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# Beneficial use of CeO<sub>2</sub> nanocatalyst for black liquor conversion under sub and supercritical conditions

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## ABSTRACT

Black liquor is an alkaline liquid residue from paper industry, containing ~80 wt% of water and ~20 wt% of organics and minerals. Hydrothermal conversion of black liquor in a batch reactor is particularly interesting towards hydrogen production, as the carbon dioxide is highly solubilized in the basic aqueous media. Thus hydrogen with higher purity than other processes is obtained. Cerium oxide nanocatalyst (cubic CeO<sub>2</sub>) is used to improve the amount of hydrogen produced and to decrease the coke formation, based on the water splitting into active species. Experiments have been carried out at sub and supercritical conditions 350 °C or 450 °C, 25 MPa) in a batch reactor for 15 min or 60 min. CeO<sub>2</sub> nanocatalyst improved the conversion of black liquor at sub and supercritical conditions as expected. The amount of carbonaceous solid recovered was decreased due to the catalytic effect. Recovered hydrogen was not significantly affected by the catalyst as it was involved in secondary reactions such as hydrogenation. Oxidations reactions, as well as O<sub>2</sub> production, were also improved using catalyst and supercritical media. Supercritical water media combined with catalyst clearly affects the fragmentation of dissolved lignin compared to subcritical conditions. Then it was assumed that water splitting occurs and produces active hydrogen and oxygen species. Thus these active species produced using catalyst are able to improve hydrogenation and oxidation reactions, as well as recombination into H<sub>2</sub> and O<sub>2</sub>.

### Keywords:

Hydrothermal conversion

Black liquor

CeO<sub>2</sub> nanocatalyst

Hydrogen

## 1. Introduction

Black liquor is an alkaline wastewater coming from Kraft process in paper industry. It results from the step of cooking wood chips with white liquor (Na<sub>2</sub>S and NaOH mixture). This step is used for delignifying the wood; corresponding to the dissolution of lignin from the fibrous part (cellulose, hemicelluloses) to kraft lignin [1]. The cooking juice recovered, namely black liquor, is an aqueous media containing dissolved lignin, fragments of cellulose and hemicelluloses, and several minerals and salts (Na, K, Ca, S. . .

carbonates, sulfates, sulfides. . .). Black liquor (BL) is a basic aqueous solution (pH ~ 13), as well as white liquor, whose the organic content presents a strong use potential. The composition of black liquor is varying as function of wood and ratio of alkaline in the white liquor. However, Demirbas reported that the molar composition could be assumed as C<sub>10</sub>H<sub>12.5</sub>O<sub>7</sub>Na<sub>2.4</sub>S<sub>0.36</sub> [2]. In industrial facilities of the Kraft process a large space is devoted to black liquor treatment. Black liquor is concentrated and incinerated for heat production (due to its high heating value) and white liquor recovery [2]. Nevertheless an extra volume of black liquor is produced, and thus useful material recovery could be investigated. Considering the amounts of water in black (~80 wt%), hydrothermal processes could be possible to use its high water content to convert its significant organic content (~100 gCL<sup>-1</sup>). Indeed, hydrothermal process uses the properties of water at high pressure and temperature to convert biomass. It has been firstly used to achieve total oxidation of waste and more recently it is used to recycle waste by generating energetic gas, building-block molecules or

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added-value solids [3]. Indeed, water over its critical point ( $T > 374^\circ\text{C}$  and  $P > 22.1\text{ MPa}$ ) is a solvent, as well as a reactant [4]. Water is a polar solvent where salts are miscible and organic molecules immiscible. However water becomes non polar at the supercritical state, and the overall physico-chemical properties change drastically. Indeed water molecules form nonpolar clusters [4] and its density sharply decreases 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 [4].

Preliminary hydrothermal conversion of black liquor have been made in batch reactor and revealed the formation of three phases [5]: gas with a high proportion of  $\text{H}_2$  ( $\sim 80\%$  at  $600^\circ\text{C}$ ), a rich bouquet of phenolic compounds in the liquid phase and an non negligible proportion of carbon converted into solid phase ( $\sim 20\text{ wt}\%$ ). This preliminary study shows the interest of black liquor conversion by hydrothermal process without catalyst such as previous work about gasification [6], liquefaction [7] or carbonization [8]. Moreover, the alkaline salts, such as those in black liquor, are commonly used in hydrothermal processes to improve hydrogen production [9].

These results have been obtained without catalyst, however a previous study about cracking bitumen [10] using  $\text{CeO}_2$  has shown that cerium oxide is an interesting nanocatalyst to improve hydrogen production and to reduce coke formation. Indeed,  $\text{CeO}_2$  has a "redox cycle" that allows fixing and releasing easily the oxygen generated by the water at supercritical conditions. During the reaction,  $\text{CeO}_2$  acts as a catalyst and splits water into two active species: H and O [10], which react during hydrothermal process.  $\text{CeO}_2$  exists with various crystalline structures (cubic, octahedral. . .); however the catalytic activity of cubic  $\text{CeO}_2$  is higher than octahedral  $\text{CeO}_2$  [10].

Considering alkali contains and  $\text{CeO}_2$  properties, this work is on the catalytic conversion of black liquor using  $\text{CeO}_2$ ; the objective is to study the amount and the proportion of  $\text{H}_2$ , as well as the limitation of coke formation. Sub and supercritical conditions were selected ( $350^\circ\text{C}$  and  $450^\circ\text{C}$ ,  $25\text{ MPa}$ ) at various reaction times in a batch reactor. In addition, the last section discusses the catalytic role of the catalyst by comparing the medias (L/V mixture vs. supercritical).

## 2. Materials and methods

### 2.1. Reagents and reactors

#### 2.1.1. Feedstock: Black liquor

Black liquor used in this study was supplied by Smurfit Kappa Cellulose du Pin in Factice, France. It was obtained from the digester after the recovery of tall oil in Kraft process. The organic and mineral contents dissolved in water represent  $23\text{ wt}\%$ . The organic compounds amounted to  $70\text{ wt}\%$  of the dry matter, which equals to  $100\text{ gCL}^{-1}$ . In this study, the original feedstock was diluted to  $10\text{ wt}\%$  in pure water.

#### 2.1.2. Catalyst: Cerium oxide

$\text{CeO}_2$  nanoparticles were synthesized by hydrothermal process [10,11]. The average size of the nanoparticles was around  $8\text{ nm}$ . The catalytic activity of  $\text{CeO}_2$  arises from its redox activity via  $\text{Ce}^{4+}/\text{Ce}^{3+}$  cycle, which is accompanied with capturing and releasing oxygen.  $\text{CeO}_2$  is known to have high oxygen storage capacity (OSC). The OSC of cubic  $\text{CeO}_2$  is  $340\ \mu\text{g-O/g-cat}$  and that is 3.4 times higher than octahedral  $\text{CeO}_2$  [10]. Due to this high OSC, cubic  $\text{CeO}_2$

nanoparticles were used in this study. The ratio of catalyst to the reactants was defined in the following equation:

$$R = \frac{\text{mass of catalyst}}{\text{mass of organic content}} \quad (1)$$

**2.1.2.1. Expected action of  $\text{CeO}_2$ .** During reaction  $\text{CeO}_2$  acts as a catalyst and splits water into two active species: H and O [10]. These hydrogen active species can form directly  $\text{H}_2$  or stabilize the reactive intermediate species reacting with organic molecules to form smaller molecules. The amount of  $\text{H}_2$  formed is also linked to hydrogenation/dehydrogenation reaction that occurred for big molecules observed in liquid phase after reaction. The role of active oxygen species were mainly involved in oxidation reactions. The more the oxidation is achieved, the more  $\text{CO}_2$  is produced. The concentration of these active species increases in the presence of  $\text{CeO}_2$  catalyst and thus the carbon conversion was enhanced.

