

DEVELOPMENT OF A PULP AND PAPER BASED BIOREFINERY: BLACK LIQUOR SUPERCRITICAL WATER GASIFICATION

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ABSTRACT

Supercritical water gasification (SCWG) is one of the most promising technologies to convert wet biomasses into a combustible gas rich in methane and hydrogen. Above the critical point, water behaves as both reactant and solvent: organic compounds are subject to hydrolysis and are then gasified to a burnable gas.

In the alkaline pulping processes, cellulose is separated from the other compounds of wood which are heavily depolymerized. The black liquor contains most of the lignin and a significant fraction of the hemicelluloses under a degraded form together with the cooking chemicals. Its water content is about 85%. Traditionally, this black liquor is burned after water evaporation in a Tomlinson boiler. An energetic valorization of black liquor avoiding the evaporation could improve the thermal and economic efficiencies of the whole pulping process. The objective of this work is to establish whether supercritical water gasification of black liquor is more efficient than the conventional recovery process with real data obtained from gasification of a black liquor from a NaOH / Anthraquinone cooking process of softwood.

Semi-batch reactor experiments of black liquor supercritical water gasification were performed. Devices allowing injection and sampling were set up. Temperatures between 430 and 470°C, pressure between 24 and 26 MPa, and reaction times between 2 and 65 minutes have been tested. The results showed that the gas produced was a mixture of mainly hydrogen (39%), methane (21%) and carbon dioxide (36%) in 60 minutes reaction time. At 470 °C, cold gas efficiency is 46 % and hydrogen conversion efficiency is 53 %. 34 % of the carbon and 53 % of the hydrogen initially present in black liquor were converted into gases. It appeared that under those conditions the thermodynamic equilibrium was not reached. Energetic process evaluations and thermodynamic calculations indicate that working at higher temperature could be an efficient way to optimize the gasification and energetic efficiencies.

INTRODUCTION

Kraft pulp mills have always been working as biorefineries, producing material (fibres), chemicals (tall oil and turpentine) and energy needed for the process: this process enables to extract cellulosic fibers from wood to produce pulp, while the main part of the lignin and a significant amount of hemicelluloses are dissolved during the cooking, ending up in the Black Liquor (BL). This liquor, with water content between 80 % and 90 %, is then concentrated by evaporation until having water content between 20 % and 30%, and burned in the recovery

boiler of the mill, with a boiler energetic efficiency of 64 % (when BL dry solid is at 80 % when entering in the boiler) [2]. Taking into account the energy needed to evaporate black liquor before the boiler, the energetic yield is lower than 39 % (respectively 30 % and 39 % when BL dry solid is at 11.5 % and 20 % after washing). The cooking chemicals are also recovered making this process at 99% self-sufficient regarding the chemicals (see figure 1).

