Supercritical Water Gasification of Waste Oils as a Source of Syngas

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A huge amount of waste oil is produced worldwide. Also substantial amount of virgin oils is available that are interesting candidates for upgrading into syngas. Supercritical water gasification (SCWG) can be considered as an aqueous phase reforming process to produce syngas from oils.

In this work, a variety of waste and virgin oils were gasified in a continuous down-flow autoclave reactor at supercritical conditions. Experiments were carried out at 430 °C and 660 °C, 25 MPa, with a residence time in the range 103-170 s, in order to investigate gasification and carbon efficiency, hydrogen yield and composition of the produced gas.

All the analysed feedstocks were suspended in water at various concentrations before gasification. Pyrolysis bio-oil showed a gasification efficiency of 74 % and 86 % for mixtures with 3 and 10 oil/water wt ratio, respectively. Waste motor oil, suspended in water at a concentration of 1 % wt thanks to the use of surfactants, was successfully gasified with a gasification efficiency of 73 %. Virgin motor oil gasification efficiency higher than 60% had been obtained for both analysed concentrations (5 % wt and 10 % wt of oil). Gasification of rapeseed oil at 5 % wt showed a gasification efficiency close to 88 %. On the contrary, the gasification of sunflower oil at 430 °C showed that this temperature is not high enough to obtain acceptable gasification efficiencies that varied from 20 % to 15 % for concentrations of oil from 2 % wt to 8 % wt, respectively. The analysis of the gas composition, in all the studied cases, showed that the obtained gas stream was rich in H_2, CH_4 and CO_2, with variable quantities of light hydrocarbons (C_2H_4, C_2H_6 and C_3H_8).

1. Introduction

The global energy demand lead researchers to the exploration of alternative sources of energy. Thermochemical and biochemical technologies can lead to a conversion of waste into green energy sources. Gasification is one of the most effective thermochemical technologies that can transform organic substrates into a hydrogen-rich syngas. This gas represents an interesting energy carrier due to its high energy content and low-presence pollutants. It can also be used as a source of hydrogen, that is a key reagent of a large number of industrial processes. Conventional gasification efficiency significantly decreases with increasing feedstocks' moisture content. About 2242 kJ per kg of water are necessary to remove the feedstocks' moisture before the gasification process begin (Basu, 2013). To overcome this drawback, Supercritical Water Gasification (SCWG) has been developed as a promising alternative for wet biomass. SCWG process can have several applications from the treatment of different type of biomass (Freitas and Guirardello, 2014) to that of landfill leachate (Gong et al., 2017). SCWG can also be considered as an aqueous phase reforming process for upgrading wet and not-wet organic liquids. Recently, SCWG has been also applied to not-wet organic matters, such as light gas oil and heavy gas oil obtained through distillation of oil sands (Rana et al., 2020) and for the valorisation of waste cooking oils (Nanda et al., 2019). Also when applied to not-wet matters, SCW gasification has many advantages with respect to the conventional one. Organic matter is solubilized in SCW, NO_x and SO_x are not produced, CO_2 can be easily separated from fuel gas without further costs of purification and the products can also be stored at high pressures without additional compression costs. There are no comprehensive studies that explore the candidacy of oils and waste oils as a potential feedstock for hydrogen-rich syngas production. This work is aimed at exploring the potentiality of SCWG as an alternative to

the traditional waste disposal and treatment through the generation of value-added products. The effect of temperature, pressure and residence time on the process were investigated using pyrolysis bio-oil, motor oil (virgin and waste), rapeseed oil and sunflower oil.

