Catalytic Conversion of Black Liquor under Sub-/Supercritical Conditions

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ABSTRACT

Black liquor is an alkaline liquid residue of paper industry, containing ~80wt% of water and ~20wt% of organic matter and minerals. Our global project explores black liquor conversion by using properties of supercritical water. Exploratory conversion experiments have been made previously without catalyst and revealed the formation of three phases; especially an interesting gaseous phase with a high proportion of H_2 (~80% at 600°C). A solid residue is also observed and results from the polymerisation of phenolic compounds together with aldehyde crosslinks. Based on these results, this study is devoted to the catalytic conversion using CeO_2 nanocatalysts to improve gasification and H_2 production as well as to block coke formation. In sub-/supercritical conditions, water splitting occurs by CeO_2 catalysts, to produce active hydrogen and oxygen species. Thus these actives species react with molecules of the medium.

Experiments are performed in sub-/supercritical conditions in batch reactor, during 15-60 min reaction time with and without catalyst. As expected, nanocatalyst of CeO_2 improved the conversion of black liquor at sub and supercritical conditions. Hydrogen production was not significantly affected by the catalyst while amounts of CO and CO_2 are reduced at short reaction time. The high basic pH of raw feedstock and remaining solutions impacts the CO_2 dissolution into carbonates. Supercritical water media and catalyst clearly affects the fragmentation of dissolved lignin compared to subcritical conditions.

INTRODUCTION

Black liquor comes from Kraft process in paper industry. It results from the step of cooking wood chips with white liquor (Na_2S and NaOH mixture). Delignification of wood corresponds to lignin dissolution from the fibrous part (cellulose, hemicellulose) to kraft lignin recovered in the cooking juice (black liquor) [1]. As white liquor is a basic mixture, black liquor is also a basic aqueous solution (pH ~ 13), containing dissolved lignin, fragments of cellulose and hemicellulose and several minerals and salts (Na, K, Ca, S.... carbonates, sulfates, sulfides...). In industrial facilities of the Kraft process, a large space is devoted to the concentration of black liquor followed by the incineration of this concentrated solution for

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heat and white liquor 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.

Supercritical water has been firstly used to achieve total oxidation of waste and more recently it is used to recycle waste by generating energetical gas, platform molecules or added-value solids. 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 condition ($T < 374°C$ and $P < 22.1$ MPa), water is a polar solvent in which salts are miscible and organic molecules are immiscible. In supercritical state, the properties of water change drastically. The water molecules form clusters [3] that results in a nonpolar solvent and thus free radical reactions are favored. Furthermore, supercritical water and gases are miscible and the diffusion of the molecules in this phase is then improved. Either platform molecules (cresol, guaiacol,…) or gases (H_2, CO, CO_2 ...) are produced depending on the temperature reaction. As black liquor is a wet biomass (~80wt%), this kind of hydrothermal process is suitable to use its high water content to convert its significant organic content (~ 140 $gC.L^{-1}$).

Preliminary batch conversion experiments have been made without catalyst and revealed the formation of three phases [4]: gas with a high proportion of H_2 (~80% at 600°C), a rich bouquet of phenolic compounds in the liquid phase and an non negligeable proportion of carbon converted into solid phase (~20wt%). Here, we propose the use of catalysts to convert black liquor more efficiently. Cerium oxide is an interesting nanocatalyst to improve hydrogen production and to reduce coke formation as mentioned in a study with bitumen [5] using cubic CeO_2. Indeed, CeO_2 has a “redox cycle” allowing to fix and release easily the oxygen generated by the water in supercritical conditions. Different morphologies of CeO_2 exist (Cubic, octahedral….); however the catalytic activity of cubic CeO_2 is better than octahedral CeO_2 [5].

These both studies lead us to consider the catalytic conversion of black liquor using cubic CeO_2 to improve the amount of H_2 into the gas phase and to reduce coke formation as well as to form more building block molecules in the liquid phase. Thus, this study focuses on the conversion of Black liquor with and without catalyst.

MATERIALS AND METHODS

1- Reagents

Black liquor

Black liquor was obtained from Smurfit Kappa Cellulose du Pin in Facture, France. It was obtained from the digester after the recovery of tall oil in Kraft process. The fraction of dried components was 23 wt% (organic and mineral) while the other part was water (77 wt%). The organic compounds amounted to 65 wt% of the dry components, which equals to 140 $g\text{-}C.L^{-1}$. In this study, the original solution was diluted to 10 wt% and used in the following experiments.

