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Glucose gasification in super-critical water conditions for both syngas production and green chemicals with a continuous process

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ABSTRACT

The paper reports on experiments of glucose gasification with water in supercritical conditions (SCW). The adoption of these process conditions revealed advantages in terms of biomass conversion efficiency as the resulting liquid phase includes some important compounds (Acetic Acid, 5-HFM, furfurals). In addition the high operative pressures allow either to consider the possibility to use this technology inside the steam cycle in order to produce power and liquid/gaseous biofuels such as synthetic natural gas and/or methanol/DME(di methyl ether). In fact, from the experimental tests, it was possible to evaluate that using glucose, that is the main intermedia of SCW gasification from wet biomass, is possible to estimate a syngas production of about 100 lt – 200 lt for each kg of glucose fed, while the global gasification efficiency was of about 10–18%. Syngas product to SCWG has been analysed and the main results shows that, in the range investigated, CO content was 40–50%vol., H_2 10–15%, CH_4 10–20%, C_2+2–8% and at the end CO_2 with a volume content of about 20–30% and then with lower calorific value of about 20 MJ/Nm^3. Analysis on the liquid phase was carried out and the main results has been an high production of both 5-hydromethil furfural and 2-Furaldehyde that have a great potential as "carbon-neutral" feedstock for fuels and green chemicals.

1. Introduction

Gasification in supercritical water condition could be a new technology for the treatment and valorization of wet biomass and organic wet substances such as digestate, municipal solid organic wastes, etc. respect to the traditional treatments in order to produce syntetic natural gas or liquid biofuels, as soon as chemicals as showed below [1–4]:

In this operative condition water exhibited different advantages with respect to traditional gasification processes, in fact water is proper reactant of the process, able to solubilise organic compounds and reducing the tars formation and do not need preliminary drying saving energy and preserving some of the energy of raw materials. The water state reduces the mass transfer resistance through interphase, ending with and increased apparent reaction rates and more effective products separation [5–10]. Furthermore the water physical properties of the water are very different respect to the normal condition indeed water is highly compressible and this variation is mainly responsible for the changes in terms of solvating capability, polarity, dielectric constant and viscosity 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 [11–26]. 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 [27].

2. Materials and methods

2.1. SCW gasification (SCWG) bench scale plant and analytical methods

The reactor used for glucose gasification in supercritical conditions was built with tubolar configuration realized by Parr Instrument Co®. It has a usable volume of about 450 mL with an internal diameter of 25 mm, external diameter of 48 mm and with total

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length of 1120 mm while the heated length is of 900 mm. The material used for the reactor is stainless steel T316 type in order to avoid the main problem of the intergranular corrosion at the temperature greater than 500 °C and pressure of about 30–35 MPa. In Fig. 1 is showed the reactor used for the experimental tests:

The reactor has two flanges at the top and bottom of the tube in order to facilitate both the cleaning and the routine maintenance of the same. At the top is located the rupture disk, analogic manometer and pressure transducer. At the same time there is a multiple thermocouple for the monitoring via Distributed Control System. At the bottom of the reactor is situated the discharge zone where it is coupled with the condenser for the separation the syngas from the water. Thermical profile inside reactor is guaranteed by electrical heater that is isolated with ceramic fiber realized by Vecstar Limited® – Furnace Division, and composed by three different zones and for each one with its power generator. Using the temperature control device it is possible to set the temperature profile and at the same time monitoring it. The maximum of electrical power for the resistances is 2.4 kW. Feed is pressurized using a pump, syringe type, producted by Teledyne Isco® Pump 500D, that have a cylinder of volume 508 ml. It is possible to obtain pressure range of 0.69–258 bar at temperature of 5–40 °C and flows greater than 0.01 till 204 mL/min.

SCWG plant is composed also by a condenser that is indirect cooled using water at the end to obtain dry pressurized syngas. DCS provided for the control and monitoring of the parameters process, such as temperature with temperature controller (TC), temperature indicator (TI), TIC for both the control and monitoring of the temperature, PG for pressure gauge and a pressure transmitter in order to regulate the pressure inlet to the SCWG plant. Product syngas such as the liquid phase in outlet are depressurized by apposite valve and analyzed on/off line. In particular, dry gas was analysed through an gaschromatography on-line HP 6890 (Hewlett Packard, USA) equipped with a conductivity detector (TDC). The liquid phase separated from the condenser, as well as the residual fraction in the reactor, were collected and analysed, in order to evaluate the residual glucose content and typical compounds from sugar thermal degradation (such as aldehydes and carboxylic acids). For aldehydes, determination an optimised analytical method based on high performance liquid chromatography (HPLC) model 1100 equipped with photodiode array detector (DAD) and Phenomenex Idro RP 80 column was used (Agilent, USA), whilst sugar and carboxylic acids amount was measured via another optimised analytical technique by using a HPCL (Dionex, USA) equipped with NUCLEOGEL ION 300 OA. The SCWG plant is also equipped of a gas line inlet for example that could be used for the inertization of the system or for the procedures of catalysts activation.