2. Materials and methods

2.1 Experimental apparatus and procedure

Figure 1 shows the P&ID of the SCWG experimental apparatus.
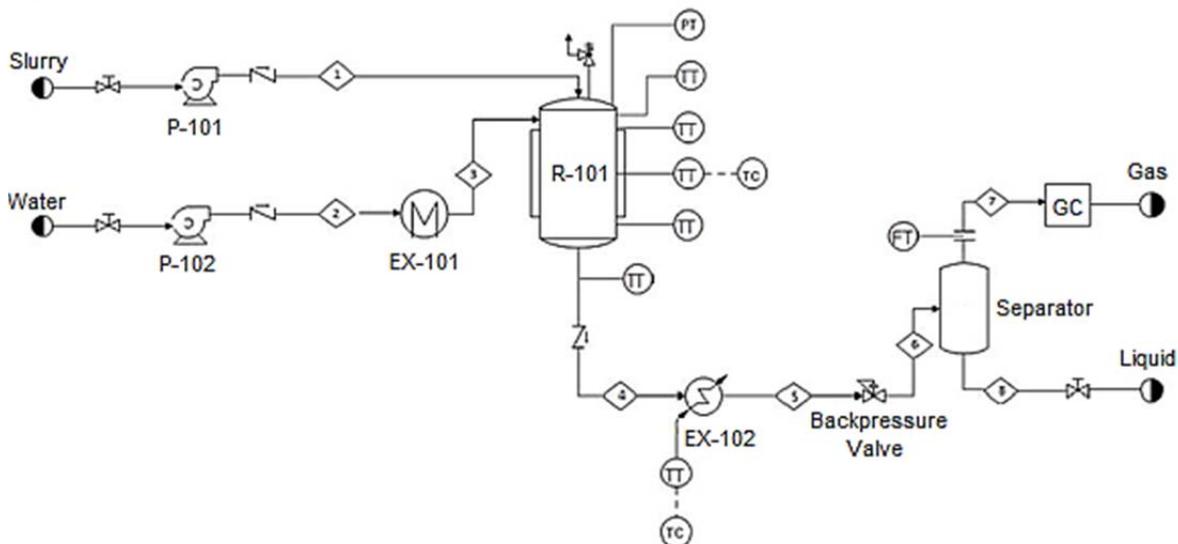
Figure 1: P&ID of the SCWG experimental apparatus.

The R-101 reactor was fed with two different streams: the slurry (oil/water mixture) and deionized water. They were sent to the reactor through two pumps (P-101/102). The aqueous stream (indicated as stream 2 in the P&ID shown in Figure 1) was pre-heated up to the reactor wall temperature through a coil (EX-101 in the P&ID). Streams were sent to the continuous down-flow autoclave reactor with an internal diameter of 2.5 cm, aspect ratio (length to diameter ratio) of 17 and a volume of 200 cm³. Heating was provided by electric heating bands. The outlet stream was cooled up to room temperature thanks to a chilling recirculation system (EX-102). A backpressure valve reduced the pressure up to 1 bar in order to separate and collect products in a glass separator. The liquid phase was collected on the bottom of the separator and the gas phase was continuously sent from the upper part of the separator to a digital mass flowmeter (FT) and then to the on-line Gas Chromatograph (GC).

Modifications to the experimental apparatus

Sunflower oil SCWG was operated in a modified version of the experimental apparatus described in section 2.1. These modifications allowed a faster and more effective heating phase, eliminating most of the transient necessary to reach the stationary regime that characterized the previous configuration of the apparatus. In particular, the autoclave reactor has been replaced with a coil reactor consisting of a 316L stainless steel thick-walled tube, with an outer diameter of 6.35 mm and an estimated volume of 66 ml. This reactor was placed inside an electric oven also with another coil necessary for the deionized water pre-heating. Then these two streams were mixed up through a T-type connection.

