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1 A study on Supercritical Water Gasification of Black Liquor  
2 conducted in Stainless Steel and Nickel-Chromium-Molybdenum  
3 reactors.

4

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7

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### 3 **ABSTRACT**

#### 4 *BACKGROUND*

5 Supercritical Water Gasification (SCWG) is presented here as an alternative treatment process  
6 for black liquor. In this research work, tests were done at different temperatures (500, 600 and  
7 700°C) at a pressure of 25MPa. The effect of temperature and catalysis on the gasification  
8 efficiency was investigated.

#### 9 *RESULTS*

10 The obtained yield and hot gas efficiencies increase with temperature while char and tar  
11 significantly decrease with it. Methanation was shown to be promoted at high temperature by  
12 Nickel catalyst and appeared faster than steam reforming in SCWG of black liquor. The  
13 addition of hydrogen on the double bond of ethylene was demonstrated to be an important step  
14 during the formation of methane. Water gas shift reactions were displaced toward the formation  
15 of CO<sub>2</sub> while the methane yield at higher temperature was favored by catalysis of Nickel-  
16 Chromium-Molybdenum alloy. CO<sub>2</sub> generation was enhanced at lower temperatures while at  
17 higher temperatures the thermal decomposition to low-weight carboxylates followed by  
18 decarboxylation was favoured producing hydrogen and methane. MS results gave information  
19 on the degradation process, char and tar formation and that heterocyclic compounds could be  
20 present in the liquid products as well as products from cyclization of acids.

#### 21 *CONCLUSIONS*

22 Results on black liquor and sucrose gave important conclusions regarding the effect of  
23 constituents. Alkali metals promote methanation reactions while nickel catalyst promote  
24 decarboxylation of high-weight organics, methanation and steam reforming at low temperature.

1 Results demonstrated that water is a reactant and it is not only the medium in which the reactions  
2 take place.

### 3 **KEYWORDS**

4 Supercritical Fluids, Wood Industry, Energy, Biomass.

### 5 **Introduction**

6 Due to the sustainability issues of fossil fuels, biomass feedstock is considered to be a potential  
7 replacement for energy supply and chemical production. Rather than 1<sup>st</sup> generation biorefinery,  
8 organic wastes could be utilized through the integration of biorefinery with industrial processes.  
9 For instance, black liquor - side stream of pulping process - has a very good potential for this  
10 purpose: it has 50% of the organic matter present in wood<sup>1</sup> along with a large number of  
11 different organic compounds including polysaccharides, carboxylic acids and extractives. ~~The~~  
12 ~~overall production of black liquor is estimated to be 240 million tons in the world annually;~~  
13 ~~furthermore, Kraft pulping process accounts for almost 60% of all pulp production.~~ In Finland,  
14 the utilization of black liquor for energy purposes accounted in 2002 for the 46% of the entire  
15 energy produced by biofuels and the 11% of the total heat and power generation<sup>2</sup>.

16 The commercial treatment of black liquor in recovery boilers has energy efficiency issue despite  
17 being considered as feasible for large-scale wood mills. This process requires evaporation and  
18 heating in order to concentrate black liquor for combustion and to enable spraying by  
19 overcoming the viscous forces<sup>3</sup>. These two steps are energy demanding operations. In addition,  
20 this treatment method has operational issues related to the transfer of highly viscous liquid, such  
21 as fouling on heat transfer surfaces and blockage in pumps. As a matter of fact, deposition of  
22 sodium carbonate and sodium sulphate salts can occur together with other forms of fouling like  
23 sodium oxalate and calcium carbonate deposition<sup>4,5</sup>. The production capacity of pulping mills  
24 could be limited by these operational issues; therefore, in case of a need to increase the capacity,

1 the only way is to build an additional recovery boiler unit with the evident risks. The recovery  
2 boilers are also limited by the heat release characteristic of the boiler; therefore, the same  
3 limitations are present regarding the mass flows and additionally to the energy flows.

4 The recent investigations mainly present two alternatives for black liquor treatment:  
5 gasification<sup>6</sup> and partial wet oxidation<sup>7</sup>. The gasification produces syngas which can either be  
6 utilized for electricity generation through gas engines or biofuel production. The gasification  
7 provides higher power efficiency compared with the commercial boiler combustion/Rankine  
8 cycle steam power plant. On the other hand, black liquor gasification also requires evaporation  
9 as pre-treatment, thus raising the same operational issues with the recovery boiler treatment.