#### 2.1.3. Reactor and experimental protocol

Experiments were performed at either  $350^\circ\text{C}$  or  $450^\circ\text{C}$  in sub- or super-critical conditions using a pressure-resistant batch reactor with an inner volume of  $5.0\text{ mL}$ . The diluted black liquor was introduced into the reactor with the cubic  $\text{CeO}_2$  nanoparticles ( $R = 0; 5$  or  $20$ ); then the reactor was capped tightly. The volume of the reactant for the reactions at  $350$  and  $450^\circ\text{C}$  was  $3.128\text{ mL}$  and  $0.449\text{ mL}$ , respectively. The reactor was initially pressured with  $\text{N}_2$  ( $\sim 0.26\text{ MPa}$ ), and then placed in an electric oven whose temperature was set to either  $350^\circ\text{C}$  or  $450^\circ\text{C}$ . After the reaction time ( $15$  or  $60\text{ min}$ ), reactor was cooled in an iced water to stop the reaction immediately, such as a quenching process. Liquid and solid products were collected after gas analysis by rinsing the reactor with tetrahydrofuran (THF). THF is purchased from Wako Pure Chemical Industries (Japan) with a purity of  $99.0\%$ . Solid and liquid phases were separated by filtration using PTFE membrane filter with pore diameter of  $0.1\ \mu\text{m}$ . The THF-insoluble fraction was called solid residue and the THF-soluble fraction form the liquid phase.

## 2.2. Analytic procedures

### 2.2.1. Gaseous residue

After quenching, the gas from the reactor was directly analyzed by  $\mu$ -gas chromatography (GC) (Agilent GC-3000) to identify and quantify following gases:  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and others hydrocarbons; with a carrier gas of Argon. Columns used are: Molesieve 5A and PorapLOT Q.

Gas volume is estimated with a calibration curve linking pressure reads by the manometer and the volume introduced.

### 2.2.2. Liquid residue

The composition of the liquid phase was analyzed by gel permeation chromatography (GPC) (HP1100) and gas chromatography coupled with mass spectroscopy (GC-MS) (GC: Agilent 7890A; MS: Agilent 5975C), the column used is HP-5MS.

### 2.2.3. Solid residue

The solid residue is dried at  $60^\circ\text{C}$  under vacuum during  $12\text{ h}$  and then weighted. The weight of coke was evaluated as the weight loss after solid calcination at  $600^\circ\text{C}$ , because the solid products contained  $\text{CeO}_2$  nanocatalyst as well as coke. Morphology of solid residue (including coke, inorganics and  $\text{CeO}_2$  nanoparticles) was observed via transmission electron microscopy (TEM, Hitachi H7650) on a copper mesh. Moreover microanalysis of solid using an energy dispersive X-ray spectroscopy (EDX) was performed. The

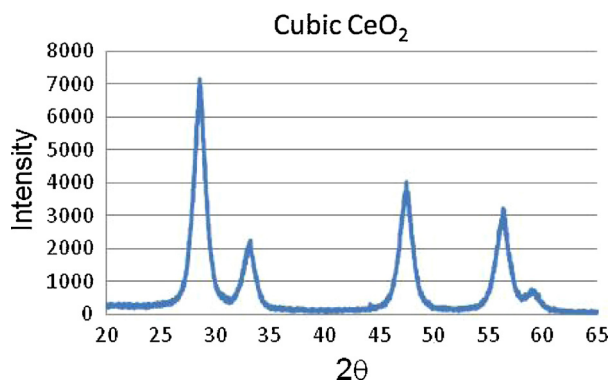


Fig. 1. XRD analysis of CeO<sub>2</sub> before and after reaction.

proportion of coke formed in the solid phase is calculated with the following equation:

$$\%C = \frac{m_{\text{Coke}}}{m_{\text{solide recovered}}} \quad (2)$$

An XRD analysis is made before and after reaction to check the composition of the catalyst (Fig. 1).

### 3. Results and discussion

Black liquor is a waste alkaline solution containing valuable organic compounds (thiolignin) and a large amount of water. Hydrothermal conversion of black liquor was studied at sub (350 °C, 25 MPa) and supercritical (450 °C, 25 MPa) conditions. The catalytic effect was evaluated as regards to hydrogen production and carbon conversion using either or not CeO<sub>2</sub> nanocatalyst. Liquid phase is also investigated to elucidate secondary reactions occurred between gas phase and molecules formed in liquid phase. Then in a third part, catalytic effect of CeO<sub>2</sub> is discussed by comparing sub and supercritical media.

#### 3.1. Supercritical conditions

Experiments at supercritical conditions were carried out in 5 mL batch autoclaves at 450 °C, 25 MPa. Reaction time of 15 min and 60 min, as well as the amount of catalyst, were investigated. The catalytic effect was evaluated towards coke formation and hydrogen production.

To highlight the reactions involved, the liquid is also analyzed and compared according to the operating conditions.

##### 3.1.1. Coke formation

Black liquor is mainly composed of dissolved lignin. During hydrothermal conversion lignin is expected to be degraded into aromatics molecules [12] such as phenolic compounds and smaller molecules such as little aldehydes, glyceraldehyde, etc. Polymerization of the phenolic molecules takes place thanks to these smaller molecules, which connect aromatics components together. Coke formation was the result of this polymerization and was formed since the splitting of lignin molecule began [13].

The solid recovered was observed with TEM. As shown in Fig. 2, the solid is shapeless (Fig. 2). An EDX analysis was simultaneously realized showing the composition was carbon, oxygen and minerals; particularly sulfur (darkest spots on Fig. 2) but minerals recovered in the solid phase are not involved in the morphology of the carbonaceous material as seen previously by Wu [14]. So, the coke recovered after reaction is composed of organic and mineral compounds that could influence the mass recovered. However as the proportion of minerals is low, the contribution of coke in the weight of solid residue is assumed to be the totality.

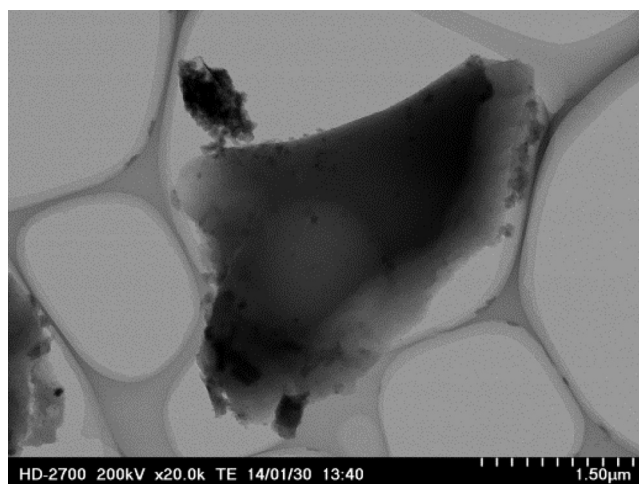


Fig. 2. solid obtained after 450 °C, 25 MPa, 15 min of reaction time, without catalyst.

Table 1

Proportion and weight of coke formed after reaction at 450 °C.