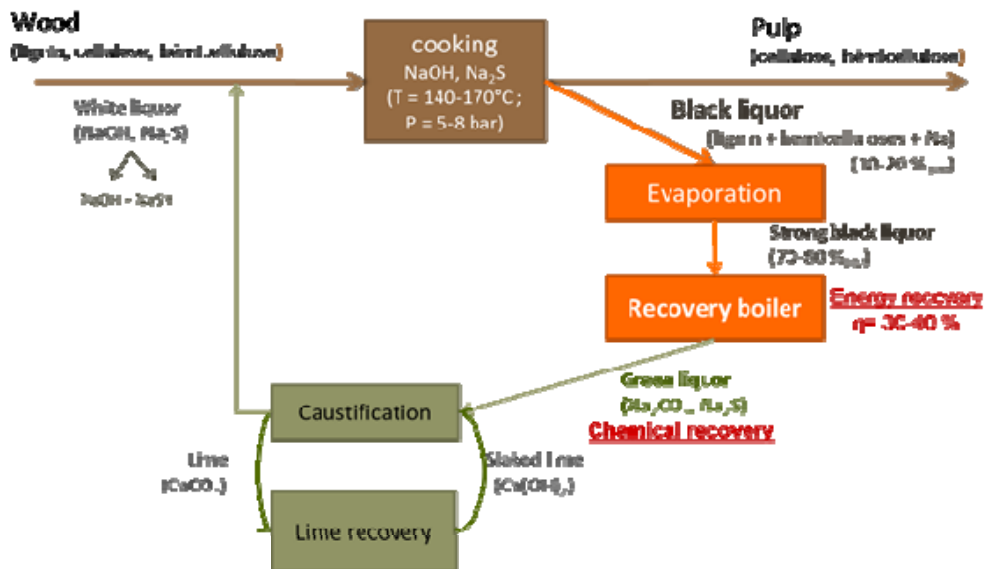


Figure 1 : Kraft process

Supercritical water gasification is particularly relevant for biomasses with high content of water like black liquor. This process is using the specific properties of supercritical water. Above its critical point (221 bar, 374°C), water behaves like a non-polar solvent, with a low dielectric constant, a high diffusivity, and a low dissociation constant. Organic matters are solubilized but salts are precipitated. Biomass components are rapidly decomposed by hydrolysis into smaller species and subsequent fragmentation up to the production of a gas mixture. This gas is mainly composed of CH₄, H₂ and CO₂. In these conditions, CO if formed is rapidly converted into CO₂ and H₂ through the water gas shift reaction, catalyzed by alkali like sodium [1].

Literature indicates that supercritical water gasification of black liquor could be advantageously integrated in a pulping process, in terms of energetic valorization of degraded lignin and of recovery of the cooking reagents [6]. However data and assumptions presented in this earlier work did not come from tests on black liquor directly but on wood. The aim of this study is to examine the supercritical water gasification of black liquor and to compare it to the usual recovery process. The black liquor used in this study is from a soda/AQ cooking of prehydrolyzed softwood chips, a cooking process developed at Pagora.

A previous study on black liquor shown that an increase of temperature enhance the gasification however a variation of pressure doesn't have a significant effect [3].

MATERIALS AND METHODS

Gasification experiments were performed in a batch autoclave (500 mL) made of stainless steel 1.4571 designed to work up to 300 bar and 500°C. The experimental pressure is related

to the selected heat up temperature, the weight of water introduced and the initial N₂ pressure (about 10 bar). An injection device was added, allowing injection of the black liquor directly at the desired temperature at pressure up to 300 bar. It takes less than 1 minute for the black liquor to reach supercritical conditions. A sampling system at the top of the reactor is used to take about 10% of the supercritical phase at the desired time. This sample is thereafter quenched and analyzed.