10 Alternatively, partial wet oxidation of black liquor presents an opportunity to produce valuable  
11 chemicals – carboxylic acids or salts of those acids - through exothermic reactions. Wet  
12 oxidation phenomena occur in liquid phase, thus no requirement of evaporation. However, the  
13 separation of downstream can give low acid and salt recovery due to dilute outlet<sup>8</sup>.

14 Another alternative for black liquor treatment is represented by Supercritical Water Gasification  
15 (SCWG). During SCWG of biomass, the organic material is gasified in water at supercritical  
16 conditions (pressure and temperature higher than 22.1 MPa and 374 °C)<sup>9</sup>. At these conditions,  
17 supercritical water (SCW) has several encouraging properties for future development of  
18 gasification technologies. It is a non-polar substance and an effective solvent for carbohydrates,  
19 gases and lignocellulosic compounds<sup>10</sup>, thus providing single phase reaction media without  
20 mass transfer limitation. SCW takes part directly into the reactions of biomass and contributes  
21 greatly to the recovery of inorganic compounds, salts and valuable chemicals since they are  
22 insoluble in SCW<sup>10,11</sup>. Additionally, SCW operates at relatively lower temperature than  
23 conventional gasification and is an ideal medium for processing hazardous chemical waste. As  
24 a result, SCWG is a very suitable process for high-moisture feedstock in contrast to  
25 conventional gasification<sup>19</sup>, i.e. very promising potential for being integrated with pulp and

1 paper industry. Weak black liquor (downstream of pulping unit) can be treated directly in  
2 SCWG without pre-treatment of evaporation<sup>6</sup> to produce syngas with high methane and  
3 hydrogen content. Furthermore, the method offers great possibilities for new ways of reactors  
4 design and operations<sup>12</sup>.

5 The reaction mechanism of thermal decomposition of biomass has five main steps:  
6 depolymerization of polymeric molecules (i.e. cellulose, hemicellulose and lignin),  
7 decomposition of monomers to intermediates, gasification of these intermediates, equilibrium  
8 reactions among gas species, and some other reactions involving solid carbon and salts. The  
9 depolymerization of cellulose gives first smaller polymers – such as cellobiose, cellotriose,  
10 cellotetraose – and then glucose. In addition, glucose generates fructose through isomerization  
11 reaction<sup>23</sup>. The hydrolysis of hemicellulose is also similar to cellulose with the monomers of  
12 mainly xylose and also mannose, galactose and arabinose. Investigations on the reaction  
13 kinetics show that hydrolysis rate becomes faster than the rate of further decomposition  
14 reactions under supercritical water conditions<sup>23,24</sup>; in addition, the reaction pathway after  
15 hydrolysis involve thermal decomposition of monomers. Therefore, depolymerization products  
16 have been studied in previous research works as model compounds for biomass feedstock  
17 constituents<sup>18,25–30</sup>. Sucrose is used in this study as a model compound of cellulose for  
18 preliminary tests in order to validate the apparatus and to have understanding about the reactions  
19 after hydrolysis. Similarly, isoeuganol is used as a model compound of lignin.

20 From the process viewpoint, the main parameters of SCWG are temperature, pressure,  
21 residence time and solute concentration. In previous studies<sup>13</sup>, reactors made of nickel,  
22 chromium and molybdenum were at 700°C and a significant increase in methanation was  
23 observed due to the metal catalysts. The reaction rate have been observed in literature to be the  
24 highest in presence of ruthenium, nickel, cobalt, iron and molybdenum<sup>14</sup>. Temperature was  
25 stated as the most influencing parameter by Y. Lu, 2012<sup>15</sup> and it is considered as more

1 influential than residence time, as also stated by Castello et al.<sup>16</sup> and Cao et al.<sup>17</sup>. In addition,  
2 the SCWG of sugars is not highly dependent on pressure in a range between 25-35 MPa<sup>18</sup>.  
3 However, further investigation is necessary for mature knowledge on reaction mechanisms and  
4 the influence of process conditions and catalysts, in order to enable process development. These  
5 facts guided the selection of conditions for the experiments of this study.  
6 The purpose of this study is to investigate the influence of black liquor constituents, catalyst  
7 and temperature on the SCWG phenomena through experimental data. First, the experiments  
8 were performed with sucrose, as a model compound for sugars, then with isoeugenol, as a lignin  
9 model compound, to determine the influence of temperature and constituents. Afterwards, as  
10 the main focus, SCWG of black liquor was experimented in two reactors, stainless steel and  
11 Nickel-Chromium-Molybdenum (INCONEL 625), in order to compare catalyst and  
12 temperature impacts together.