2.2 Analysis of SCWG products

The carbon content of the collected liquid phase for each experimental tests was analyzed using a total organic carbon analyzer (TOC) (Shimadzu Corporation, Japan). Three different efficiency values were calculated in order to evaluate process' performances (Caputo et al., 2016): gasification efficiency (GE%), carbon efficiency (CE%) and hydrogen yield ($H_{2\ yield}$ %). They can be calculated as:

$$GE[\%] = \frac{Gas\ mass\ flow\ rate\ out}{Dry\ Feedstock\ mass\ flow\ rate\ in} \cdot 100 \tag{1}$$

$$CE[\%] = \frac{Moles\ of\ carbon\ in\ the\ gas\ product}{Moles\ of\ carbon\ in\ the\ feed} \cdot 100 \qquad (2)$$

$$H_{2\ yield}[\%] = \frac{Moles\ of\ hydrogen\ in\ the\ gas\ product}{Moles\ of\ hydrogen\ in\ the\ feed} \cdot 100 \qquad (3)$$

The composition of the gas was determined using a gas chromatograph (GC) to quantify all the gaseous products including H_2, CO_2, CO, CH_4 and C_2-C_3 compounds. The GC was an Agilent 7890 B, with thermal conductivity detector (TCD) and a flame ionization detector (FID). The temperature of the column was maintained at 250 °C and the temperatures of the TCD and FID were kept at 230 °C. Argon was used as carrier gas. The concentration of each component was calculated against standards. Gas samples were analyzed at least in triplicates for the accuracy, repeatability and reproducibility of the collected data.

3. Results and discussion

3.1 Pyrolysis bio-oil

In this case, the gasified pyrolysis bio-oil was artificially reproduced in laboratory referring to a typical composition found in literature (Lehto et al., 2013) and whose elemental analysis is shown in Table 1.

Table 1: Pyrolysis bio-oil elemental analysis.

	C	H	O
% wt	13.28	10.24	76.48

Bio-oil density was also determined and equal to 1.07 g/cm^3. Experimental tests were conducted at 660 °C, 25 MPa and various oil/water ratios (3 % wt and 10 % wt, respectively) with a residence time (τ) of 128 seconds, in order to study the effect of the biomass concentration on the overall process. Process' yields are shown in Table 2.

Table 2: Process' yields for pyrolysis bio-oil gasification at 660°C, 25 MPa and τ=128 s.

	3 % wt	10 % wt
GE %	74.1	86.1
CE %	80.6	89.1
H_2 yield %	76.5	56.3

The gasification efficiency (GE%) increases from 74.1 % to 86.1 % when the biomass concentration in the slurry is increased from 3 to 10 % wt. The hydrogen yield, instead, decreases with increasing biomass concentration from 76.5 % to 56.3 %. On the other hand, the carbon yield (CE%) shows a less significant variation compared to the others. These results are in agreement with those of Migliori *et. al* (Migliori et al., 2011).
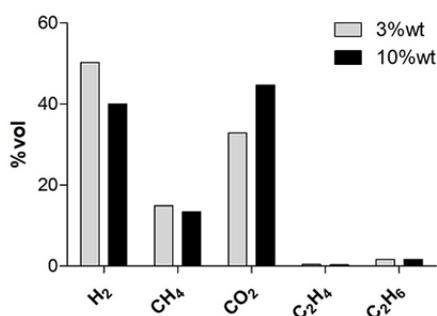
Figure 2: Comparison between the composition of the gas phase produced from pyrolysis bio-oil SCWG at two different concentrations (T = 660 °C, P = 25 MPa and τ=128 s).

The main components of the produced gas phase are H_2, CO_2 and CH_4. As the bio-oil concentration varies, a significant increase of the concentration of carbon dioxide and a decrease of methane and hydrogen can be

observed. This behavior can be explained through the reaction mechanism and, in particular, to the methane gasification and the water-gas shift reactions. There is a nearly negligible concentration of light hydrocarbons such as ethane and ethylene (C_2H_4 and C_2H_6) due to the long residence time in the reactor that allows to complete the degradation reactions of all organic molecules with the consequent formation of lighter compounds.

3.2 Virgin and Waste motor oil

The gasified virgin motor oil was *Eni i-Sint 10W-4.* The gasified waste motor oil, instead, comes from the engine of a car, considered a special waste. Table 3 shows the elemental analysis of the waste motor oil.

Table 3. Waste motor oil elemental analysis.

