Valorization of Black Liquor under Sub-/ Supercritical Water

H.Boucard[1*], E. Weiss-Hortala[1], R. Barna[1]

[1]Université de Toulouse; Mines Albi; CNRS; Centre RAPSODEE, Campus Jarlard, F-81013 Albi Cedex 09, France

ABSTRACT

Black liquor is a waste of paper industry containing important concentration of carbon (140 $gC.L^{-1}$) minerals (Na^+, K^+, Ca^{2+}, S^{2-}, SO_4^{2-},…) and quantity of water (77wt%). This high contain of water allows to consider a treatment by supercritical water. The goal of our work is to study the potentiality of black liquor valorization using hydrothermal conversion in batch reactor.

This paper characterizes phases obtained as regards to the operating conditions of the batch hydrothermal conversion of 10wt% black liquor solutions.

INTRODUCTION

Biomass and organic residues are interesting for valorization in two ways: energy and/or platform molecules, used in chemical industry. This study is focused on a residue of paper industry: black liquor which comes from the step of wood cooking, in Kraft process. The mixture of NaOH and Na_2S called white liquor is used to dissolve lignin as thiolignin [1]. This alkaline aqueous phase is mainly composed of dissolved lignin, but contains also hydrolyzed cellulose, hemicellulose and different salts (carbonates, sulfates, sulphides etc) of Na, K, Ca…. In industrial facilities of the Kraft process, a large space is devoted to white liquor recovery from black liquor. In this process, incineration of black liquor led to minerals and heat recovery [2]. Nevertheless an extra volume of black liquor is produced, and thus black liquor would be valorized. As a result, an alternative process is to convert black liquor by using properties of supercritical water. In fact some authors discussed that the energy consumes to reach the critical point of water is lower than the evaporation step currently processed [3-4]. The goal of our work is to study the range of operating conditions leading to alternative valorization as gas, liquid or solid valuable organics by hydrothermal conversion in supercritical water.

Supercritical water has been firstly used to achieve total oxidation of waste and more recently it is used to turn waste into valuable products (gas, organics, oil or solid). Indeed, the water in these conditions ($T > 374°C$ and $P > 22.1$ MPa) has the distinction of being both a reactant and a solvent. In subcritical conditions ($T < 374°C$ and $P < 22.1$ MPa), water is less polar, however salts are still miscible and organic molecules are immiscible. In supercritical state, the properties of water change drastically. The clusters formed by water molecules [5] results in a nonpolar solvent. As a result, heterolytic and homolytic reactions are favored in sub and supercritical water respectively. As black liquor is a wet biomass (~80wt%), hydrothermal processes would befit this waste with high water and organic content (~ 140 gC.L-1).

---

[*] Corresponding author : helene.boucard@mines-albi.fr

Preliminary batch conversion experiments have been made without catalyst and revealed the formation of three phases as mentioned by authors [6]. Hydrothermal conversion of BL solutions in sub/super-critical conditions is a complex process of gasification, liquefaction and carbonization. This paper deals with the hydrothermal conversion of black liquor under sub-/supercritical water and its potentiality of valorization.

MATERIALS AND METHODS

1- Reagents

Black liquor comes directly from paper industry Smurfit Kappa Cellulose du Pin in Facture, France. It was recovered from the digester after tall oil separation in the Kraft process. The dry matter is of 23wt% (organic and mineral) while the other part is water (77wt%). Moreover, the organic compounds represent 65 wt% of the dry mass that equals to 140 $gC.L^{-1}$.

2- Experimental protocol

Hydrothermal experiments were performed in pressure-resistant batch autoclaves (5mL) at 25 MPa, using various temperatures [350°C-600°C]. The black liquor is introduced into reactor which is capped tightly. 5 autoclaves are prepared in parallel. Reactors are placed in an oven. The reaction time starts when oven has reached target temperature. The reactor is filled at atmospheric temperature and pressure, with the amount of black liquor required to reach the temperature and pressure of the reaction. After reaction time [15 or 30 min] reactor is cooled by ambiant air (slow cooling). After reaction gas, liquid and solid are collected. Liquid and solid fractions were separated by filtration.

3- Analysis of gas, liquid and solid phases

Gas phase:
Gas phase was analyzed by gas chromatography (Agilent GC-3000) with 4 columns and 4 TCD detectors for H_2, CO_2, CO, CH_4, C_2H_6, C_2H_4 and C_3H_8. H_2S produced during the process was not yet quantified but identified with mass spectroscopy (OMNI star Pfeiffer).
Liquid phase:
Total Organic Carbon was quantified using a TOC-analyzer (Shimadzu TOC-5050). the pH of the solution was measured at room temperature.
Solid phase:
Solid phase is analyzed by environmental scanning electron microscopy (ESEM, Philips XL 30 FEG), optical microscopy and FTIR (PERKIN ELMER 200 FTIR).

