BLACK LIQUOR SUPERCRITICAL WATER GASIFICATION IN BATCH REACTOR FOR BIOFUEL PRODUCTION

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ABSTRACT: The H2020 Pulp&Fuel project intends to make a significant contribution to biofuel development by taking advantage of the synergy between dry gasification and supercritical water gasification. The project has chosen to demonstrate its applicability to pulp industry that have both dry and wet wastes available. The process produces sludge as wet waste and an excess of black liquor in chemical pulp mills. Supercritical water gasification (SCWG) is considered the most suitable route as no drying step is required to transform wet waste as black liquor in syngas (mainly composed of H_2, CH_4 and CO_2). The objective is to maximize organic matter conversion of black liquor into a gas and to maximize H_2 yield production. Black liquor gasification is studied in two kinds of reactors in the CEA platform: batch and continuous reactor. This paper focuses on batch experiments. Some batch experiments (55 runs) have been performed to characterize gasification efficiency, gas composition and carbon conversion in liquid, solid, and gaseous phase.
Keywords: Supercritical water gasification, hydrothermal gasification, biofuel

1 INTRODUCTION

The H2020 Pulp&Fuel [1] project intends to make a significant contribution to biofuel development by taking advantage of the synergy between dry gasification and supercritical water gasification. The project has chosen to demonstrate its applicability to pulp industry that have both dry and wet wastes available. These wastes are today either recycled in low value fuel for combustion or are disposed at great cost. The mechanical and chemical processes provides large amounts of bark and wood co-products as dry waste. It also produces sludge as wet waste and an excess of black liquor in chemical pulp mills.
Supercritical water gasification (SCWG) is considered the most suitable route as no drying step is required to transform wet waste as black liquor in syngas (mainly composed of H_2, CH_4 and CO_2). The objective is to maximize organic matter conversion of black liquor into a gas and to maximize H_2 yield production. CH_4 is a side product as well as CO_2. Associating this syngas with the one from bark dry gasification, allows fulfilling the H/C ratio adapted for Fischer-Tropsch fuel synthesis (Figure 1). The final objective of the project is to help the design of black liquor hydrothermal gasification unit at 100 kg/h. The challenges studied to drive this design are carbon conversion, salt management and inorganic recycling, energy efficiency, co-products valorisation (Grenoble INP studies the degradation of black liquor organic components during its hydrothermal treatment. to find optimal conditions to recover small phenolic compounds and extract them, for valorisation in high added value applications), and mechanical stress and corrosion management.

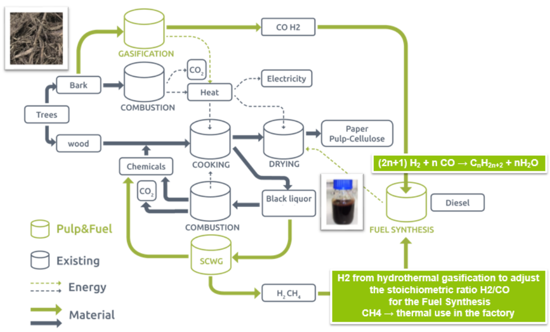

Figure 1: Pulp&Fuel biorefinery concept

Black liquor gasification is studied in two kinds of reactors in the CEA platform: batch and continuous reactor. Batch experiments allow to obtain quick results on small quantities of resources, avoiding any injection and product separation issues, to explore several operating conditions, to extrapolate the results to a continuous operation mode, and to feed the energy integration model.
Continuous experiments allow to process larger quantities of feedstock, to operate the "injection / hydrothermal conversion / product separation / analysis" unit at the same time, and to validate operational conditions and performance.

This paper focuses on batch experiments, and more particularly on carbon conversion.

2 MATERIALS AND METHODS

2.1 Reactor

Figure 2 and Figure 3 show a schematic view and a picture of the reactor. The reactor has a theoretical volumetric capacity of about 500 ml. The reactor height is 130 mm for a diameter of 70 mm.

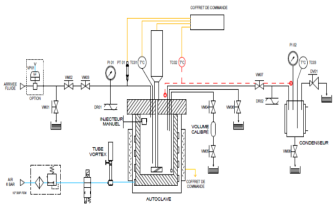

Figure 2: Schematic view of the batch reactor

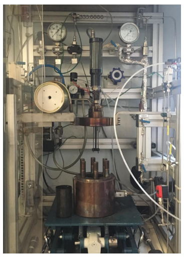

Figure 3: Picture of the batch reactor

The maximum admissible pressure in the reactor is 300 bar. In supercritical conditions, the pressure is not limited by the vapour pressure, but is controlled by the temperature and total amount of water and gasses in the fixed volume. For each experiment, 60 g of black liquor is introduced in the reactor. The reactor is then closed. A first step of the procedure consists in verifying that the reactor is well sealed and that there is no leak. For that, 100 bar of nitrogen is injected into the reactor, a few minutes are necessary to let the pressure and the gas to stabilise. This operation is repeated a second time. Once it is certain that the reactor is correctly sealed, 7 bar of nitrogen are injected in the reactor (no air, and so no oxygen are still in the reactor). Afterwards, the reactor was heated to the desired temperature (for example, 90 minutes are necessary to achieve the temperature of 600 °C). Once the temperature reached, the temperature is maintained for the desire holding time (for example 30 or 60 minutes). Finally, the reactor is cooled down to 20 °C (see example of temperature and pressure profiles in Figure 4).