	C	H	Others
% wt	83.39	12.77	3.84

SCWG was carried out at 660°C and 25 MPa with a residence time of 128 s for both oils. Three concentrations of the slurry were gasified (5 % wt and 10 % wt for virgin motor oil, 1 % wt for waste motor oil). In the case of waste motor oil two surfactants (Span 80 and Tween 80) have been added to the oil/water mixture in order to ensure a better mixing. A 1 % wt mixture was obtained with a percentage of the two surfactants of 0.164 % wt and 0.149 % wt for Span 80 and Tween 80, respectively. Results are summarized in Table 4.

Table 4: Process' yields for virgin and waste motor oil gasification at 660°C, 25 MPa and τ=128 s.

	Virgin		Waste
	5 % wt	10 % wt	1 % wt
GE %	61.49	62.78	72.91
CE %	43.08	47.60	49.58
H_2 yield %	13.00	12.88	19.43

Virgin motor oil shows lower yields of about 60 % that do not vary in an appreciable way with the concentration of the input stream. As regards the waste motor oil, it can be observed a higher gasification yield, due to the lower concentration used, while the presence of surfactants does not significantly affect the SCWG process.
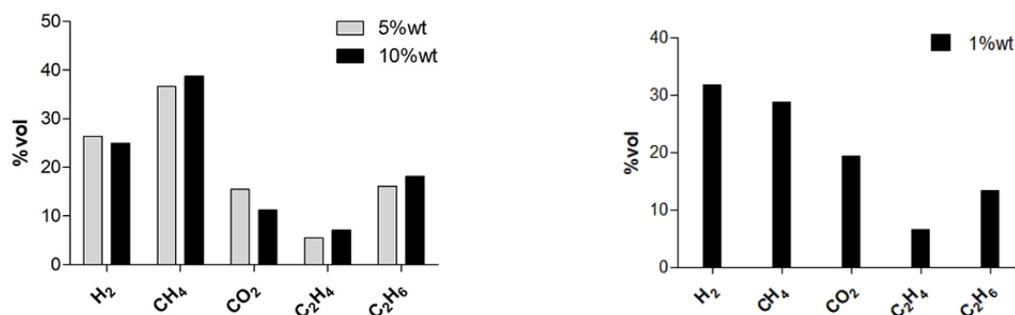
Figure 3: Comparison between the composition of the gas phase produced from virgin (on the left) and waste (on the right) motor oil SCWG at different concentrations (T = 660 °C, P = 25 MPa and τ=128 s).

The main components of the gas phase, as expected, are H_2, CH_4, CO_2. In this case a non-negligible concentration of ethane and ethylene were detected due to the different composition of the motor oil with respect to the pyrolysis bio-oil. The former is made up of species with higher molecular weight that favour the formation of heavier hydrocarbons with a consequent decrease in hydrogen content.

3.3 Rapeseed oil

Table 5 shows the elemental analysis of the gasified rapeseed oil.

Table 5: Rapeseed oil elemental analysis.

	C	H	O
% wt	76.74	11.84	11.42

Results are shown in Table 6 and Figure 4. A 5 % wt slurry was gasified at 660 °C and 25 MPa with a residence time of 128 s.

Table 6: Process' yields for rapeseed oil gasification at 660°C, 25 MPa and $\tau=128$ s.

	5 % wt
GE %	87.83
CE %	50.67
H_2 yield %	17.26
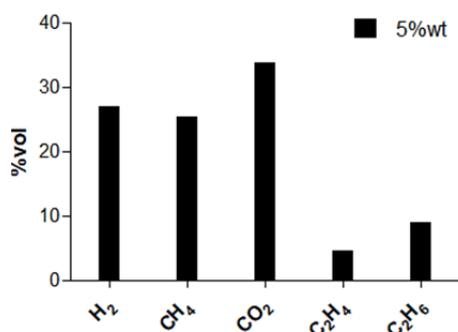
Figure 4: Composition of the gas phase produced from SCWG of rapeseed oil (T = 660 °C, P = 25 MPa and $\tau=128$ s).