RESULTS

The hydrothermal conversion of black liquor in sub and supercritical water was investigated. Taking into account a proximate molar composition of the liquid [2], the complete gasification can be expressed as follow:

$$C_{10}H_{12.5}O_7 + 13H_2O \rightarrow 10CO_2 + 12.75H_2 \qquad (1)$$

Eq. 1 indicates that one equivalent mol of black liquor can produce more than 10 mol of hydrogen. For this reason, researches are developed for the gasification process. However, the high content of lignin favors also the studies about carbon conversion.

Influence of temperature

The initial black liquor solutions were dark brown with an initial pH superior to 12. Figure 1 reveals the discoloration progress, a qualitative parameter for the conversion process of the black liquor solutions. In the subcritical region (350°C) and close to the critical point the color is close to the initial one. However, the air bubbles observed at 400 and 450°C seem to indicate the formation of surfactants during the process. Moreover, the formation of a non water miscible phase could be possible but not observed. A study realized at 300 and 350°C showed the increase of oil production with temperature and the slight reduction of water soluble fraction. These colors were observed in other studies [6] in a continuous process. However, they observed a lighter color at 450°C in a shorter reaction time (<12 s). The heating process seems to influence the composition of the solution prior to reach the target temperature, as studied by Wu for model molecules [11].

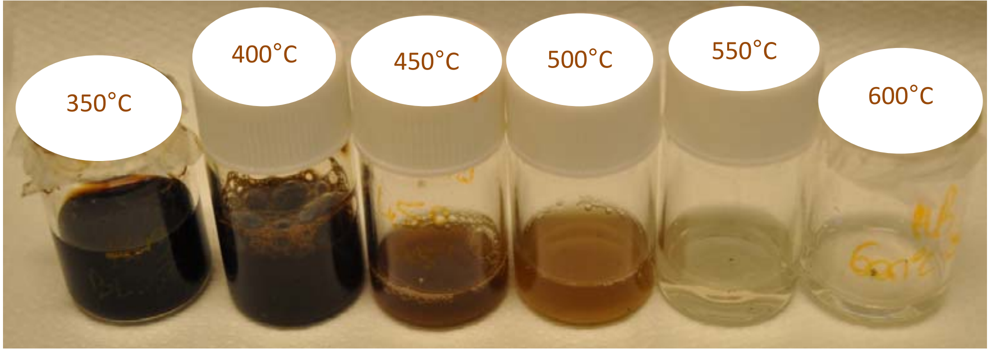

Figure 1:. Collected black liquor solutions after treatment versus temperature. (black liquor at 10 wt%, 25 MPa, 15 min, batch autoclave).

The effect of temperature was also studied by measuring the total organic carbon in the solution. Proportion of carbon converted from liquid phase is estimated by TOC values in the liquid phase and increased when the temperature increased (5% at 350°C and 95% at 600°C) meaning that a more or less significant part of organic carbon was distributed to solid and/or gaseous phases (Figure 2).

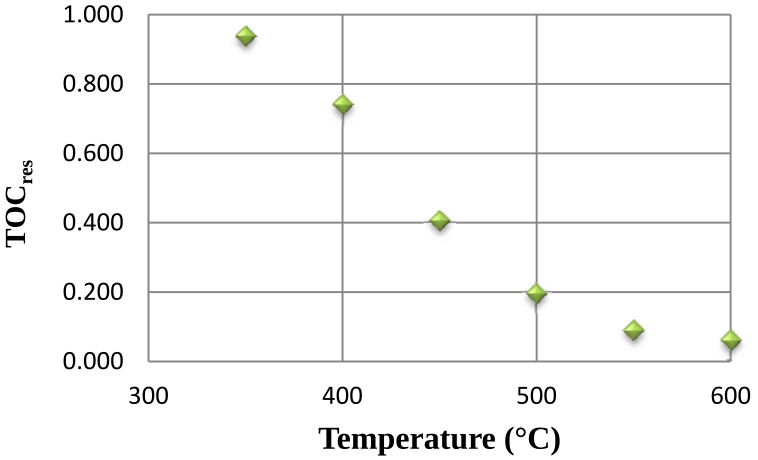

Figure 2: Variation of normalized TOC in the liquid phase during the SCWG of black liquor (black liquor at 10 wt%, 25 MPa, 15 min, batch autoclave).