	$m_{\text{coke+cat}} = (\text{g})$	$\%_{\text{coke formed}}$	$m_{\text{coke}} = (\text{mg})$
60 min R=5	3.31E-02	13.87%	4.59
60 min	1.17E-02		11.7
15 min R=5	1.00E-03	54.55%	0.50
15 min	1.00E-03		1.00

The amount of coke was evaluated for the set of experiments and summarized in Table 1. The mass of coke produced during the reaction is about two times lower with using CeO<sub>2</sub> catalyst. This result confirms that the use of catalyst reduces the coke formation. However, the amount of coke is ten times higher by increasing the reaction time. This same order of magnitude is observed using either or not the catalyst.

Using supercritical conditions, radical reactions are favored and result in the efficient degradation of lignin into phenolic compounds. As a result, several condensation reactions [15] are expected to take place and explain this non negligible amount of coke formed. Reaction time increased these phenomena; results Table 1 confirmed that point.

Indeed, as described previously, CeO<sub>2</sub> catalyst is able to oxidize organics more efficiently or rapidly than supercritical water. Thus, the whole organics (aromatic and aliphatic molecules) are subjected to efficient oxidation reactions. Small molecules such as aldehyde, are known as promoter for polymerization of phenolic compounds [13]. In presence of catalyst, the kinetics of aldehyde oxidation is expected to be enhanced that results in a decrease of polymerization reactions if the oxidation is complete and then a decrease of coke formation. Simultaneously, this complete oxidation of aliphatic compounds would increase the amount of CO<sub>2</sub> released in the gas phase.

##### 3.1.2. Gas formation

The gas phase is analyzed directly after reaction. For each condition, gas phase is composed of H<sub>2</sub>, CO, CO<sub>2</sub>, and light hydrocarbons. However the proportion changes slightly regarding parameters studied (reaction time and catalyst). Indeed, reaction time, as well as the catalysts, played an important role in the carbon conversion and enhanced the gasification particularly H<sub>2</sub> production. Moreover a large amount of CO<sub>2</sub> is dissolved as carbonates due to the pH of the remaining solutions which are equal to 10.

Fig. 3 presents the proportion of carbon recovered in gas phase versus reaction time. The main part of carbon in the gas phase was CO and CO<sub>2</sub>, which were produced from the oxidation and

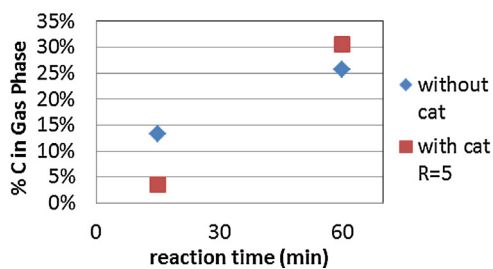


Fig. 3. Proportion of carbon converted into gas phase at 450 °C, 25 MPa.

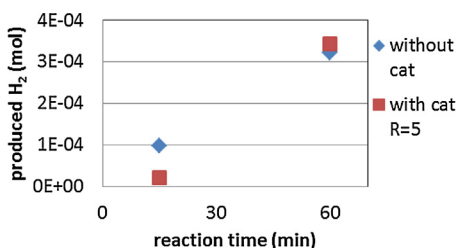


Fig. 4. H<sub>2</sub> produced into gas phase after reaction at 450 °C, 25 MPa.

water–gas shift reactions. Fig. 3 shows that the amount of carbon in gas phase increases with reaction time using or not the catalyst.

At long reaction time, the analyses of the gaseous phases obtained by micro chromatography indicated that the compositions of both gaseous products are almost similar. The main difference concerns the amount of carbon dioxide, and to a lesser extent carbon dioxide and methane, in the catalytic experiment. CO, CH<sub>4</sub> and CO<sub>2</sub> are thus increasing the amount of carbon recovered in the gaseous phase as shown in Fig. 3.

As regards to the catalytic effect, Fig. 3 shows that the amount of carbon converted to the gaseous phase is slightly higher at long reaction time (60 min). At short reaction time, carbon conversion to gas phase is surprisingly lower using catalyst. Indeed the gas produced using catalyst contains six times fewer methane and three times fewer CO<sub>2</sub> and light hydrocarbons. Moreover the amount of CO was under the detection limit and was not quantified using catalyst. This means that the oxidation is quite achieved in gas phase. As the volume of gas produced is almost the same in both experiments, the amount of carbon is thus lower using catalyst and would be due to concurrent reactions. Indeed the amount of oxygen in gas phase is triple using catalyst and reaches 145 μmol. Taking into account the role of catalyst on water splitting, these results would indicate that oxygen active species are recombined into O<sub>2</sub>. These results indicate that the carbon gasification efficiency using catalyst is affected by reactions between oxygen active species. Kinetics of reaction between oxygen active species is expected to be higher than that of oxygen active species on organics, for short reaction time. This result underscores that the recombination of oxygen activated species could be a preliminary reaction in the global oxidation reaction on organics. Nevertheless, for a higher reaction time (450 °C–60 min), competition occurs between water gas shift reaction and extreme oxidation of organic molecules that released of CO<sub>2</sub> also. This double production generates more CO<sub>2</sub>. After reaction equilibrium between liquid and gas should occurs and limits the capture of CO<sub>2</sub> in the liquid phase, which explain the existence of CO in gas phase and more amount of CO<sub>2</sub> in the presence of catalyst.

Considering the global reaction of CeO<sub>2</sub> on hydrothermal conversion, this catalyst increased the conversion of carbon into CO<sub>2</sub> by promoting oxidation and water gas-shift reactions.

During the catalytic hydrothermal conversion of black liquor, hydrogen activated species is also expected. Fig. 4 shows the

amount of H<sub>2</sub> produced for same operating conditions as previously. For a long reaction time (60 min), the amount of H<sub>2</sub> was slightly affected by the catalyst ratio ( $R=0$  or  $5$ ). The amount of H<sub>2</sub> obtained for this reaction time reached 345 μmol and 322 μmol using or not catalyst, respectively. Demirbas reported that more than 10 mol of H<sub>2</sub> was produced from 1 mol of black liquor if the formula C<sub>10</sub>H<sub>12.5</sub>O<sub>7</sub>Na<sub>2.4</sub>S<sub>0.36</sub> is considered [2]. Applying this calculation to our case, the maximal value of H<sub>2</sub> from black liquor gasification would be 360 μmol. Considering this value and CeO<sub>2</sub> activity, H<sub>2</sub> is expected to be higher. Nevertheless the amount of H<sub>2</sub> measured was related to its production and its consumption. Active hydrogen species that was produced from water splitting would easily and continuously react with another active hydrogen to form H<sub>2</sub>; as the amount of light hydrocarbons is lower using catalyst; the consumption of H<sub>2</sub> could be related to hydrogenation or/and capping reactions with organic molecules to form smaller molecules in liquid phase.

For short reaction time, the amount of H<sub>2</sub> is 5 times lesser using catalyst. This low amount of H<sub>2</sub>, while the amount of O<sub>2</sub> is high, indicated its consumption in other reactions. As described previously, the amount of light hydrocarbons is also lower using catalyst meaning that H<sub>2</sub> produced could be consumed in reactions such as hydrogenation in liquid phase.

To conclude, at long reaction time the catalyst improves carbon conversion, mainly for CO<sub>2</sub>, and H<sub>2</sub> production. At short reaction time, the catalyst has a strong effect on O<sub>2</sub> production while H<sub>2</sub> and C amounts in gas phase are lower than without catalyst. The proportion of carbon converted into gas phase suggested that exchange can occur between gaseous and liquid phase. In this case, hydrogenation reactions with liquid phase are supposed to play an important role.