## 13 **2. Materials and Methods**

### 14 **2.1 Reactor Setup and Experimental Procedure**

15 Two tubular reactors with the same dimensions were tested. The reactors were made of stainless  
16 steel 316 and INCONEL 625. Table 1 shows the reactors' dimensions and Table 2 shows their  
17 composition. The major difference in reactor compositions occurs in iron, nickel, chromium  
18 and molybdenum. Stainless steel reactor has mainly iron and very less of other elements  
19 whereas INCONEL 625 reactor has nickel as the main element, higher content in other  
20 mentioned elements except iron. The reactor made of stainless steel was used as a reference  
21 reactor to have a better estimation of the catalytic effect given by the INCONEL 625 alloy.

22 Table 1. Dimensions of tubular reactors utilized for SCWG of biomass

Specification	Value
Internal diameter	1.1 cm
External diameter	2.5 cm
Length	50.8 cm

Length with couplings	58.4 cm
Design pressure	1379 bar
Capacity	81 ml

1

2

Table 2. Composition of catalytic and stainless steel tubular reactors

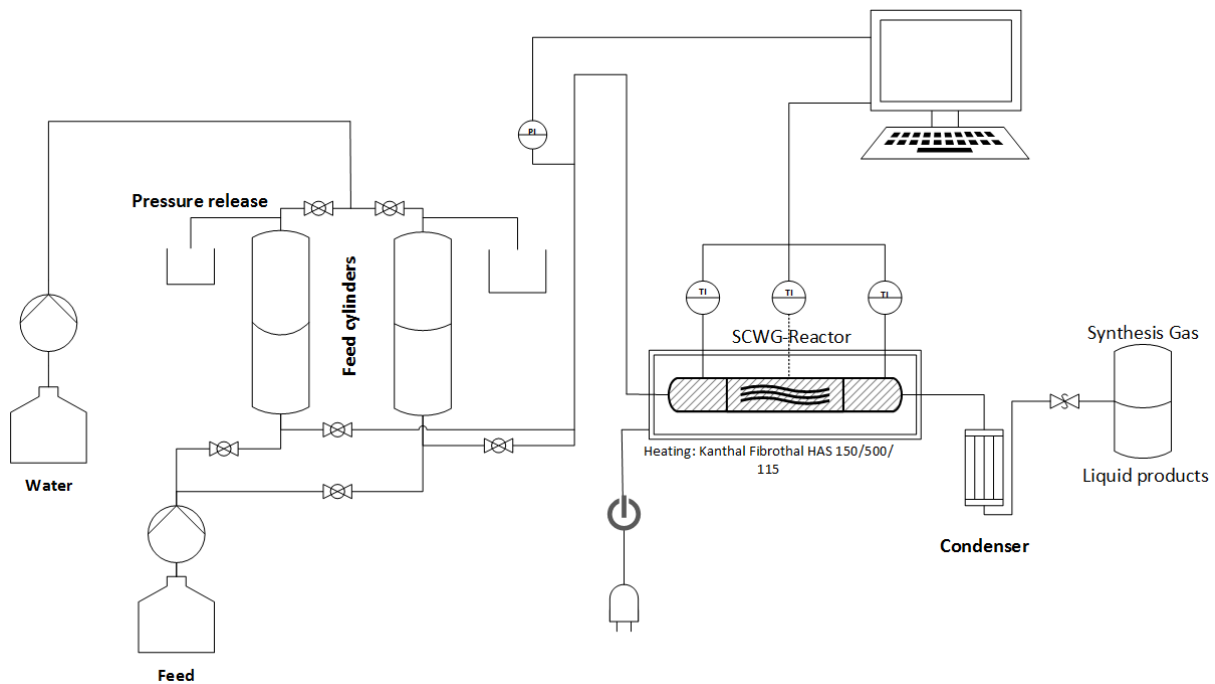
Material (wt%)	Stainless steel 316	Inconel 625 (High Nickel alloy containing Chromium)
C	0.01	0.037
S	0.02	<0.0003
Mn	1.48	0.04
Si	0.65	0.07
Cr	16.54	20.89
Mo	2.04	8.51
Co	0.14	0.1
Fe	69.4	4.53
Cu	0.28	0.03
Ni	10.20	61.36
P	0.022	0.006
Ti	-	0.31
Al	-	0.28
B	-	0.003
Zr	-	<0.01
Cb	-	3.78
Ta	-	<0.01
W	-	0.06
V	-	0.01