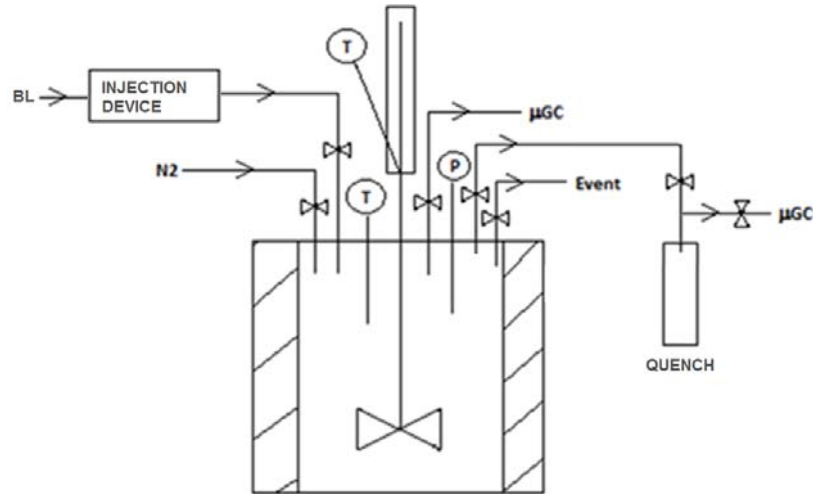


Figure 2: process scheme of the batch reactor

Initial and final organic carbon in the aqueous phase is measured with a Shimadzu TOC-L CSH. Black liquor is supplied by our project partner at PAGORA. Its initial carbon content is 61 g/L and Na concentration is 16 g/l. Black liquor is a high alkaline solution with pH≈13 due to the cooking conditions. This black liquor is sulfur free. After each experiment three different phases are recovered: an aqueous phase, a gas phase and a solid phase. Gas composition is determined with a μGC Varian CP-4900. Total carbon content for solids and liquids is measured with a TOC meter (Shimadzu VCSH). Sodium concentration in the liquid phase is measured by Ion Chromatography (Dionex ICS-3000) and GC-MS (Perkin Elmer Clarus 500/Clarus 600S) was performed on the ethylacetate extract of the liquid phase. Gas yield is characterized by the percentage of C or H initially in black liquor measured in the gas phase. Energy efficiency is calculated with the Low Heating Value (LHV) of the gases.

Cold Gas Efficiency is calculated via this formula: $CGE = \frac{\sum LHV_{gases}}{LHV_{black\ liquor}}$ (1)

As the reactor is heated with a small quantity of water, after injection the black liquor is diluted to 11.5% of solid content and a total Carbone content of 51 g/L.

RESULTS

Gasification of the black liquor was performed at three different temperatures (430, 450 and 470 °C), different reaction times (between 2 and 64 min) and at a resulting pressure between 24 and 27 MPa.

Evolution of total organic carbon (TOC)

Black liquor is not defined by a specific molecule but is composed by a large variety of molecules (mainly phenolic compounds from lignin), that's why it is impossible to study its

evolution directly. The TOC measures the amount of carbon in organic compounds and will be used as an indicator of degradation of black liquor, including the measurement of the black liquor constituents and their intermediates of degradation.

The effect of variation of gasification time on TOC at different temperature is given figure 3:

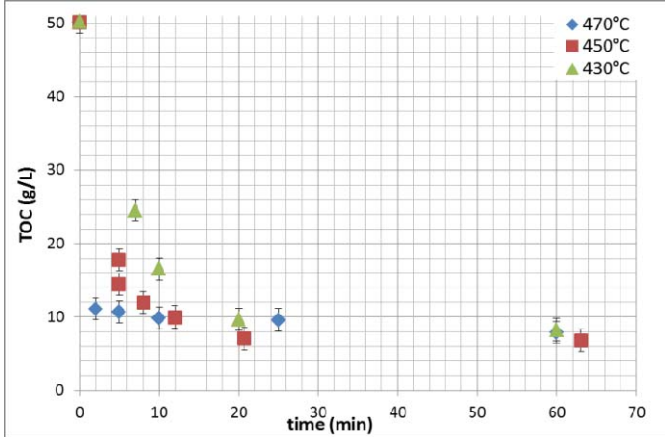


Figure 3: influence of time and temperature on the total organic carbon

The TOC decreases drastically in the first minutes of gasification and reaches a plateau at about 20% of its initial concentration. Moreover, the higher the temperature is, the faster is the degradation.