The deep color of the solution corresponds to high residual TOC at 350 and 400°C while the colorless solutions are obtained at 550 and 600°C where the TOC is minimal. Therefore, the deep color is clearly related to the composition of the solution which contains probably phenols and oligomers coming from the degradation of lignin during reaction. The composition of liquids after SCWG at 500, 600 and 650°C was previously studied [8] and showed that phenol and derivatives are almost present in the solution above 500°C and the polymerization of phenolic compounds started immediately after production. Further investigations are needed to understand the great breakdown of the TOC variation around 450°C through the phenols concentration.

The pH and the salt concentration were also measured in the outflow. A diminution of salts concentration (~30%) indicated by the ICP values suggests the transfer of salts from the liquid to the others phases specially in solid phase [8].

The pH of the collected residual aqueous phase remains alkaline (pH>10). In a continuous process, the pH of the outflow was measured in the neutral region [6]. The authors processed the pH measurement during the cooling phase and showed that the pH was increasing. This phenomenon was due to the solubilisation of alkaline salts which were deposited on reactor walls at supercritical conditions. In our batch reactor the solubilisation is achieved before the recovering of the phases that explains our alkaline pH after reaction.

Temperature influences clearly the color and the carbon content of the solution. Gasification was improved by the temperature and the gas was recovered above 450°C that corresponds to the removal of 60% of TOC. Gas composition revealed by the micro-GC, was particularly rich in hydrogen and controlled by the temperature: about 30% at 450°C while about 85% at 600°C. MS measurements revealed the presence of H_2S in the gas mixture that was not quantified. The composition of the gaseous phase changes with the temperature: low hydrocarbons are detected at 450°C: H_2, CO_2, CH_4, C_2H_6 they disappear at 600°C: H_2, CO_2, CO, H_2S.

The litterature data show the efficient production of hydrogen but the molar percentage was systematically lower than 60% [4, 7, 8].

Hydrothermal process revealed the formation of three interesting phases whose one is solid phase althought non solid is present at the begginning. Indeed, into black liquor conversion, phenolic compounds polymerize together with aldehydes that is related to temperature reaction. This solid phase represents ~20wt% of the total carbon. After reaction, solid is recovered and filtered. Fig 3 shows ESEM pictures of solid residues obtained by hydrothermal conversion of a solution of 10wt% black liquor, after 15 min of reaction and under 25 MPa of pressure for different temperatures.

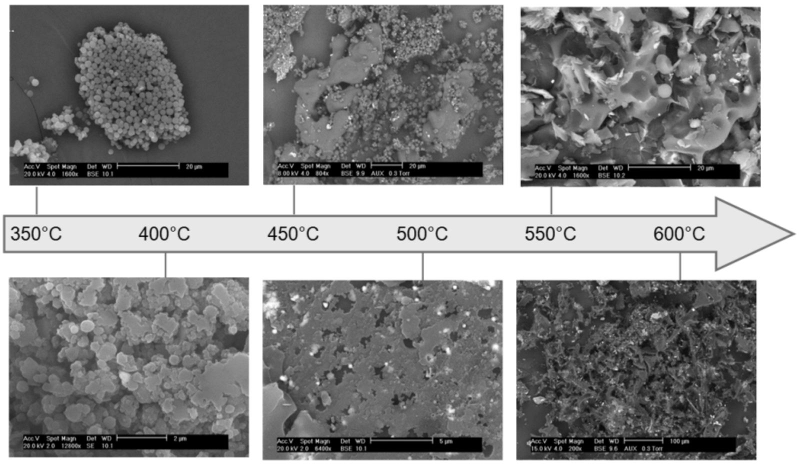

Figure 31 : ESEM pictures of solid residue

Composition of the solid phase is already the same: carbon, oxygen and minerals. However, minerals are not involved in carbonaceous surface morphology [9]. The morphology evolves from microparticles at 350°C to sharpless structure using high temperatures. The strucuture becomes denser and could be due to an evolution of microparticles by sintering or agglomeration of particles. Indeed at 350°C, under subcritical conditions, spherical microparticles are observed. As the system is composed of two phases (an aqueous and a non-aqueous), polymerization of phenolic compounds can probably occur. Thus the shape of the microparticles can come from the oil-in-water dispersion.

This shape is particularly interesting for material recovery. Energy recovery should be considered for a solid with high LHV in substitution of coal. Material recovery will be justified if the solid is porous (catalyst support, adsorbent ...), if it contains minerals or metals (new catalyst, hollow spheres), if it has structural or crystalline qualities (electrochemical applications, nanotubes carbon ....). All current challenge is to develop future materials from waste and / or renewable resources with specific textures.