3

4 A description of the experimental apparatus is shown in Figure 1. In the feed system, the desired  
5 pressure is provided by water pumped through a high-pressure pump. This would allow for a  
6 greater flexibility and for continuous mode of operation. A similar solution for biomass feeding  
7 has been adopted in studies of SCWG of different kinds of feedstock<sup>15,20</sup>. The cylinders are  
8 made of stainless steel 316 L and have a maximum pressure tolerance of 40 MPa. The heating  
9 system surrounding the reactor consists of two semi-cylinder of Fibrothal, prefabricated heating  
10 modules with metallic heating elements and ceramic fiber insulation, from Kanthal. The unit  
11 power has a capacity of 2600 W. For temperature measurements, chromel-alumel K-type  
12 thermocouples with operating range of approximately -200 to 1350 °C were utilized. After the



1 reactor, a condenser was put in place and the system pressure was regulated by a back-pressure  
2 regulator.



3  
4 Figure 1. Flow diagram of the experimental setup.

5 The reactor was brought to the experimental temperature by electrical heating elements which  
6 were positioned within the insulation around the reactor. The heating rate was regulated to 0.04  
7  $\text{K}\cdot\text{s}^{-1}$  in order to minimize the thermal stress on the reactor metal. Then, biomass feed was  
8 inserted into the reactors through the feed cylinders. The Black Liquor (BL) samples as received  
9 were diluted with water to a final BL/water ratio of 0.35 by volume. The sucrose feed  
10 concentrations are given in Table 3 while the composition of BL as received is given in Table  
11 4. After gasification under supercritical water conditions, the product stream was cooled to  
12 room temperature and separated into gas and liquid products at atmospheric pressure. Finally,  
13 the gas and liquid samples were collected to be analysed. This operation was repeated for both  
14 feedstock materials with an inlet flow rate of  $6 \cdot 10^{-5} \text{ L}\cdot\text{s}^{-1}$  at the reactor temperatures of 500,  
15 600, 700°C under the same pressure of 25 MPa. Sucrose solution was tested only with stainless  
16 steel reactor whereas black liquor was tested in both reactors.

## 2.2 Feedstock and Product Analysis

The preliminary experiments were conducted with sucrose ( $C_{12}H_{22}O_{11}$ ) solution in water with the volume of 0.5 L. Table 3 shows the sucrose solutions used in SCWG experiments.

Table 3. Characteristics of the sucrose solutions

	Mass of Sucrose (g)	Molarity (M)	Weight (%)
MIX A → Test 500°C	11.69	0.068	2.32
MIX B → Test 600°C	23.00	0.134	4.52
MIX C → Test 700°C	13.16	0.077	2.61

Black liquor feedstock was obtained from a pulp mill using hardwood and softwood mixture as raw material with the weight fractions of 0.3 and 0.7, respectively. The black liquor sample as received was taken from the downstream of the pulping unit, without any treatment. Table 4 shows the analysis of the black liquor sample as received. The Brix degree was determined by refractometry analysis at a constant temperature of 20°C, while the conductivity was evaluated on the crude sample and also on a diluted sample at 24° Brix. The dry solid content was evaluated by drying of the sample in oven at 110°C and the ashes content was evaluated by drying at 750°C. The samples were treated for 16h.

Table 4. Physical analysis conducted on Kraft black liquor as received.