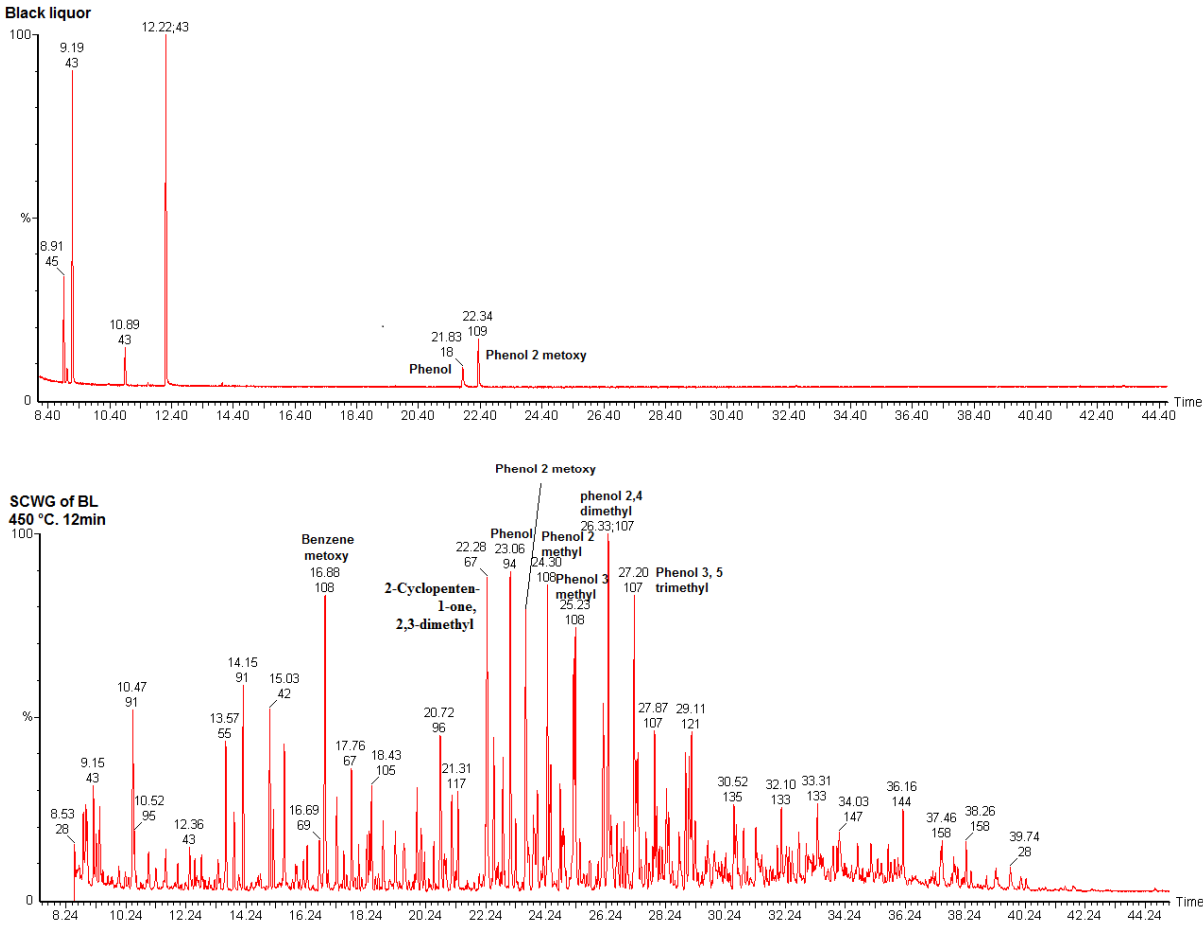


Figure 4 GCMS analysis of the aqueous phase after gasification of black liquor at 450°C

As black liquor is mainly constituted of degraded lignin and as phenolic compounds are reported to be difficult to gasify at a temperature inferior to 600 °C due to resonance-stabilized phenoxy radicals [4]; this can explain the low conversion at these conditions. This hypothesis is confirmed by the results of GCMS analyses of the residual organics extracted from the aqueous phase after gasification (see figure 4) in comparison with the analysis of the organic extracted from black liquor.

Production of gases

The gas phase is mainly composed of carbon dioxide, hydrogen and methane, with a small amount of C₂ (sum of C₂H₄ and C₂H₆) and C₃H₈. No CO was measured; this is explained by the high concentration of sodium in black liquor promoting the water gas shift reaction, which consumes CO and generates H₂ and CO₂.

Individual gas yield is given for CH₄ and H₂ figure 5. The trend for CO₂ is similar so it is not reported below.

