be obtained.

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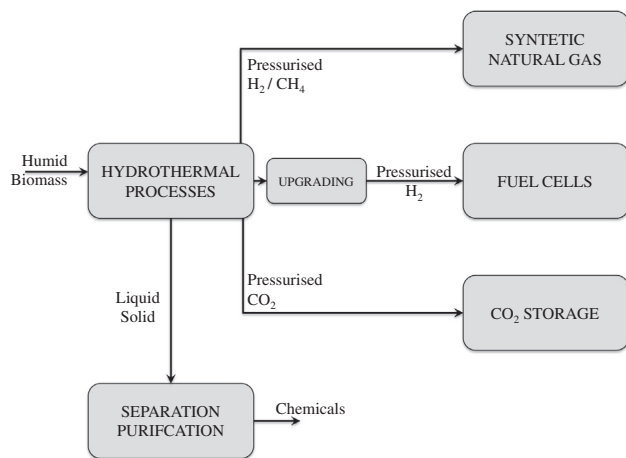


Fig. 1. Product distribution for SCWG.

- iii. The water state reduces the mass transfer resistance through interphase, ending with an increased apparent reaction rates and more effective products separation.

1.1. Hydrothermal processes classification

Hydrothermal processes can be classified on the base of the increasing operative temperature, in liquefaction, catalytic and high temperature gasification (Fig. 2).

At pressure below or near critical value (374 °C and 22 MPa), changes in temperature affect the water physical properties ending with characteristics very different from those of the liquid at low pressure. Close to critical pressure, the increase of temperature up to the critical value allows to control either the hydrolysis rate or to change the reaction paths leading to different products. Close to critical point, water is highly compressible, as the density drops from 800 kg/m³ at 300 °C to 150 kg/m³ at 450 °C, this sharp variation is mainly responsible for the changes in terms of solvating capability, polarity, dielectric constant and viscosity as summarised in Table 1. The polarity is connected to the dielectric constant DC, in particular at high DC corresponds a polar solvent such as water in normal condition while apolar solvent are characterized by low DC. Particularly change in polarity affect the water ability to act as a solvent for polar species and also the solubility of most inorganic salt drops down when exceeding the critical point [1,6].

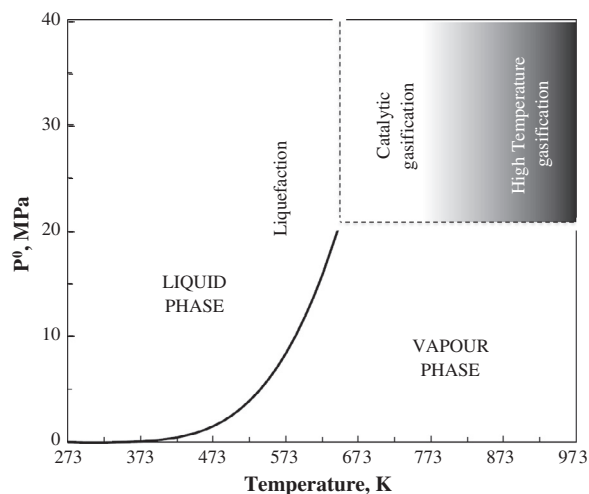


Fig. 2. Hydrothermal processes in water phase diagram.

Table 1

Water physical properties as a function of p and T [9,13,11]. Data into square bracket are at SATP.

Near- and sub-critical conditions		
Temperature (°C) [25]	250	350
Pressure (MPa) [0.1]	5	25
Density (g/cm ³) [1]	0.8	0.6
Dielectric constant (F/m) [78.5]	27.1	14.07
Ionic product (pKw) [14]	11.2	12
Specific heat (KJ/kg °C) [4.22]	4.86	10.1
Dynamic viscosity (mPa s) [89]	0.11	0.064
Super-critical conditions		
Temperature (°C) [25]	400	400
Pressure (MPa) [0.1]	25	50
Density (g/cm ³) [1]	0.17	0.58
Dielectric constant (F/m) [78.5]	5.9	10.5
Ionic product (pKw) [14]	19.4	11.9
Specific heat (KJ/kg °C) [4.22]	13	6.8
Dynamic viscosity (mPa s) [89]	0.03	0.07

These severe process conditions, requested to have proper water characteristics for gasification, act negatively on materials used for reactor manufacturing. In fact, acid and highly oxidant conditions, promote corrosion phenomena such as pitting or inter-crystalline and stress corrosion. Therefore some selected materials, exhibiting the adequate mechanical resistance, (such as Hasteloy C-276 or Inconel 625) can be used in gasification with water near critical conditions [11,13,14]

1.2. Glucose gasification

Glucose is a simple molecule, acting as primary intermediate when gasifying lingo-cellulosic biomass. It represents a key compound for reaction mechanism and kinetic comprehension.

Different studies [8–10,12,16] have defined a reaction path (Fig. 3) starting from carbohydrates hydrolysis to monosaccharides followed by isomerisation, leading to glucose and fructose presence. These compounds can be used to understand reaction mechanism as fructose degrades rapidly through isomerisation, dehydration and recombination pathways. The range of products is wide, involving phenols, furans, acids and aldehydes that can reconverts into gas (supercritical conditions) or liquid/solid species (near critical conditions) [17–20].

Also lignin, together with cellulose and hemicellulose, is among the main constituents of the biomass; it is constituted by a hetero aromatic polymer with a high resistance to chemical and enzymatic degradation [21] although during the hydrothermal processes degrades in different types of phenols. Experimental results [22–24] of hydrothermal processes with the lignin, in the range of 350–400 °C showed the formation of compounds such as catechol, phenols and cresols, with a yield in the liquid phase in the range 58–79% and in the range 12–37% for the solid phase. The liquid phase obtained is not of type oily, but an aqueous phase in which are dissolved organic compounds. In this paper, results are presented of almond shells gasification with water near critical point, with special attention to liquid phase yield and composition.

2. Materials and methods

Gasification tests were performed in a semi-continuous system equipped with an autoclave-reactor (free volume of 275 ml) mod. Limbo li (Büchi, Switzerland). High pressure water was fed using an AGP-1 Gradient Pump (Dionex, USA) whilst the solid phase was initially placed in the reactor. During the test, the internal pressure was maintained in the range 300–330 bar using an on-off valve (Mod.462007/4000, Büchi).

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