### 3.1.3. Liquid phase

The original black liquor is dark brown. The color of the liquid phase obtained after reaction is linked to its conversion and the effectiveness of the catalyst.

At 450 °C, the liquid was yellow, almost transparent. The color became lighter with increased reaction time. The observed color variation was caused by the conversion of oligomer molecules to either smaller colorless molecules (such as acids, aldehydes, alcohols...), polycyclic (2 or 3) aromatics molecules and/or to solid residues. This observation was supported by gel permeation chromatography (GPC). GPC separates molecules towards their molecular weight. The profiles of the curves are plotted in Fig. 5, where the intensity is reported as function of the molecular weight. The profile obtained for black liquor indicates that molecules have mainly a molecular weight centered at  $\log M = 2.05$ . Moreover, a significant amount of molecules presents higher molecular weight up to  $\log M = 3.5$ . First, the profiles of liquids recovered after reaction is the sharp decrease of the number of molecules between a  $\log M$  of 2.7 and 3.5. Hydrothermal conversion, whatever the conditions used, is efficient to either convert organics into smaller structures (C removal) or hydrogenate molecules (O removal and H addition). Catalyst and reaction time are improving this phenomenon. Nevertheless this strong decrease could be also attributed to coke formation.

For experiments performed with catalyst, intensity at low molecular weight is higher, meaning that CeO<sub>2</sub> improved degradation of black liquor. At longer reaction time and using catalyst, the number of heavy molecules decreases while that of medium molecules increases with a molecular weight center at  $\log M = 1.77$  and explain the higher release of carbon to gas phase. Simultaneously, GC–MS analyses were carried out and confirmed that smaller molecules were detected in the presence of catalyst.

At 15 min: 3-butanolic acid; propane; 3-methyl butanal; phenol, etc.

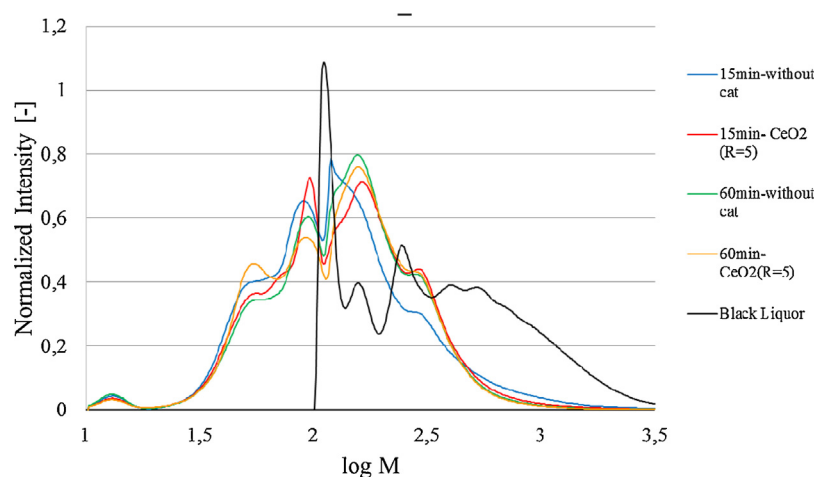


Fig. 5. catalyst influence on molecular weight at 450 °C, 25 MPa.

At 60 min: acetone; cyclopropane, 1-ethyl-2-methyl-, cis-; butanal, 3-methyl; phenol, etc.

The degradation of black liquor during reaction is confirmed by the presence of these smaller molecules. No molecules more oxidized were detected meaning that oxidation by  $\text{CeO}_2$  on the black liquor is a complete oxidation leading to the release of  $\text{CO}_2$  into gas phase.

The basicity of the liquid phase after reaction is preserved ( $\text{pH} > 10$ ),  $\text{CO}_2$  is captured by liquid phase until equilibrium between liquid and gas is achieved. The saturation of molecules in liquid phase does not change that it suggested no hydrogenation but capping reaction occurred.

#### 3.1.4. Conclusions about the catalytic effect of $\text{CeO}_2$ under supercritical conditions

$\text{CeO}_2$  nanocatalyst was selected to decrease coke formation and improve hydrogen production. The objectives have been achieved considering gas and liquid analysis. Under supercritical conditions splitting of water occurred efficiently, with the use of cubic  $\text{CeO}_2$ ; forming oxygen and hydrogen activated species. On the one hand, complete oxidation happened for smaller molecules to release  $\text{CO}_2$ . A first step of oxygen activated species recombination into  $\text{O}_2$  has to be considered. On the other hand, the hydrogen activates species seemed to react into homolytic reaction to form  $\text{H}_2$  and also into capping reaction to form smaller aromatics molecules.  $\text{CeO}_2$  improved water-gas shift reaction that can explain also the higher amount of  $\text{H}_2$ , higher amount of  $\text{CO}_2$  and lower amount of  $\text{CO}$ .

Under subcritical conditions properties of water are intermediate between atmospheric conditions and supercritical condition. In addition, most of the reactions occurred into liquid phase.

### 3.2. Subcritical conditions

Experiments at subcritical conditions were carried out in 5 mL batch autoclaves at 350 °C, 25 MPa. Reaction time of 15 min and 60 min, as well as the amount of catalyst, were investigated. The catalytic effect was evaluated towards coke formation and hydrogen production as previously.

#### 3.2.1. Coke formation

At 350 °C, under subcritical conditions, reaction media is made by the mixture of three phases: aqueous phase, oily phase and gaseous phase. Due to the pressure, it assumed that the gaseous phase is minority. During the conversion, polymerization of phenolic compounds occurred, and formed at macroscopic scale a nuclei non miscible with aqueous phase. Because of non-miscibility oily

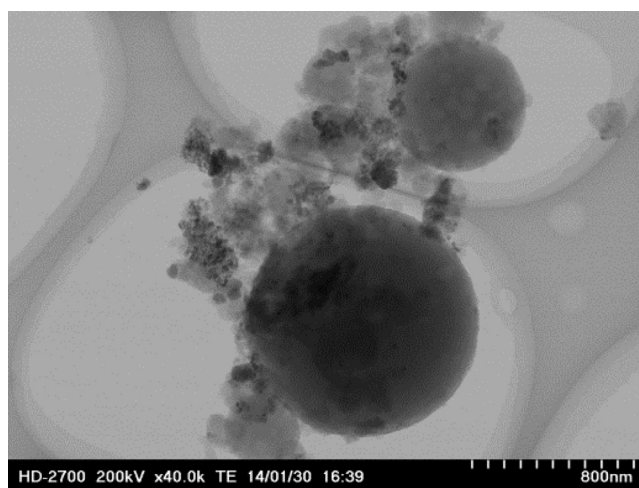


Fig. 6. Solid obtained after 350 °C, 25 MPa, 60 min of reaction time, without catalyst.

Table 2

Proportion and weight of coke formed after reaction at 350 °C.

	$m_{\text{coke+cat}} = (\text{g})$	%coke formed	$m_{\text{coke}} = (\text{mg})$
60 min R=20	9.85E-01	1.56%	15.4
60 min R=5	1.34E-01	3.81%	5.1
60 min	9.30E-03		9.3
15 min R=5	2.51E-01	2.70%	6.8
15 min	1.01E-02		10.1

drops appeared into aqueous phase to give the morphology of coke obtained under subcritical conditions: spherical micro-particles (Fig. 6). Coke from black liquor at 350 °C is still composed by carbon, oxygen and minerals. Sulfur (darkest spots on pictures) is still detected. Minerals are observed as independent crystals to the coke.