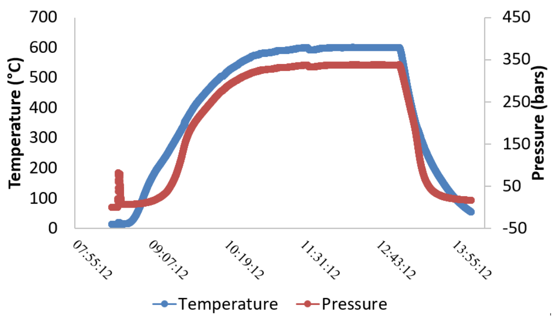

Figure 4: Temperature and pressure profiles during a batch reactor test (example for a test at 600 °C and a holding time of 60 minutes)

The gas composition is measured with a μGC for few minutes. Once the gas is evacuated, the reactor is opened. The crucible with the reaction products and the agitator are weighed. The content in the crucible is filtered with a Buchner filter to separate the aqueous to the solid phase.
All the apparatus used are let dried overnight and weighted the day after in order to determine the amount of solid. The amount of carbon in the solid is determined by elemental analysis CHNS and the carbon in the aqueous phase with the Total Organic Carbon (TOC) analyser.

2.2 Feedstock

Three black liquors are studied in this work: softwood and hardwood black liquors produced in the Fibre Excellence factory of Saint Gaudens with the Kraft process, and hardwood sulphur free black liquor using non-sulphur reagents (SODA process) produced in a Fibre Excellence innovative pilot. The use of sodium sulfide is mandatory in Kraft process to obtain a pulp suitable to make paper. However, it is possible to produce another kind of pulp, the dissolving pulp, by the addition of a hydrolysis prior to the Kraft cooking to remove the hemicelluloses. In this case, cooking is easier and then can be performed only with soda.

The chemical composition of black liquor is complex and thus it is difficult to obtain an accurate analysis. For example, black liquor contains a non-negligible content of volatile compounds such as alcohols, carboxylic acids, and when the sample are heated at 105 °C these molecules are evaporated with the water. An important work of characterisation has been performed to determinate the more accurate analysis for carbon content, dry content, inorganic content, elemental analysis...

Kraft black liquor has an amount of carbon of about 60 g/L ([C] = 5 mol/L), is rich in Sodium and in Sulfur ([Na] = 1.7 mol/L, [S] = 0.3 mol/L), and its pH is very high (pH = 13.5).

Table 1: Kraft Black liquor caracteristics

	Dry Matter	Ash Content	HHV [MJ/kg]
Basis	As received	Dry basis	Dry Basis
Kraft Black liquor	18.6%	72%	9.7%
Sulfur-free Black Liquor	20.7%	61%	8.8%

3.3 Operating conditions

Some batch experiments (55 runs) have been performed to characterize gasification efficiency, gas composition and carbon conversion in liquid, solid, and gaseous phase. Mass and Carbone balance have been realised for each run. Run reproducibility have been investigated. Batch experiments have been performed at different temperatures [225, 250, 280, 300, 350, 400, 450, 500, 550, 600°C], for four reaction times [0, 5, 30 and 60 minutes]. Runs have been also performed with diluted black liquor [dilution factor 2 and 5], with ethanol addition, and with black liquor addition option.
A lot of repeatability tests have also been realized.

3 RESULTS

The overall mass balance of the batch experiments are satisfactory but the carbon balance of the batch experiments are less good (see Figure 5).

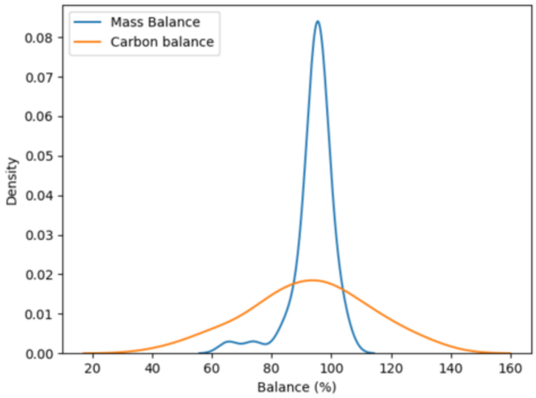

Figure 5: Continuous probability density of the Mass and Carbon balances

The gas yield increases slowly with the temperature before supercritical water temperature point, and strongly increases after (see Figure 6).