Cerium oxide: CeO_2

CeO_2 nanoparticles were synthesized by Adschiri's group in Tohoku University, Japan [5], [6]. The average size of the nanoparticles was around 8 nm. The catalytic activity of CeO_2 arises from its redox activity via Ce^{4+}/Ce^{3+} cycle, which is accompanied with capturing and releasing oxygen. CeO_2 is known to have high oxygen storage capacity (OSC). The OSC of cubic CeO_2 is 340 µg-O/g-cat and that is 3.4 times higher than octahedral CeO_2 [5]. Due to this high OSC, cubic CeO_2 nanoparticles were used in this study. The ratio of catalyst to the reactants was calculated and shown as a parameter in the following study.

$$R = Catalyst/Organic\ Matter \quad (1)$$

Equation 1 : ratio of catalyst

2- Experimental protocol

Experiments were performed at either 350°C or 450°C in sub- or super-critical conditions using a pressure-resistant batch reactor with an inner volume of 5.0 mL. The diluted black liquor was introduced into the reactor with the cubic CeO_2 nanoparticles (R= 0, 5, 20), then the reactor was capped tightly. After adding N_2 gas into the reactor (~0.26 MPa), the reactor was placed in an electric oven whose temperature was set to either 350°C or 450°C. After the reaction time (15 or 60 min) passed, reactor was cooled in an iced water to stop the reaction immediately. After quenching, the gas inside the reactor was analyzed by µ-GC without exposing to air. Liquid and solid products were collected after gas analysis by rinsing the reactor with THF. The collected products were separated by filtration using PTFE membrane filter with pore diameter of 0.1 µm. The THF-insoluble fraction was called coke and the THF-soluble fraction form the liquid phase. The weight of coke was evaluated as the weight loss of the solid products during calcination until 600°C, because the solid products contained CeO_2 nanoparticles as well as coke.

3- Analysis of gas, liquid and solid phases

Gas, liquid and solid phases were analyzed and characterized after reaction.

Gas phase:

The gas products were analyzed by µ-Gas Chromatography (Agilent GC-3000) to quantify following gases: H_2, O_2, N_2, CO, CO_2, and hydrocarbones.

Liquid phase:

The composition of the liquid phase was analyzed by complementary techniques of Gel Permeation Chromatography (GPC) (HP1100) and Gas Chromatography coupled with Mass spectroscopy (GC-MS) (GC: Agilent 7890A; MS:Agilent 5975C).

Solid phase:

Morphology of solid residue (coke) was observed via transmission electron microscopy (TEM, Hitachi H7650).

RESULTS

1- Gaseous phase

During the hydrothermal process of black liquor, H_2 is expected to be produced. Demirbas reported that more than 10 mol of H_2 was produced from 1 mol of black liquor if the formula $C_{10}H_{12.5}O_7Na_{2.4}S_{0.36}$ is considered [2]. The use of CeO_2 nanocatalysts possibly results in higher gas productions [7]. Figure 1 shows the results of gas phase analysis at both sub- (Fig. 1a) and supercritical (Fig. 1b) conditions. In both cases, carbon species were formed during reaction. However, gasification of carbon was enhanced under supercritical conditions. CeO_2 acts as a catalyst and splits water into actives species [5]. Active hydrogen species stabilize the reactive intermediate species and active oxygen species involves in oxidation reactions. Although radical reactions are mainly involved at supercritical conditions, they remain significant at subcritical conditions. These hydrogen active species can form directly H_2 or react with organic molecules to form smaller molecules. Simultaneously, alkenes are formed at subcritical conditions and release H_2 in gas phase by deshydrogenation reaction. The role of active oxygen species were mainly involved in oxidation reactions. The more the oxidation is achieved, the more CO_2 is produced. The concentration of these active species increases in the presence of CeO_2 catalyst and thus the carbon conversion was enhanced.

Figure 1 shows that the amount of carbon (~2 or 3%) is lower at subcritical conditions than at supercritical conditions. This tendency was in accordance with the lower quantity of gaseous products (not shown). Proportion of carbon at 350°C can be also explained by the remaining basic pH of the solution that dissolves a large amount of CO_2 in the liquid phase.