Components	Amount	Units
Alkali-soluble lignin, UV 280	162600	mg/L
Calcium, Ca, ICP	180	mg/kg
Iron, Fe, ICP	5.02	mg/kg
Potassium, K, ICP	8128	mg/kg
Sodium, Na, ICP	34171	mg/kg
Sulphur, S, ICP	15372	mg/kg
Silicon, Si, ICP	325	mg/kg
Molar mass, lignin, Mn, SEC	2572	
Molar mass, lignin, Mw, SEC	4532	
Molar mass, lignin, Peak maximum, SEC	2086	
Molar mass, lignin, PD, SEC	1.77	
Arabinose, acid hydrolysis, HPAE-PAD	1966.6	mg/L
Rhamnose, acid hydrolysis, HPAE-PAD	0.0	mg/L
Galactose, acid hydrolysis, HPAE-PAD	2387.9	mg/L
Glucose, acid hydrolysis, HPAE-PAD	575.5	mg/L

Xylose, acid hydrolysis, HPAE-PAD	4932.0	mg/L
Mannose, acid hydrolysis, HPAE-PAD	222.8	mg/L
Carbohydrates, acid hydrolysis, HPAE-PAD, total	10084.8	mg/L
Gross calorific value	14.4	MJ/kg
Ash 700°C (black liquor)	46.8	wt%
pH	13.3	
Brix	57	wt%
Conductivity	62.6	mS/cm
Dry solid content	41.7	wt%
Ashes	35.4	wt%
Density	1.19	kg/L

UV 280 refers to the spectroscopy at 280nm, ICP, Inductively Coupled Plasma mass spectrometric analysis; SEC, size exclusion chromatography; HPAE-PAD, High-Performance Anion-Exchange Chromatography with Pulsed Amperometric Detection.

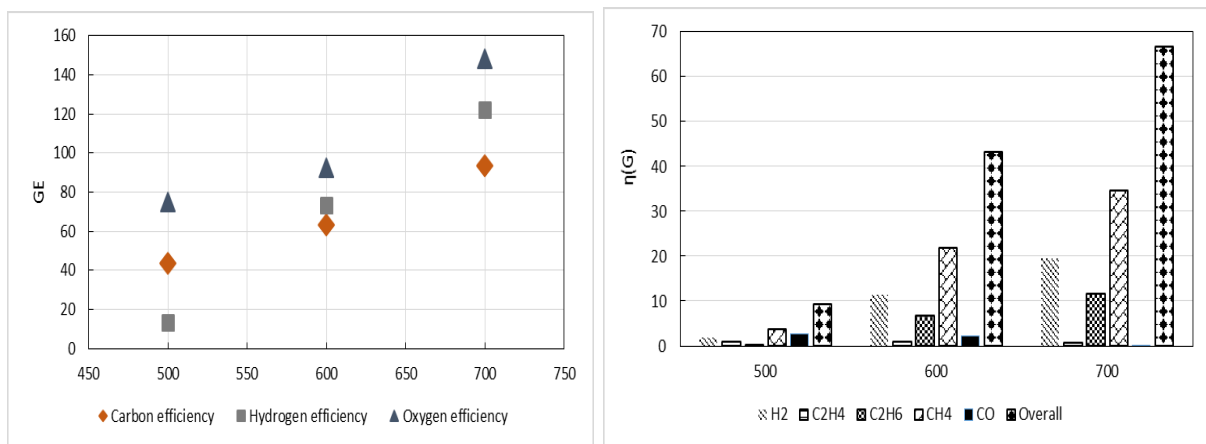
1  
2 The composition of gas products was analysed with a gas chromatograph, Perkin Elmer Clarus  
3 500 (with a TCD detector) by Arnel. The liquid products were analysed for organic content,  
4 nitrogen content and sugar, carboxylic acid contents and mass spectrometry. The TOC (total  
5 organic carbon) measurements, or more accurately under the conditions of this method as Non-  
6 Purgeable Organic Carbon (NPOC), is carried out by means of the TOC-V CPH analyzer  
7 produced by Shimadzu. In addition to the TOC, the organic matter content has been also  
8 verified in terms of COD (chemical oxygen demand) following the Finnish standard procedure  
9 SFS 5504<sup>21</sup>. The analyses on the nitrogen content followed the SFS-EN ISO 11905-1<sup>22</sup> and the  
10 standard method 4500 B. Mass Spectrometry, MS, analyses were conducted on a Waters  
11 Micromass LCT Premier with ionization method ES+ on the SCWG products obtained from  
12 Kraft black liquor samples at temperatures of 500°C, 600°C and 700°C. Low-molecular-weight  
13 carboxylic acids, alcohols and sugars are quantified through High Pressure Liquid  
14 Chromatography, HPLC. The instrument used was a WATERS 2690 Alliance with a Refractive  
15 Index Detector WATERS 2414, Column Hi-Plex H with the size of 300 x 7.7mm; column  
16 temperature as 65 °C and a flow of 0.6 ml·min<sup>-1</sup>. The eluent is 0.005 M H<sub>2</sub>SO<sub>4</sub>. Liquid product