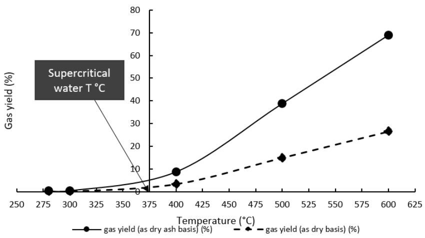

Figure 6: Gas yield for Sulphur free black liquor at 30 min for different temperatures

The best results in term of carbon conversion of the feedstock in gas phase have been obtained for 600 °C and a holding time of 60 min. On dry basis, the carbon conversion of the feedstock in gas is 34 % for the Sulfur-free hardwood black liquor and 32.5 for the hardwood Kraft Black Liquor. On dry ash free basis, the conversion is 78.5 % and 84.3 % for Sulfur-free and Kraft black liquor respectively.

In the Figure 7 is plotted the carbon repartition in the different phases for these two best runs. A lot of carbon remains in the solid phase (char), we could think that higher temperature would enable to convert more feedstock into gas. Unfortunately, it is not possible to work at higher temperature than 600 °C in the batch reactor at CEA.

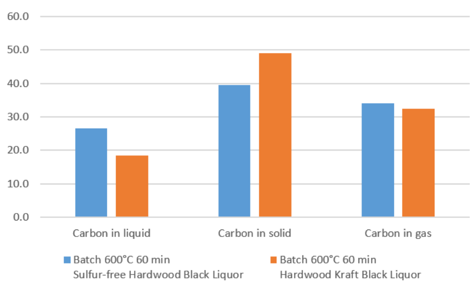

Figure 7: Carbon conversion (%w on dry basis) in the liquid, solid and gas phase

The best gas production composition for the Sulfur-free and Kraft Hardwood black liquor are showed in the Figure 8.

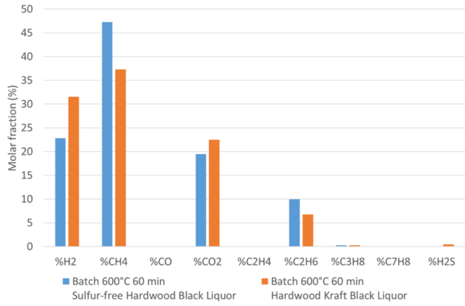

Figure 8: Molar fraction composition for Sulfur-free black liquor and Hardwood Kraft liquor (%)

At 600°C, the gas is mainly composed of H2, CH4 and CO2. The best result for H2 production is obtained with the hardwood Kraft black liquor.

On the Figure 9 is presented the composition in terms of gas production in moles per kg of dry feedstock.

The H2 gas production for the two black liquor are almost the same, but there is a significant difference for the CH4 production.

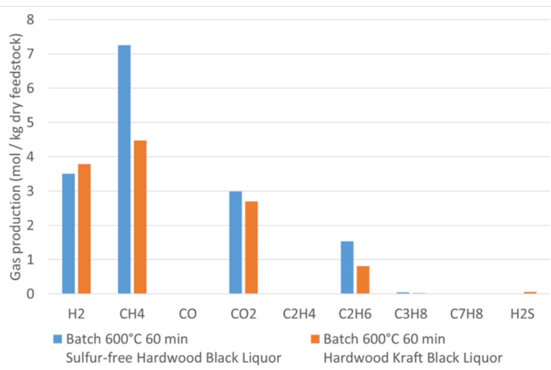

Figure 9: Gas production (mol / kg of dry feedstock)

The CEA used machine-learning algorithm on this 55 data batch set in order to better understanding the results and to identify the most sensitive parameters in black liquor conversion (library Scikit-Learn in Python). Example of results is showed in the Figure 10. It clearly appears that the gas yield is extremely sensitive to the temperature. It is surprising to see that the holding time does not appear to affect the gas yield. However, there is no surprise that the Sulfur concentration affect the H_2S production. In addition, it appears that adding ethanol is a good way to increase gas production.

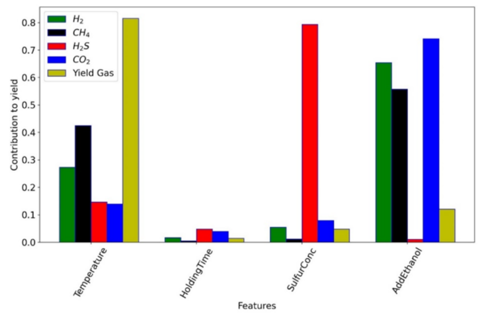

Figure 10: Identification of the sensitive parameter

4 CONCLUSIONS

The supercritical water gasification tests at CEA SCWG in batch reactor showed that to increase the carbon conversion efficiency, black liquor has to be converted at high temperature than 600 °C (it would favour H_2 production to the detriment of CH_4 production). A pre-treatment of the black liquor could also help the conversion. Experimental tests are in progress to investigate solutions to increase carbon conversion. Moreover the problems linked to salt precipitation that appeared in the continuous runs is still investigated in the CEA from modelling and experimental approaches.

5 REFERENCES

[1] https://pulpandfuel.eu/

6 ACKNOWLEDGEMENTS

- This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grand agreement N° 818011.
- We thank Fibre Excellence partner for providing the feedstock for this study.
- We thank GRENOBLE INP for their participation in the experimental data.

7 LOGO SPACE