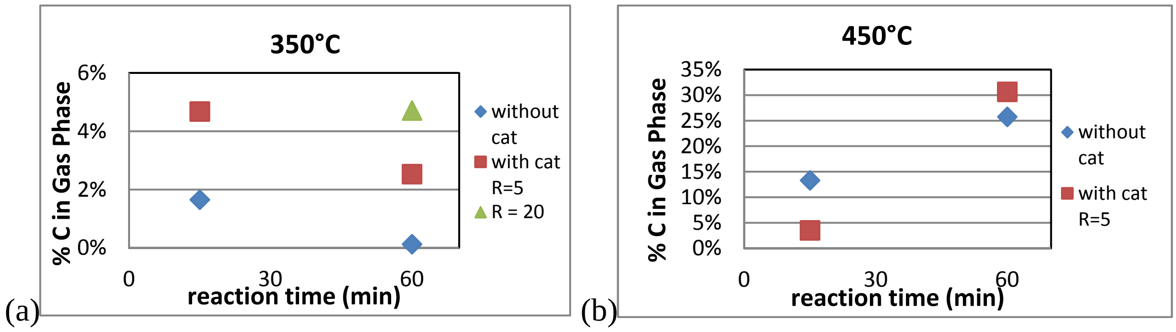


Figure 1: Proportion of carbon converted into gas phase at 350°C and 450°C

The gas mixtures are composed of the same gases: H_2, CO, CO_2, and light hydrocarbons. However the composition changes slightly in the presence of the catalyst. The main part of carbon in the gas phase was CO and CO_2, which was produced from the oxidation and water-gas shift reactions. The amount of CO_2 after quenching the reaction was low, because CO_2 could dissolve into basic aqueous solution to form carbonates. The amount of CO was also low due to either its consumption through the water gas shift reaction, which is promoted by alkaline salts ([4], [8]), or the strong oxidation strength of the CeO_2 catalyst.

Reaction time, as well as the catalysts, played also an important role in the carbon conversion. At 350°C, the influence was not significant. However, longer reaction time resulted in enhanced gasification at 450°C. Catalysts increased the conversion of carbon by promoting water gas-shift reaction. The quantification of gaseous phases by µ-GC confirmed this result. Indeed, at 450°C and 15 min, a low quantity of CO was detected while no CO was detected after the experiment with the catalysts. The simultaneous action of catalyst and short reaction time may explain that no CO was detected in the gaseous phase due to thermodynamic equilibrium of CO_2 and kinetics.

Figure 2 shows that the amount of produced H_2 significantly increased in the presence of the catalysts at 350°C and 60 min. The other experimental conditions demonstrate a moderate effect of the catalysts. As H_2 is mainly produced from water splitting, its amount would be higher with the catalyst. Active hydrogen species that was produced from water splitting would easily and continuously react in gas phase to form H_2. H_2 was also prouduced by hydrogenation reaction from alkane. However the increase in active hydrogen species would simultaneously increase reactions with organic molecules. Thus, the amount of H_2 was related to both the production and consumption of hydrogen actives species. The slight effect of the catalyst seems to indicate an increase of both phenomena. Concerning the experiments carried out at 350°C and 60 min, the amount of H_2 was multiplied by 10 using CeO_2 as a catalyst.

This means that H_2 consumption was higher at long reaction time without catalyst while H_2 production would be higher using catalyst. As the gas-liquid equilibrium was expected for these experiments due to sub-critical water conditions, limitative diffusion of hydrogen from gas to liquid phase could explain its low consumption.