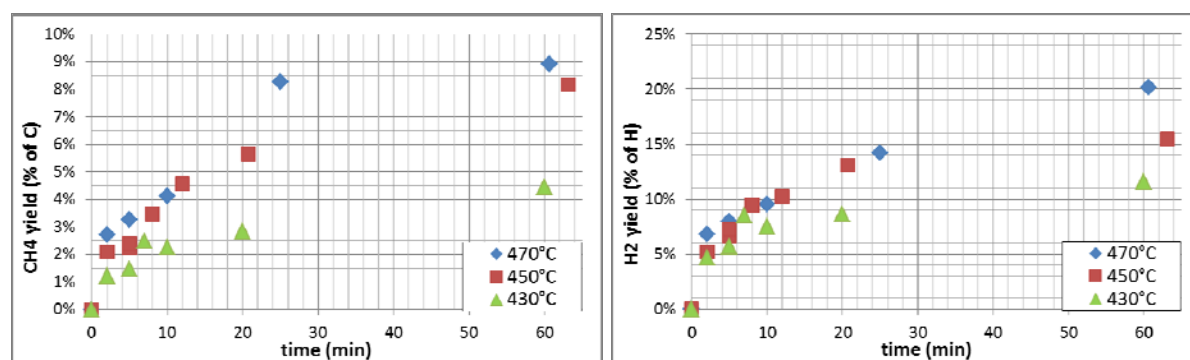


Figure 5: Experimental yields of CH₄ (left) and H₂ (right) in SCWG of black liquor

The results show that gas yield increases with temperature and time. Yield reaches a plateau with a value increasing with temperature (11.6 % for H₂ at 430 °C and 20.2 % at 470 °C).

Moreover, increasing the temperature allows gas yield to be closer to the thermodynamic equilibrium. Figure 6 shows that at 430 °C, yield of CH₄ is at 7.7 % of its equilibrium value whereas it is at 16.1 % at 470 °C.

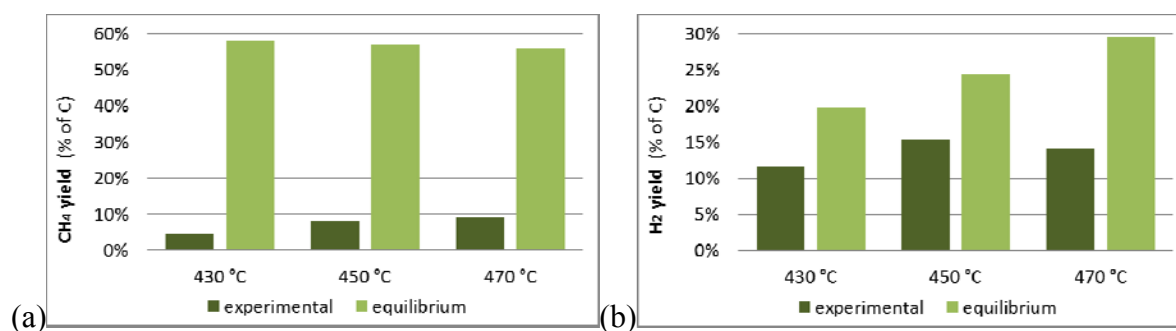


Figure 6: experimental and at thermodynamic equilibrium gas yields for CH₄ (a) and H₂ (b) (60 min).

According to this results and results from literature, we can expect to be close to thermodynamic equilibrium at 700 °C.

Finally H₂ and CO₂ are closer to equilibrium than CH₄: at 470°C and 60 minutes, only 16.1 % of the CH₄ that could be formed at equilibrium was measured whereas 68 % of H₂ was measured. This confirms the effect of water gas shift catalyzing the formation of CO₂ and H₂.