However, in the presence of catalyst, spherical particles disappeared and the amount of coke formed is less. Coke is not visible by TEM observation, only the nanoparticles of catalyst as shown in Fig. 7. Thus the coke is not recovered as particles but as deposit on the catalyst surface. Simultaneously, the color of the virgin catalyst changed from yellow to dark brown after reaction.

The mass of coke was also evaluated after experiments and summarized in Table 2. At both reaction times, the amount of coke is almost halved using the catalyst. The proportion of coke formed decreased in the presence of catalyst.

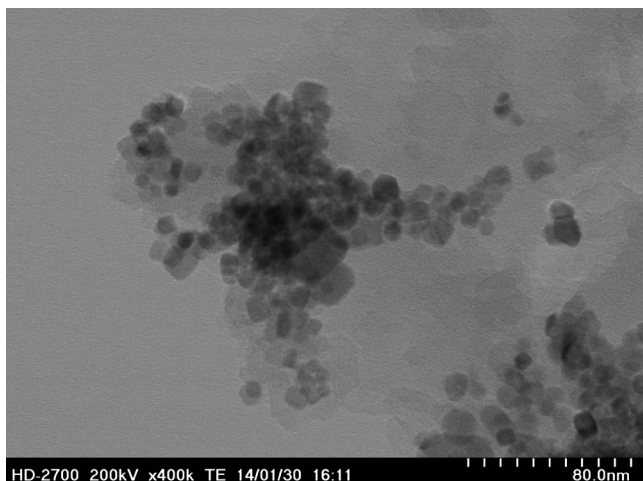


Fig. 7. Solid obtained after 350 °C, 25 MPa, 60 min of reaction time, with catalyst.

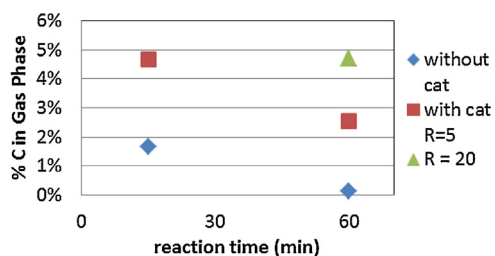


Fig. 8. Proportion of carbon converted into gas phase at 350 °C, 25 MPa.

A second experiment was carried out using higher catalyst ratio ( $R=20$ ) for 60 min reaction time. The total amount of coke formed was higher in mass (15.4 mg at  $R=20$  compared to 5.1 mg at  $R=5$ ) but lower in mass percentage in the solid (1.56 wt% compared to 3.81 wt% at  $R=20$  and 5, respectively). A hypothesis was an antagonist effect of  $CeO_2$  as catalyst and as carrier of coke formation. In addition, probably oxidation is not complete because catalyst efficiency is low under subcritical conditions and water properties are less optimal for reactivity.

Analyze of gas phase can give first information on the level of oxidation made by  $CeO_2$  on aromatics molecules regarding in particular carbon conversion.

### 3.2.2. Gas formation

After the experiments carried out at 350 °C, 25 MPa the volumes of the gaseous phases are quite similar meaning that it is not strongly affected by reaction time and catalyst. Fig. 8, shows that even if the amount of carbon species under subcritical conditions is low, the amount is higher with catalyst and confirmed that more carbon is converted into gas in the presence of catalyst. The low quantity conversion is due to subcritical temperature which improves reactions in liquid phase exclusively. Furthermore in these conditions water is enough reactive to react with  $CeO_2$ , which was confirmed by the rising amount of carbon converted into gas phase with increasing the ratio of catalyst.

Considering only the proportion of carbon converted (Fig. 8) in the gaseous phase, it is impossible to conclude significantly so the proportions are low.

Indeed, in subcritical conditions with catalyst, as coke is decreased, higher conversion of carbon into gas phase could be expected. The main compound is  $H_2$ , and to a lesser extent  $CO_2$  and  $CH_4$  are produced. Some light hydrocarbons were also detected in the gas produced. This tendency was in accordance with the lower quantity of gaseous products. Proportion of carbon at 350 °C can

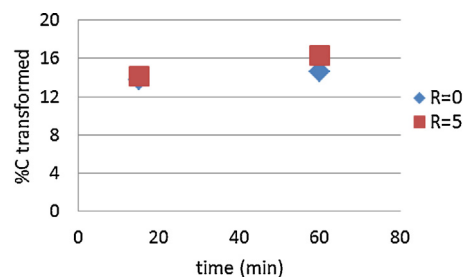


Fig. 9. Distribution of initial organic carbon in gas phase and dissolved carbonates at 350 °C, 25 MPa.

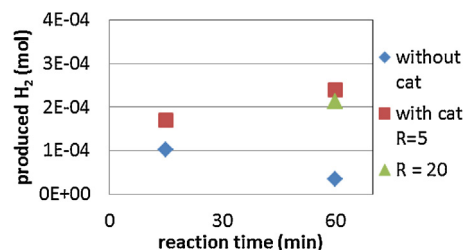


Fig. 10.  $H_2$  produced into gas phase after reaction at 350 °C, 25 MPa.

be also explained by the remaining basic pH of the solution that dissolves a large amount of  $CO_2$  in the liquid phase.

So to understand the catalytic conversion of black liquor under subcritical conditions, we choose to consider the percentage of initial carbon transformed and recovered in the gaseous phase, as well as dissolved carbonates (inorganic carbon in liquid phase) and presented Fig. 9. For both reaction times, the amount of organic carbon converted increased using the catalyst.

Under subcritical conditions, gas composition changes a little; depending on operating conditions but it is mainly composed of  $H_2$ ,  $CO$ ,  $CO_2$ , and light hydrocarbons. For example, concerning the total amount of  $CO_2$  (in gas phase and dissolved as carbonates), it is significantly higher using catalyst at higher reaction time. For short reaction time using the catalyst, the amounts of light hydrocarbons are 2 to 3 times higher while at higher reaction time, the amount of  $CH_4$  increased significantly in presence of catalyst (10 times higher). For short reaction time, carbon monoxide was also detected. Comparing Figs. 8 and 9, it is evident that under subcritical conditions,  $CO_2$  is formed but stored in liquid phase.  $CO_2$  stays in liquid phase as carbonates due to solubility equilibrium between gas and liquid phase. Indeed, at 350 °C, all the reactor volume is filled by black liquor solution. As with catalyst, the proportion of carbon is higher, the catalyst enhances the reactivity of the media.

Probably, the action of  $CeO_2$  on water under subcritical conditions is the same as supercritical conditions with lower effectiveness. Into subcritical conditions, in the same way as supercritical conditions, hydrogen active species can form directly  $H_2$  or react with organic molecules. Simultaneously, others probably reactions occurred in subcritical conditions like alkenes are formed and release  $H_2$  in gas phase by dehydrogenation reaction.

Fig. 10 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.