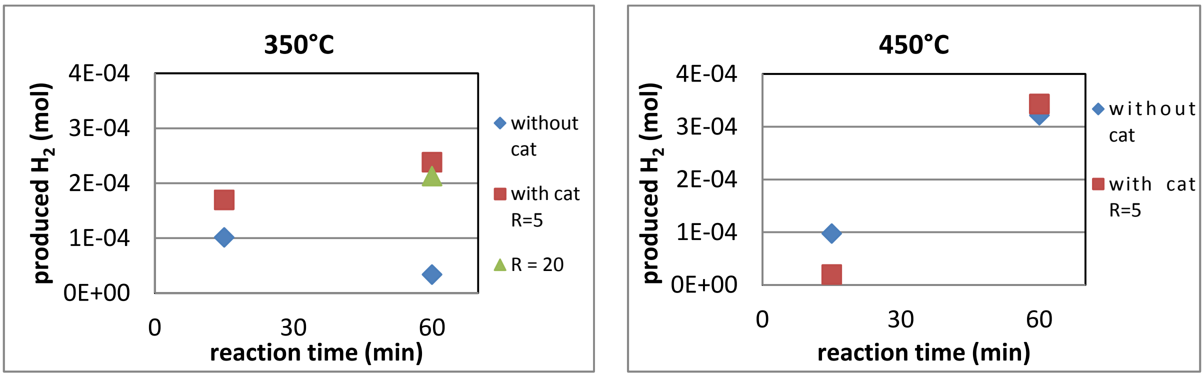


Figure 2: H_2 produced into gas phase after reaction at 350°C and 450°C

The amount of H_2 was not affected by the catalyst ratio (R= 5 or 20, 350°C and 60 min). As the amount of H_2 produced from water splitting would be higher, the mass transfer at the interface would be also enhanced by this high concentration. As a result, produced H_2 would be used for capping reaction in liquid phase to produce smaller molecules.
To conclude, carbon conversion to gas phase was more influenced by the use of the catalyst that will consequently affected the composition of the liquid phase.

2- Liquid phase

The orignal black liquor is a dark brown liquid with a basic pH (>12). The conversion of black liquor is partially related to colour evolution of the liquid products (fig 3). The deep color is due to the presence of phenolic compounds [9].

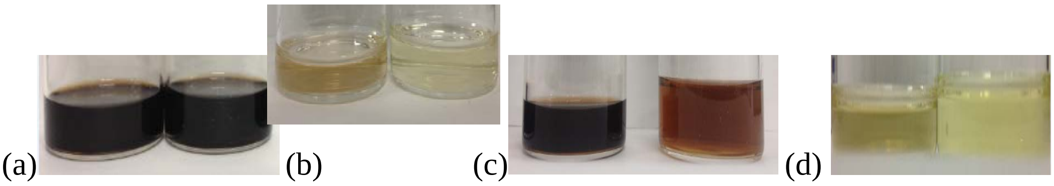

(a) (b) (c) (d)

Figure 3: liquid obtained after 15min and 60 min without catalyst; (a) at 350°C (b) at 450°C, liquid obtained after 15min and 60 min with catalyst (c) at 350°C (d): 450°C, 15 and 60 min

In subcritical conditions, at 350°C, the liquid was still brown and no colour variation was observed within the reaction time. However at 450°C, the liquid was yellow and almost transparent. The colour became lighter with increased reaction time. The observed colour variation was caused by the conversion of oligomer molecules to either smaller colourless molecules (such as acids, aldehydes, alcohols…) and/or solid residues. This observation was supported by gas permeation chromatography (GPC, fig 4). GPC separates molecules towards their molecular weight. This first global result was interesting to compare the degradation efficiency. Indeed, the curve at 450°C was shifted to low molecular weight compared to the curve at 350°C; that suggests molecules into liquid phase are smaller at high temperature.

This assumption is in accordance with the increase of gasification efficiency at high temperature.