1 samples had already the pH values of the required range for analysis (5 to 9); therefore, acid  
2 treatment was not applied to those samples. The samples were filtered through 0.2 $\mu$  filters.

### 3 **Results and Discussion**

#### 4 *SCWG of Sucrose*

5 In this study, sucrose has been tested as a model compound of sugars in the absence of the lignin  
6 and alkali metal constituents in black liquor.



7

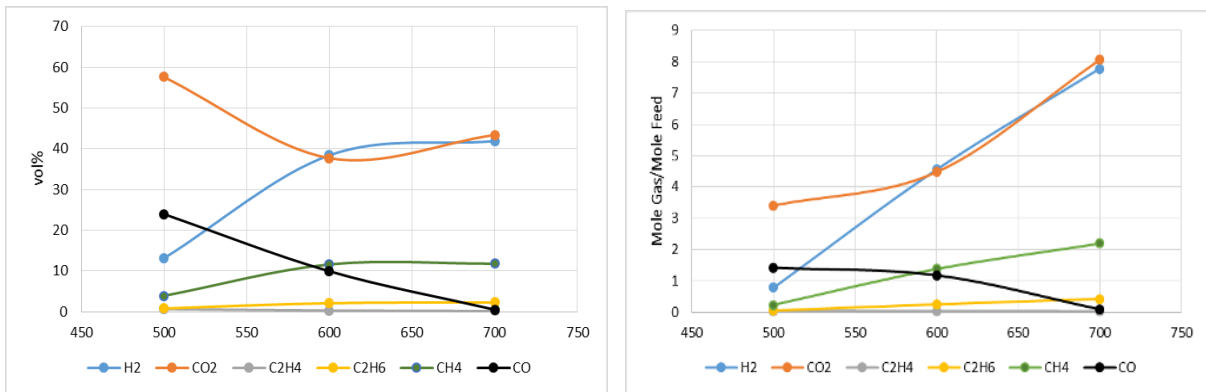
8 Figure 2. Left: Carbon, hydrogen and oxygen gasification efficiency, (CGE, HGE, OGE).  
9 Right: Energy recovery expressed as Hot Gas Efficiency, HGE\*.

10

11 Figure 2 shows the Hot Gas Efficiency,  $\eta(G)$ , and gasification efficiencies of carbon, hydrogen  
12 and oxygen at different temperatures. For the  $\eta(G)$  estimation, the sensible heat of the gas  
13 produced is taken into account together with the heating value, while the heating value of the  
14 feed is calculated on a dry basis<sup>31</sup>. Higher Heating Values, HHVs, of ethylene, ethane, carbon  
15 monoxide, methane and hydrogen are taken from Domalski<sup>32</sup>. The gasification efficiencies  
16 (CGE, HGE, OGE) were calculated as the ratio of the total moles of each element in the gaseous  
17 products on the total moles of the same elements in the dry feed. Carbon efficiency is usually  
18 mentioned as a measure of the gasification degree of the process and it is reported to always  
19 increase with the temperature. Efficiency values increase with temperature as expected. The hot

1 gas efficiency increases with temperature and reaches a value of nearly 65 % at 700 °C. It is  
 2 noticeable that hydrogen and methane have the major role in this trend, besides ethane  
 3 becoming significant at higher temperature.  
 4 In addition, it is important to notice that the gasification efficiency of oxygen and hydrogen  
 5 increases over 100%, i.e. there is more hydrogen and oxygen in the gaseous products than in  
 6 the dry biomass portion of the feedstock. These efficiency values determine the participation of  
 7 water to the gasification reactions and prove that more water reacts to form gases than the  
 8 amount produced in the whole reaction mechanisms. Hydrolysis and steam reforming are the  
 9 major reactions consuming water while methanation produces it. Especially, hydrolysis  
 10 consumes much more water in lignocellulosic biomass gasification than in sucrose gasification,  
 11 due to polymeric structure. In the literature, these results are confirmed processing samples with  
 12 low concentration by weight, with this technology<sup>17</sup>.