Influence of reaction time

Figure 4 shows the color variation of solutions obtained after various reaction times (0, 8, 15 and 30 min) at 500°C and 25 MPa. The deep brown color disappears at 15 min reaction time leading to an orange color. After 30 min treatment the solution is totally clear. This variation is also accompanied by a decrease of the residual TOC. Commonly, reaction time increases the gasification but the composition of gaseous phase can be affected [9].

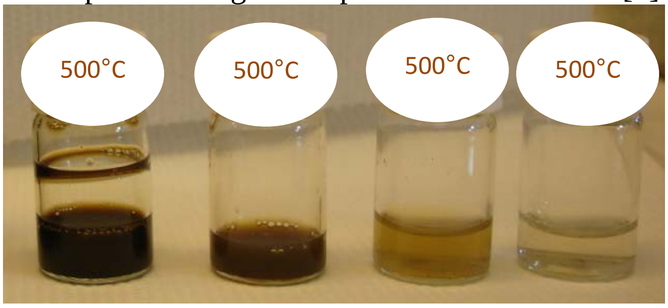

Figure 4. Collected black liquor solutions after treatmentversus reaction time. (black liquor at 10 wt%, 25 MPa, 500°C, batch autoclave).

The composition of the gaseous phase was estimated by µ-GC at 600°C for two reaction times. Table 1 illustrates gas compositions at 600°C for 15 and respectively 30 min reaction time, excepting H_2S. H_2 content is remarkably high in the quantified gas and compared to the percentage of CO_2. In fact, taking into account Eq. 1, the production of hydrogen and CO_2 would be in the same range. However, the basic pH of the solution indicates that the solubilisation of CO_2 into carbonates was improved and can explain the poor concentration of CO_2 into the gas phase. Carbon monoxide was also recovered into the gas phase. Its low part can be explained by the enhancement of the water gas shift reaction (which consumes CO) in presence of alkaline salts. This results is in accordance with the literature either using batch or continuous process [4, 6].

600°C, 15 min	**600°C, 30min**
H_2 = 84,7 %	H_2 = 87,8 %
CO_2 = 14,2 %	CO_2 = 11,5 %
CO = 1,1 %	CO = 0,7 %

Table 1. Comparative composition of gas. (black liquor at 10 wt%, 25 MPa, 600°C, batch autoclave).

Finally, the analysis of the solid phase at high temperature (600°C) and for two reaction times was also realized. The structure and the composition of the solid were not affected by the reaction time using the ESEM images. The solid phase was mainly composed by carbon (more than 90%), oxygen and minerals.

CONCLUSION

These preliminary experiments, performed at small scale in steel batch reactor highlight interesting conversion of black liquor solutions in valuable compounds. Finer investigations of the composition of the obtained liquid phase is under progress.

A high proportion of hydrogen and a low proportion of CO_2 was revealed by the GC analyses and MS measurements revealed the presence of H_2S in the gaseous mixture. The composition changes: H_2S is produced at higher temperature, while volatile hydrocarbons are produced at lower temperature.

For the liquid phase, containing phenolics compounds, Proportion of carbon converted increased with temperature increase; meaning that a part of organic carbon was transferred to solid and/or gaseous phase. A diminution of salts concentration (~30%) observed in ICP analysis suggests salts transfer to the others phases, specially into solid phase. The final pH of solutions is alkaline (>10).

The solid phase, whose morphology is variable, was mainly composed of carbon, oxygen and minerals. The morphology at 350°C seems to be particularly intersting. Further experiments will be performed at this temperature to explore the potentiality of this solid.

REFERENCES

[1] LEASK, R.A., Pulp and Paper Manufacture. Joint Textbook Committee of the Paper Industry, **1987**

[2] DEMIRBAS, A., Energy Convers. Manage., Vol. 43, **2002**, p. 877

[3] VOGEL, F., DINARO, J., MARRONE, P., RICE, S., PETERS, W., SMITH, K., TESTER, J., J. Supercrit. Fluids, Vol. 34, **2007**, p. 249

[4] SRICHAROENCHAIKUL, V., Bioresour. Technol., Vol. 100, **2010**, p. 638

[5] KRUSE, A., DINJUS, E., J. Supercrit. Fluids, Vol. 39, **2007**, p. 362

[6] CAO, C., GUO, L., CHEN, Y., GUO, S., LU, Y., Int. J. Hydrogen Energy, Vol. 36, **2011**, p. 13528

[7] RÖNNLUND, I., MYREEN, L., LUNDQVIST, K., AHLBECK, J., WESTERLUND, T., Energy, Vol. 36, **2011**, p. 2151

[8] SUGANO, M., TAKAGI, H., HIRANO, K., MASHIMO, K., J. Mater. Sci., Vol. 43, **2008**, p. 2476

[9] WU, Q., PhD Thesis, Toulouse University, **2012**