Evolution of the Cold Gas Efficiency (CGE)

The CGE is a way to evaluate the gasification efficiency and represent the percentage of energy (via LHV) in the gases initially present in black liquor. Its evolution in time and temperature is given figure 6:

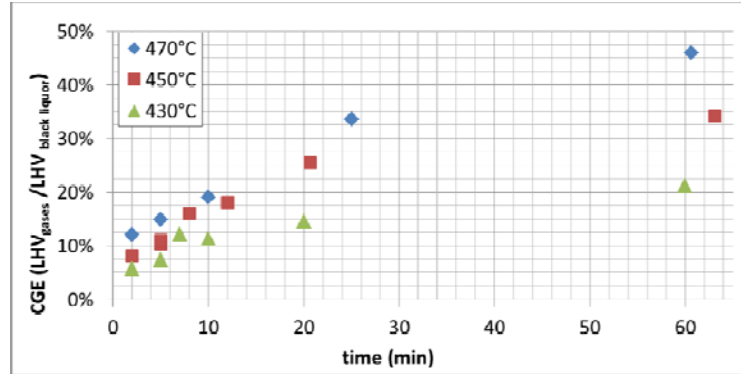


Figure 6: effect of time and temperature on CGE

Evolution of CGE corresponds to the one of gas yield: increasing with time and temperature and reaching a plateau with time. The value of the plateau increases with temperature and reaching 46 % at 470 ° and 60 min (CGE double between 430°C and 470°C). Moreover, increasing temperature will bring CGE closer to its equilibrium value (218 % at 470 °C). Indeed CGE can be higher than 100 % considering that water is a reactant of SCWG and H₂ can be formed with H derived from water.

Process simulation

In order to take into account the energy needed to bring black liquor to the SCWG conditions and the energy recovered, we simulated a continuous process with a flow of a black liquor of 1kg/h (at 11.5 %_{WT}) via the software Prosim+. The influence of inorganics is not considered in this balance. The process scheme is given figure 7.

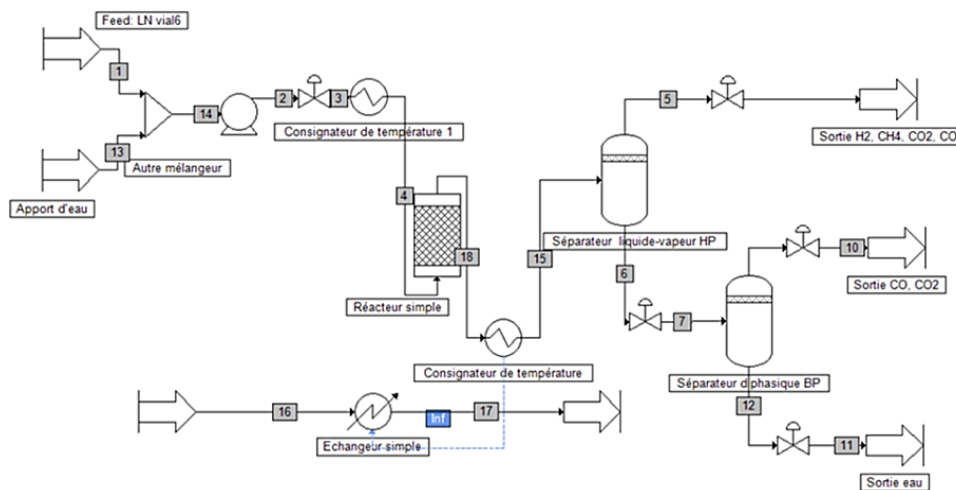


Figure 7: process scheme of SCWG of black liquor

Dry black liquor (1) is mixed with water (13) in *autre mélangeur*. This weak black liquor is then pressurized and pre-heated at 350 °C (in *consignateur de température 1*). In the reactor (*réacteur simple*) black liquor reacts with a set reaction at a set temperature (430, 470, 700 °C). The products are then cooled to 20 °C in *consignateur de température* and are separated

at high pressure in a liquid-vapor separator. The liquid phase is then depressurized to 5 bar and gases and water are separated.