Process' yields are significantly high. The gasification efficiency is about 88 % and the carbon efficiency is slightly higher than 50 %. The main components of the produced gas phase are H_2, CH_4, CO_2, C_2H_4 and C_2H_6.

3.4 Sunflower oil

Experimental tests were carried out at lower temperature and pressure and with variable residence times in order to study the effects of these parameters on the SCWG process. In particular, the process was carried out at 430 °C and 23 MPa. The experimental apparatus was modified as explained in section 2.1. A simplified composition was assumed for the sunflower oil, whose main components are: palmitic acid (6.6 % wt), stearic acid (4.9 % wt), oleic acid (27 % wt), linoleic acid (61.5 % wt). The slurry sent to the reactor was 2 % wt, 4 % wt and 8 % wt, respectively. Results are summarized in Table 7 and Figure 5.

Table 7: Process' yields for sunflower oil gasification at 430°C, 23 MPa and different residence times.

	2 % wt	4 % wt	8 % wt
τ [s]	110	103	170
GE %	20.1	16.2	15.3
CE %	20.2	15.5	15.1
H_2 yield %	31.2	23.5	23.7

The gasification yields significantly decrease with respect to the previous analysed experimental tests which operate at higher temperature and pressure. Process' yields decrease passing from a slurry concentration of 2 % wt to 4 % wt, as expected. This decrease is more significant due to a decrease of the residence time. Longer residence times lead to a greater gasification time inside the reactor and, consequently, to higher process yields. This behaviour is confirmed if one notices that when the slurry concentration varies from 4 % wt to 8 % wt, the decrease of the process' yields is less significant because it is balanced by the increase of

the residence time. These results demonstrate how the operating temperature of 430 °C is not high enough to have acceptable gasification yields and confirms that residence time and, above all, temperature strongly influence SCWG process.
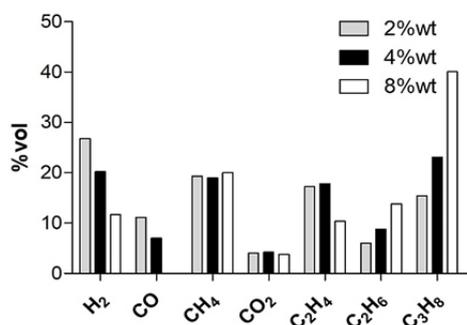
Figure 5: Comparison between the composition of the gas phase produced from sunflower oil SCWG at three different concentrations (T = 430 °C, P = 23 MPa and different residence times).

The main components of the produced gas phase are H_2, CH_4, CO_2, C_2H_4, C_2H_6 and C_3H_8. The 8 % wt oil/water mixture showed a higher concentration of propane. The amount of methane is almost constant for each analysed slurry concentration.

4. Conclusions

In this work the SCWG process of oils was studied. The gasification of pyrolysis bio-oil showed gasification yields of 74 % and 86 % for mixtures with 3 % wt and 10 % wt of oil, respectively. Waste motor oil was successfully gasified obtaining a gasification yield close to 73 %. Promising results also in the case of virgin motor oil with measured gasification yields higher than 60 % for each concentration studied (5 % wt and 10 % wt). A gasification yield close to 88 % was calculated in the case of supercritical gasification of rapeseed oil at 5 % wt. Sunflower oil SCWG showed that the temperature of 430 °C is not high enough to obtain acceptable gasification yields. Gasification efficiencies varied from 20 % to 15 % for concentrations of oil from 2 % wt to 8 % wt. H_2, CH_4 and CO_2 are the main components of the produced gas phase with variable quantities of light hydrocarbons such as C_2H_4, C_2H_6 and C_3H_8, depending on the processed feedstock. This preliminary study shows the potentiality of oils and waste oils as feedstock for hydrogen-rich syngas production through SCWG. This process could be a valid alternative to the traditional waste disposal and treatments.

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