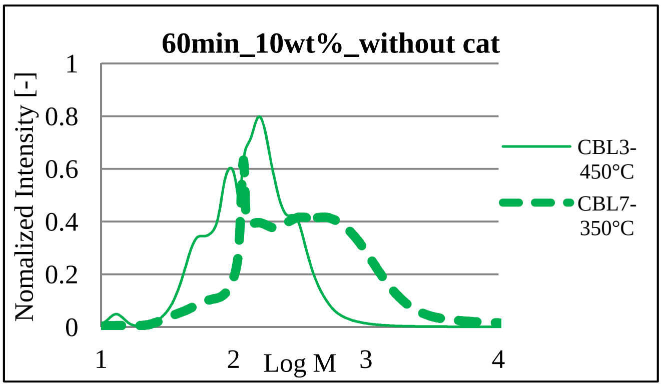


Figure 4: influence of the temperature without catalyst on the molecular weight

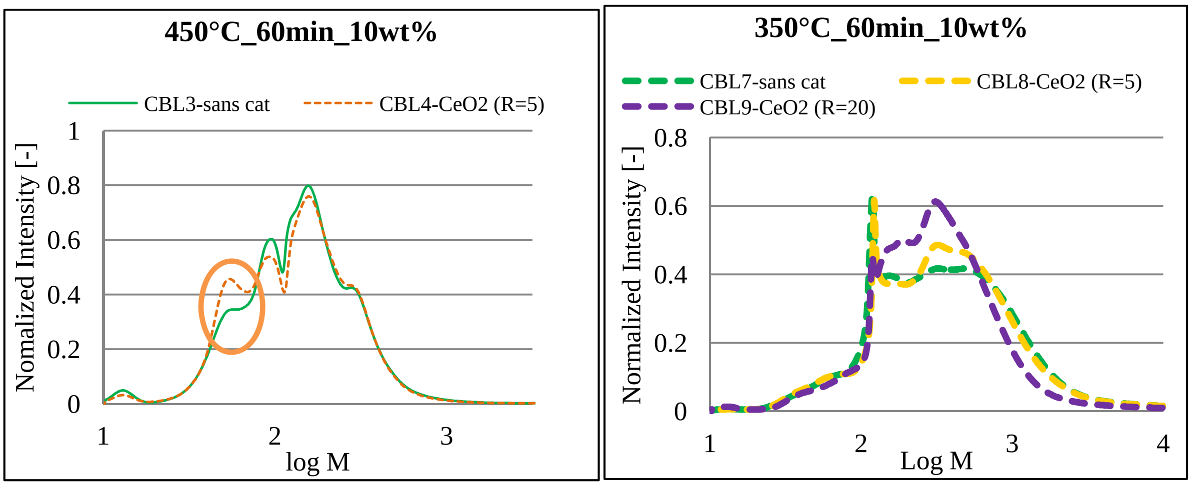


Figure 5: catalyst influence on molecular weight at 450°C and 350°C

The presence of catalysts during reaction promoted the degradation. As a result, the products showed a lighter colour as shown in Fig. 3 and had lower molecular weight distribution. At 450°C the coupled effect of reaction time and the catalysts created a new population of molecules whose the molecular weight is center at log M = 1.77 (M = 5.87 g/mol). This different composition can then explain the higher release of carbon to gas phase. At 350°C, the impact of the catalyst at a ratio of 5 is limited as regards to GPC results. The sharp peak at log M = 2 suggests one small species was selectively obtained in high quantity. Its disparition and the shift of the curve for R=20 means other populations of molecules were created. For this temperature, all curves are stackable to Log M = 2; so no smaller molecules are formed. This result was confirmed by GC-MS results and also by the change in the colour of the products. In the presence of catalyst, oxygenation of molecules has also to be considered, more oxidized molecules have been detected by GC-MS in the presence of catalyst. Especially at 350°C and R=20 and R=5, the same alkenes are detected, so hydrogenation reaction should be in competition with capping reactions. This tendency can explain why the amount of H_2 remains the same. Slight amounts of small aliphatic molecules (such as aldehydes) are detected in the presence of catalyst, while a high amount of aromatic compound was obtained into liquid and less coke was formed.

3 Solid phase

Without catalyst, polymerisation of aromatic compounds occurred since their production began during reaction. This polymerisation resulted from the reactions between aromatic molecules and small molecules such as aldehydes. Coke formation was the result of this polymerization and was formed at both temperatures. At 350°C, solid was micrometric particles of carbon (fig 6) whereas at 450°C, the solid was shapeless (fig 7). The composition was always the same: Carbon, oxygen and minerals, particularly sulfur (darkest spots on pictures) but minerals did not play a role on the surface morphology [10].

Fig 6:

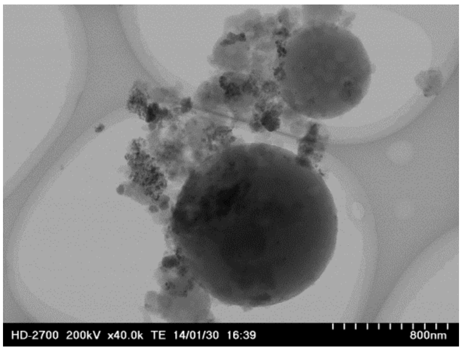


Fig 7

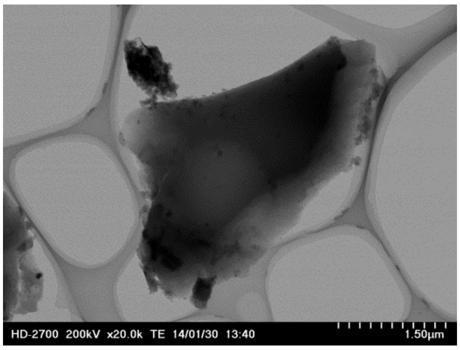


Figure 6: solid obtained after 350°C, 60 min of reaction time, without catalyst

Figure 7: solid obtained after 450°C, 60 min of reaction time, without catalyst

In the presence of cubic CeO_2, carbonaceous solid was not visible by TEM but the cartography was able to measure some carbon (fig 8). The morphology of nanocatalyst changes after reaction with black liquor from cubic structure to heterogeneous structure (fig 8) for both temperatures.