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 produced by water-gas-shift reaction and by hydrogenation reaction from alkane. However the increase in active hydrogen species would simultaneously increase reactions with organic molecules. Concerning the experiments carried out at 350 °C and 60 min, the amount of  $H_2$  was multiplied by 10 using

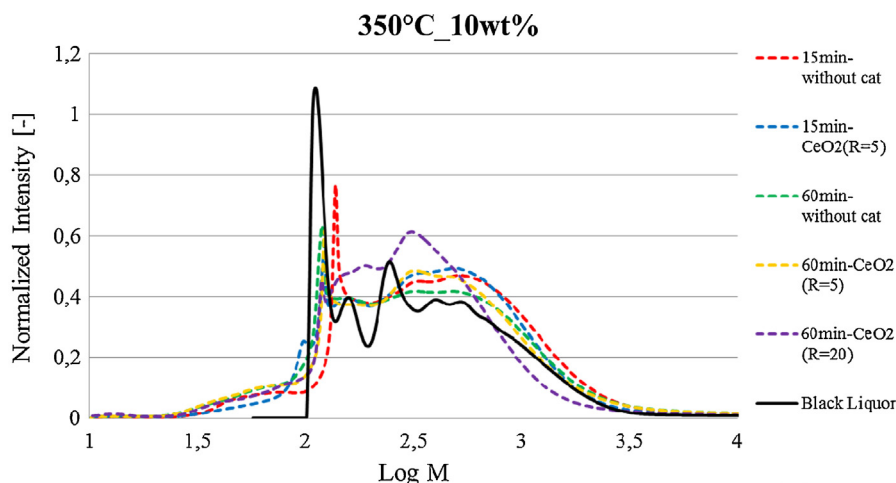


Fig. 11. Catalyst influence on molecular weight at 450 °C and 350 °C.

CeO<sub>2</sub> as a catalyst. This means that H<sub>2</sub> consumption was higher at long reaction time without catalyst while H<sub>2</sub> 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.

The amount of H<sub>2</sub> was not affected by the catalyst ratio ( $R=5$  or  $20$ , 350 °C and 60 min). As the amount of H<sub>2</sub> produced from water splitting would be higher especially for  $R=20$ , the mass transfer at the interface would be also enhanced by this high concentration. As a result, produced H<sub>2</sub> would be used for capping reaction in liquid phase to produce smaller molecules; also committed into hydrogenation/dehydrogenation reaction.

Conversion of carbon is not high at long reaction time that can suggested oxidation is not complete to release CO<sub>2</sub>. H<sub>2</sub> seemed to be limited or used with fast kinetics into reactions. The analysis of liquid phase should help to better understand.

### 3.2.3. Liquid composition

From gas phase analysis, black liquor conversion is expected to be less than under supercritical conditions. As the proportion of converted carbon is less also, partial oxidation of liquid molecules

is expected using catalyst. Regarding catalyst action, as previously, the focus is made on hydrogenation and oxidation reactions.

The oxidation of molecules is noticed; by GC-MS in the presence of catalyst, especially at 60 min;  $R=20$  and  $R=5$ ; with oxidized molecules like 1(3*H*)-isobenzofuranone, 6,7-dimethoxy-3-[2-(2-methoxyphenyl)-2-oxoethyl]. Alkenes were also detected (2-Methylphenylacetylene; 3,4,5-trimethyl-2-cyclopenten-1-one; 10,18-bisnorabieta-8,11,13-triene, etc) so reaction of dehydrogenation occurred in the same time as retroaldol reactions. As a result, these reactions compete with capping reactions. Probably kinetics (at 350 °C) for dehydrogenation reaction is higher than kinetics for capping reaction. This tendency can explain why the amount of H<sub>2</sub> remains the same. A high amount of aromatic compound was obtained into liquid and less coke was formed.

Some heavy molecules were remained into liquid phase (cf.: GC-MS results). This result was supported by liquid color. The deep color is due to the presence of phenolic compounds [7].

The liquid was still brown and no color variation was observed within the reaction time. The color became lighter with increased reaction time and for a high ratio ( $R=20$ ). These results mean that degradation is slow under subcritical conditions and most of

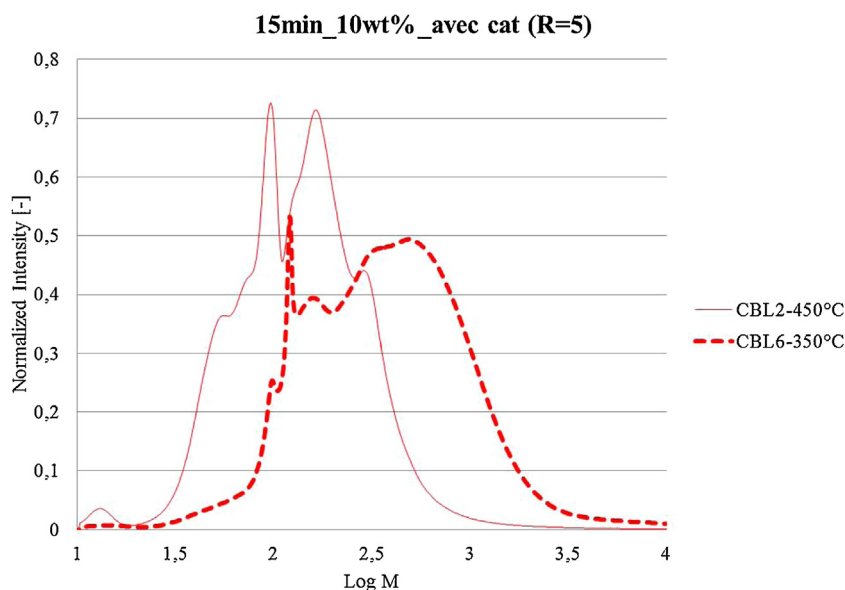


Fig. 12. Comparison of GPC results at 350 and 450 °C.  $t=15$  min and  $R=5$ .



molecules were still polycyclic molecules. This observation was supported by gas permeation chromatography (Fig. 11).

The main peak of  $\log M$  observed for original black liquor is slightly decreased using catalyst. The curve obtained after 15 min reaction time without catalyst presents a shift of the main peak to higher molecular weights. This significant increase of  $M$  would be due to O or C addition rather than H addition. For the whole set of conditions, the molecules in the region of  $\log M$  comprised between 2.2 and 2.5 seem to be particularly reactive as the peaks of the original BL are smoothed. However the intensity of  $\log M$  in the region of 2.5 to 3 suggests recovery of polycyclic molecules.

The shift of the curve for  $R=20$  means other populations of molecules were more represented. For this temperature, all curves are stackable to  $\log M=2$ ; so no smaller molecules are formed.

### 3.2.4. Action of $\text{CeO}_2$ in the conversion under subcritical conditions

Under subcritical conditions, splitting of water occurred by  $\text{CeO}_2$  making water more reactive. From results obtained, most of reactions were in liquid phase. On the one hand, H is used into hydrogenation/dehydrogenation reaction to form alkene and

saturated cycle like indane. On the other hand, O is used to oxidize molecules but under these conditions oxidation is partial. That can explain the low percentage of carbon that was converted into gas phase and into coke. Under subcritical conditions retro-aldol reactions occurred also that decreased the availability of small aldehyde to connect phenolic compounds into coke.

Action of  $\text{CeO}_2$  on water is the same under sub and supercritical reaction but main reactions differ between these both conditions

### 3.3. Comparison between the catalytic conversion of black liquor under sub-/supercritical conditions

#### 3.3.1. Carbon conversion

The quantity of coke was increased in the supercritical conditions; due to the efficiency of water under these conditions on the high degradation of lignin in phenolic compounds. Radical reactions were increased in supercritical conditions so a high level of condensation reaction is expected and explain that no negligible weight of coke is formed. Reaction time increased this phenomenon.