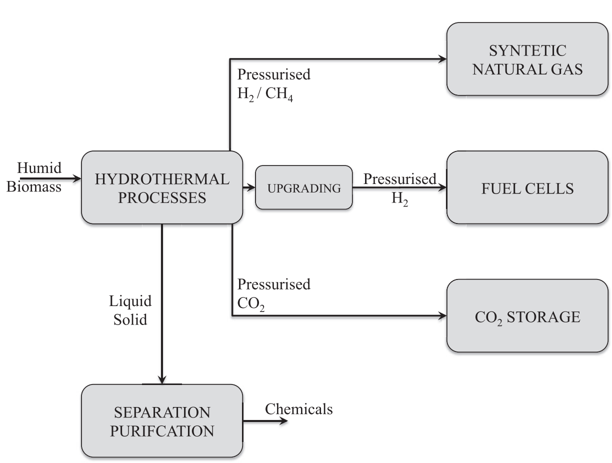

Fig. 1. Product distribution for SCWG.

2.2. Experimental procedure

Experimental tests in supercritical condition were carried out using an aqueous solution of glucose at different concentrations. The SCWG plant was preliminarily fulfilled, pressurized to 250 bar and heated at 550 °C, afterward the solution was feed to the system at the fixed flow rate. Preliminary nitrogen sweeping flux was maintained for 10 min in order to eliminate any air in the loop. After this step, demi water was fed for a period of about the residence time τ and after this, glucose with the same flow was fed to the bench scale plant. Glucose used for the experimental tests was in the anhydrous form with purity greater than 99% (Carlo Erba Reagents®, IT). Gas composition was quantified using a flux meter (GILMONT Instruments flow meter, Range 0–15 STD l/min) and in order to obtain the total value of syngas product; it was collected in apposite envelopes of fixed volume. The syngas was analyzed every 3 min, while the liquid condensate product was analyzed for several time ranges for each test. In the period equal to τ only water condensed was obtained, while after this also syngas was produced. Two are the main parameters that were monitored: fixed glucose flow at 5 ml/min, its concentration was varied from 50 to 200 g/l while at fixed glucose concentration of 150 g/L, its flow rate from 1 to 10 mL/min was changed as it's possible to see in the table below:

Table 1 shows the experimental tests carried out at 550 °C and 250 bar. In the first set tests (A–D) was evaluate the glucose concentration influence while in the second one (E–I) the influence of the flow rate has been evaluate in term of gas quality and liquid composition.

All the experimental tests were carried out fixing the temperature at 550 °C with 250 bar of pressure as previously mentioned.

In the first set plan of experimental tests (A–D tests), fixed the flow rate of glucose to 5 ml/min, the effect of glucose concentration from 50 g/l to 200 g/l was investigated in term of quality and quantity of gas production and also for the liquid phase, while in the second set plan experimental tests fixed the glucose concentration to 150 g/l, the effect of glucose flow from 1 ml/min to 10 ml/min (E–I tests) was investigated in order to understand their effect on the main performance parameters for this process.

The main parameters that will be shown for the tests are:

- *Production ratio* (*PR*): Represents the ratio between dry syngas volume, dry basis, and the glucose mass;
- *Global gasification efficiency* (*GGE*): Ratio between syngas, massic basis, and the glucose fed;
- *Elementary gasification efficiency* (*EGE*): Ratio between mole of C, H, O in the syngas product, dry basis, and in the glucose fed [7];

Table 1
Experimental setup.

Test	Conc. Solution [g/L]	Flow [mL/min]	T [°C]	P [bar]
A	50	5	550	250
B	100	5	550	250
C	150	5	550	250
D	200	5	550	250
E	150	1	550	250
F	150	3	550	250
G	150	5	550	250
H	150	8	550	250
I	150	10	550	250