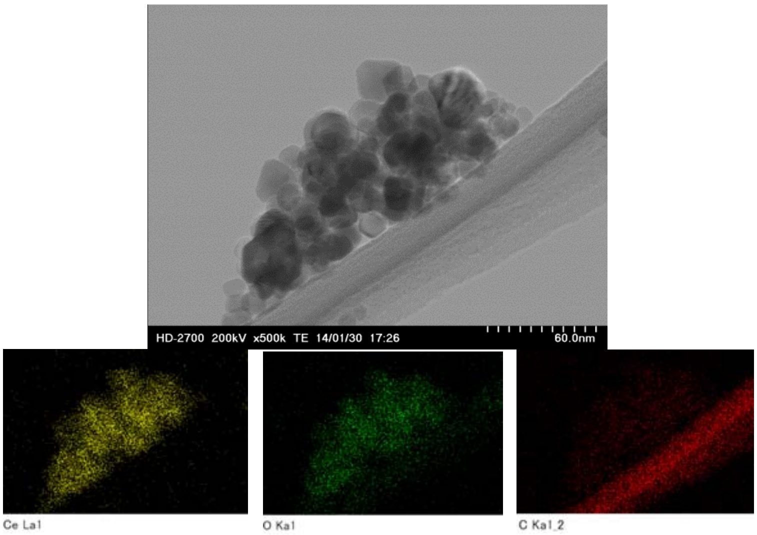
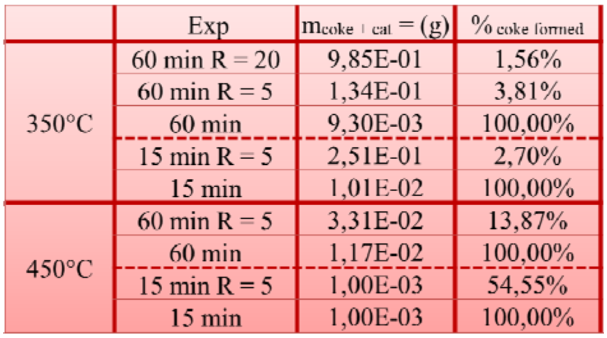


Figure 8: Cubic CeO_2 nanoatalyst obtained after reaction

For both temperatures, coke was formed (table 1); its quantity was increased in the supercritical conditions; so at 450°C, the amount of coke was higher than at 350°C. The proportion of coke formed decreased when R of catalyst increases at 350°C. The efficiency of catalyst seems to be higher at low temperature (subcritical conditions). However, for R=20, the amount of coke formed seems to be important. A hypothesis was an antagonist effet of CeO_2 as catalyst and as carrier of coke formation.

Table 1: Proportion of coke formed after reaction



	Exp	$m_{coke + cat}$ = (g)	% $_{coke\ formed}$
350°C	60 min R = 20	9,85E-01	1,56%
	60 min R = 5	1,34E-01	3,81%
	60 min	9,30E-03	100,00%
	15 min R = 5	2,51E-01	2,70%
	15 min	1,01E-02	100,00%
450°C	60 min R = 5	3,31E-02	13,87%
	60 min	1,17E-02	100,00%
	15 min R = 5	1,00E-03	54,55%
	15 min	1,00E-03	100,00%

CONCLUSION

The catalytic conversion of black liquor with cubic CeO_2 allows to split water molecules into active hydrogen and oxygen species. Active hydrogen species leads to H_2 molecules in gas phase, H_2 molecules can also be formed by hydrogenation reaction from alkane. A part of these active species can react also with liquid molecules by capping to form smaller molecules (less complex). GPC and color of liquid attested this degradation. Active oxygen species oxidized organic molecules in liquid phase, which was confirm by GC-MS results. When oxidation was extreme, some CO_2 was released to gas mixture; CO_2 was also due to the consumption of CO by the water gas shift reaction; which was promoted by alkaline salts and CeO_2 catalyst. Formation of very small molecules like aldehyde seems to be blocked which limits the polymerisation of phenolic compound. Indeed coke formation was limited, the compounds detected by GC-MS was higher in the presence of catalyst and the carbon conversion into gas increased that goes to an improvement of conversion of the black liquor using CeO_2.

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