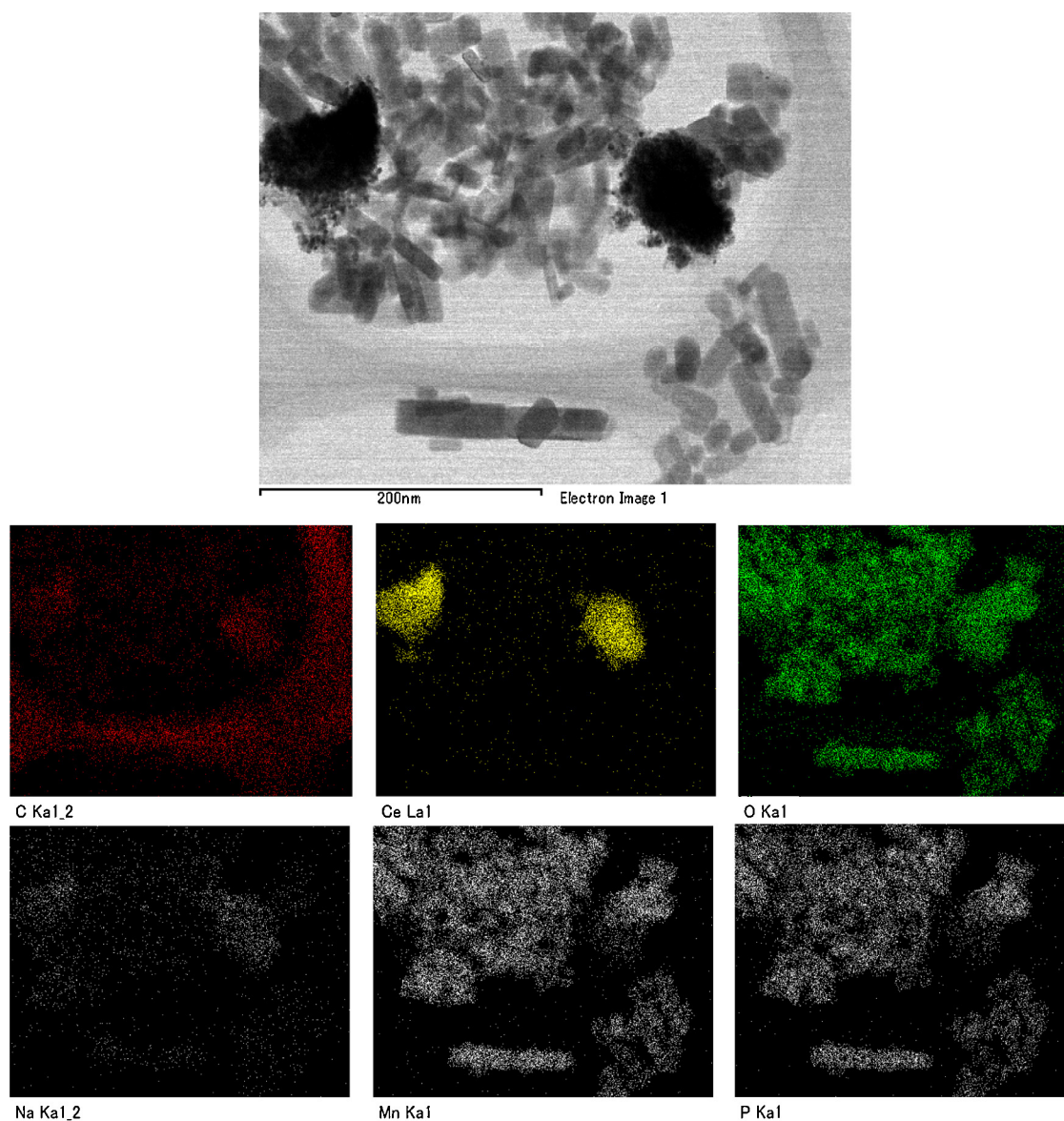


Fig. 13. TEM image (a) and micro-analysis (b)–(g) of solid recovered after experiment ( $450^\circ\text{C}$ ,  $t=60$  min,  $R=5$ ).

The degradation of organic carbon to gas phase (or inorganic carbon) is higher at 450 °C as expected. So gasification is favored under supercritical conditions. Indeed ~20 wt% of initial carbon is converted into gas phase at 450 °C whereas only 5 wt% max is converted into gas phase under subcritical conditions. This observation suggested that efficiency of catalyst is higher under supercritical conditions especially due to oxidation reactions. At the same time, the analyses of liquid phases (GPC, GC-MS and color) confirm the production of molecules with lower molecular weights at high temperature as reported in Fig. 12 (GPC results). As a result, partial oxidation was obtained at subcritical conditions while the process is more achieved at high temperature.

As regards to coke formation, for both temperatures, coke was formed (Tables 1 and 2); its quantity was increased in the supercritical conditions. 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). Indeed the mass of coke formed after 15 min reaction time is in the same order of magnitude for both temperatures (around 10% of initial organic content). On the contrary, the amount of solid at 450 °C

is higher for 60 min reaction time using the same calculation. For example, the mass of solid using catalyst represents 10% and 43% of initial organic content at 350 and 450 °C, respectively. Under subcritical conditions, amount of coke would be lower due to a combined effect of catalyst and retro-aldol reaction. Thus the efficiency of the catalyst towards the reduction of coke formation seems to be higher at subcritical conditions. The analysis of the solid morphologies reveals some differences. Indeed, Fig. 13a presents TEM images of solid recovered at 450 °C (60 min, using catalyst). A micro-analysis with EDX detector was performed and showed the presence of mineral content in the solid formation (Fig. 13b-f).

The pictures from Fig. 13a and b shows a rod-shape solid. However this rod-shape is not attributed to the carbonaceous solid (i.e. coke) as regards to C distribution (Fig. 13a and b). Oxygen is a main element recovered in the catalyst (Fig. 13c and d), as well as in the solid formed (Fig. 11b and d). However this solid formed is not only composed of carbon as minerals, such as Na, Mn, P (Fig. 13e-g) or Ca, S (not showed), are also recovered. These analyses highlight the high use of oxygen active species for oxidation or