Hypotheses are the following:

- Composition at equilibrium is calculated by Gibbs energy minimum;
- Dry black liquor molecule $C_{600}H_{939}O_{156}$ is calculated from its CHON constitution. As we know its HHV, its LHV and enthalpy of formation were calculated. Thermodynamics properties of guaiacol were used for calculations.
- Cooling enthalpy is recovered at 70 % and is used to heat the black liquor ;
- The reminder of energy is brought by a bark boiler with a yield of 80 %;
- Energy is recovered from gases by cogeneration with a yield of 80 % [5];
- The remaining organic compounds are represented by xylene C_8H_{10} (measured by GC-MS in the liquid phase) and char is represented by biphenyle $C_{12}H_{10}$ (a char precursor).

The **total yield** is then defined by the equation 1:

$$\frac{\sum \text{energy recovered}}{\sum \text{brought energy}} = \frac{0.8 \cdot \sum_{\text{gases}} \text{LHV}}{(\text{LHV}_{\text{BL}} + \sum_{\text{C}_8\text{H}_{10}} + \sum_{\text{C}_{12}\text{H}_{10}} - 0.7 \cdot (\sum_{\text{H}_2\text{O}} - \sum_{\text{H}_2\text{O}})) / 0.8} \quad (1)$$

Total yields for different scenario are given table 2, aiming at comparing the efficiencies of the usual recovery (evaporation + combustion in Thomlinson boiler) with SCWG of black liquor (experimental yields and equilibrium calculated yields).

Thomlinson recovery	yield at 430 °C	yield at equilibrium at 430 °C	yield at 470 °C	yield at equilibrium at 470 °C	yield at equilibrium at 600 °C
30 %	12 %	68 %	20 %	67 %	64 %

Table 1: total yield under different conditions

The total yield is 20 % at 470 °C (12 % at 430 °C) whereas the yield of usual recovery system is 30 % with the same conditions. At thermodynamic equilibrium total yield of SCWG of this black liquor is of 67 % at 470 °C and 68 % at 430 °C. At 700°C, the total yield at equilibrium is at 64 %. Increasing temperature at 700 °C will permit to increase gas yield close to thermodynamic equilibrium and to have a yield larger than recovery cycle in the pulp mill: the increasing of gas conversion will highly compensate the raise of energy needed to heat the water to 700 °C.

Alkali behavior

When the temperature is above the critical point, the dielectric constant is inferior to 5 thus the inorganics compounds are insoluble. We assumed that the sodium was precipitated in the reactor during gasification. As the sampling is at the top of the reactor, alkalis are not taken with the liquid during sampling. The inorganics precipitated in supercritical water will solubilize in the liquid remaining in the reactor during the cooling.

We compared the concentration of sodium in the liquid phase took during the sampling and the liquid phase remaining in the reactor: the concentration of sodium was approximately of 0.5 g/L in the sampling phase and 15.8 g/L in the remaining: this confirms the precipitation of sodium containing salts during the gasification.

Finally, the quantity of sodium in the liquid remaining in the reactor is between 90% and 105% of the quantity introduced in the reactor. This sodium carbonate could be then converted to caustic soda by causticizing of sodium carbonate.

CONCLUSION

Gasification of sulfur free black liquor was performed in a semi batch reactor at temperatures between 430°C and 470 °C and time between 2 and 64 minutes. The results show that at a temperature inferior to 470 °C, a substantial part of aromatic compounds from black liquor degradation, stable at this condition, are not completely converted during supercritical water gasification. The Sodium initially present in black liquor catalyzes the water gas shift reaction and enhances the formation of H₂ and can be recovered for the chemical autonomy of the mill.

At 470 °C, the total yield of SCWG of a sulfur-free black liquor with 11.5%_{WT} dry mass is about 20 % whereas it is at 30 % with a similar black liquor for the standard process.

Increasing the temperature will accelerate the reaction and permit to have a better gas yield because more gas is produced. Moreover, product composition will be closer to thermodynamic equilibrium at high temperature as 700 °C. The total yield is expected to be higher, going up to the equilibrium yield of 64 % at 700 °C.

Additional experiments will be done in a continuous pilot, in order to have inputs for the process calculations and to validate the temperature effect and also the interest of this process in continuous for an industrial application.

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