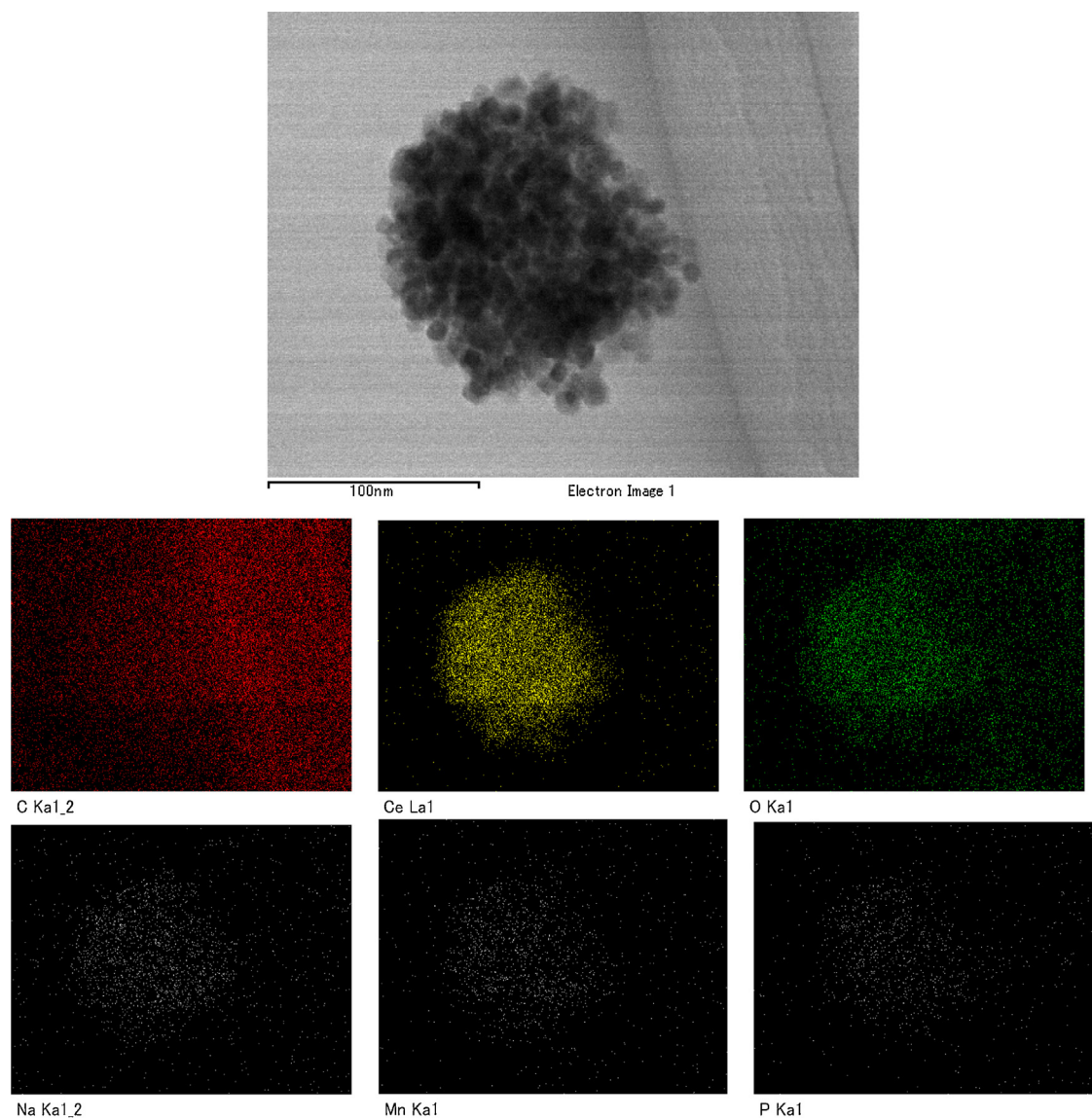


Fig. 14. TEM image (a) and micro-analysis (b)–(g) of solid recovered after experiment (350 °C,  $t = 60$  min,  $R = 5$ ).

complexation reactions, either with organics or minerals. To conclude, the solid obtained from catalytic conversion at supercritical conditions seems to contain higher amounts of minerals compared to carbonaceous material.

On the contrary, in the presence of cubic CeO<sub>2</sub>, carbonaceous solid was not visible by TEM but the cartography was able to measure some carbon (Fig. 14). Fig. 14 presents the TEM pictures and micro-analysis of solid residue recovered at subcritical conditions (350 °C, *t* = 60 min, *R* = 5). The shape of the solid recovered is different from that obtained at supercritical conditions. Fig. 14b and c shows that carbonaceous solid is dispersed on the catalyst. The amount of oxygen is still high but seems to be more distributed between organic and mineral solids. The amount of minerals, especially oxygenated compounds, seems to be lower at subcritical conditions. Aside from the quenching that would lead to high amounts of precipitate salts at supercritical conditions, oxygen species from water splitting seems to be less available for mineral oxidation at subcritical conditions. Thus the effect of catalyst towards oxygen release seems to be higher at 450 °C as regards to oxidation reactions in solid phase. In addition, the carbon conversion to solid phase requires an elemental analysis to be calculated. As regards to the local micro-analyses, the amount of solid recovered contains the mass of coke and minerals, and thus the value of 43% calculated previously is manifestly excessive.

### 3.3.2. H<sub>2</sub> production

As mentioned previously the effect of catalyst has to be evaluated towards coke inhibition and hydrogen production. To compare the results, the amount of H<sub>2</sub> produced (in μmol) was divided by the mass of organic content introduced (mg). The values obtained are close to 2 at subcritical conditions while this ratio reaches 10 to 40 at supercritical conditions. So the amount of hydrogen produced is clearly enhanced by temperature. Concerning the gaseous phase composition, light hydrocarbons with single bonds (C<sub>2</sub> and C<sub>3</sub>) are in higher concentration at supercritical conditions compared to C<sub>2</sub> and C<sub>3</sub> compounds with double bonds. On the contrary, concentrations of alkenes are higher than alkanes at 350 °C. So these results indicate that hydrogenation is enhanced at 450 °C. Hydrogenation reactions would be favored as the amount of hydrogen, such as hydrogen active species or dihydrogen, is higher at 450 °C.

Hydrogen formed by water splitting is used to react with organic molecules. Reactions pathways are guides by operating conditions. Under subcritical conditions, hydrogenation/dehydrogenation is favored whereas, under supercritical conditions, capping reaction is predominant.

## 4. Conclusion

The goal of the study was to investigate the catalytic effect of cerium oxide nanocatalyst towards hydrothermal conversion of black liquor. The use of catalyst would lead to an increase of hydrogen production and an inhibition of the coke formation. First the analyses of gaseous phases reveal that catalyst seems to improve hydrogen production, as well as the temperature and the reaction time. Although this amount at 450 °C, short reaction time and using catalyst was lower than without catalyst, the amount of hydrogenated products was increased. The produced coke without catalyst was lower than that with catalyst.

As expected, cerium oxide nanocatalyst is efficient to improve black liquor conversion.

As the trends observed for hydrogen concentration was not clearly defined, the mechanism or action of catalyst was also investigated. The hypothetic action was suggested through water splitting into hydrogen and oxygen active species. This active species are either able to react with organic and mineral

compounds (i.e. hydrogenation, oxidation) or with other actives species. Indeed, H<sub>2</sub> molecules can be formed by hydrogenation reaction from alkane or is released when dehydrogenation occurred. A part of these active species can react also with liquid molecules by capping to form smaller molecules (fewer complexes). GPC and color of liquid attested this degradation. Thus active hydrogen species leads to H<sub>2</sub> molecules, which could be involved in hydrogenation reaction to form alkane at high temperature or in the liquid at subcritical conditions. H<sub>2</sub> could be also released from dehydrogenation.

Active oxygen species are able to oxidize organic molecules that release CO<sub>2</sub> and CO at the final stages. The low amounts of CO suggested its consumption in water gas shift reaction; which was promoted by alkaline salts and CeO<sub>2</sub> catalyst. As the oxidation would be almost complete using catalyst, the amount of alcohols or aldehydes was limited compared to acids. When oxidation was extreme, some CO<sub>2</sub> was released to gas mixture; CO<sub>2</sub> was also due to the consumption of CO by the water gas shift reaction; which was promoted by alkaline salts and CeO<sub>2</sub> catalyst. Thus polymerization of phenolic compounds and aldehydes is limited.

We also noticed that the amount of O<sub>2</sub> and H<sub>2</sub> at 450 °C, short reaction time and using catalyst was significantly modified compared to the experiment without catalyst. Indeed, a high O<sub>2</sub> content was measured and hydrogenated products (such as alkanes) were identified. By increasing reaction time, O<sub>2</sub> would be used for oxidation reaction that increases CO, CO<sub>2</sub> and intermediates of oxidation. In the same way the amount of mineral oxide in the solid phase seems to be favored by catalyst and temperature increase. Moreover the ratios between oxygen (or hydrogen) and initial organic content showed that the reaction were improved at high temperature where the splitting would be favored. So the water splitting into active species would be suitable to describe the system.

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