13



14

15 Figure 3. Left: Volume percentage of different components in gas products against  
 16 temperature. Right: Gas product yields expressed as molar ratio.

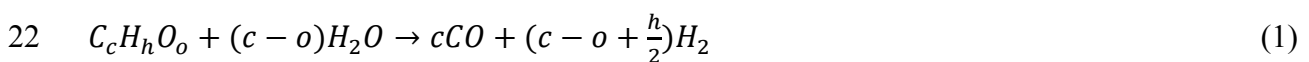
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18 Figure 3 illustrates the volume percentage of different compounds in the gas products and yields  
 19 as the molar ratio of each compound to the moles of dry sucrose in the feed. It can be noticed  
 20 that hydrogen and methane volume fractions increase with temperature while the fraction of  
 21 carbon monoxide decreases in the gas product. The volume fraction and yield of ethane also

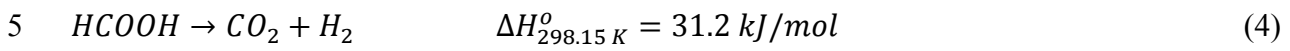
1 increase with temperature. This is a result consistent with the research work of Picou and co-  
2 workers<sup>28</sup> which had close conditions to the experiments in this study. In addition, the yield of  
3 carbon dioxide increases slightly while its fraction decreases with temperature.

4 Regarding the order of gas-generating reactions, carbon and oxygen gasification appears faster  
5 than hydrogen gasification. This statement is supported by the trends of atomic gasification  
6 efficiencies and composition of the gas product. Figure 2 shows that CGE and OGE are much  
7 higher than HGE at 500°C and increase slightly with temperature. In contrast, HGE sharply  
8 increases with temperature when biomass conversion increases. Furthermore, Figure 3 shows  
9 that CO<sub>2</sub> fraction is very high (close to 60%) and CO has the next highest fraction at 500°C;  
10 nevertheless, the fraction of CO<sub>2</sub> decreases with temperature whereas fractions of hydrogen-  
11 containing species increases with temperature. Similarly, yields of hydrogen-containing species  
12 have much sharper increase.

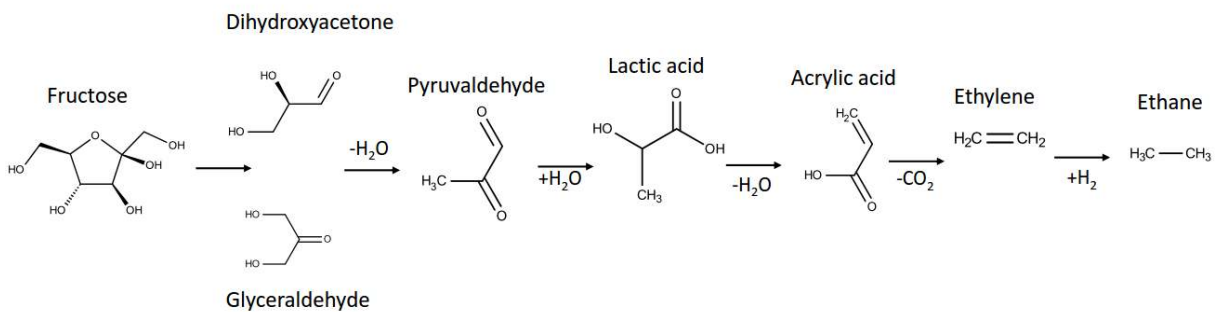
13 The formation of gas species start with the decomposition of monomers generated in hydrolysis.  
14 Glucose and fructose are decomposed to aldehydes, erythrose and 5-HMF (5-hydroxymethyl-  
15 2-furfural) which are then decomposed to carboxylic acids with subsequent release of water  
16 and carbon dioxide<sup>23,36</sup>. Xylose and arabinose, hydrolysis products of hemicellulose, are  
17 decomposed to glycolaldehyde, glyceraldehyde and furfural<sup>36</sup>. Then, the reactions continue  
18 with the reforming of the decomposition products of the monomers. This step produces the  
19 desired syngas; therefore, it is important to determine the process conditions enhancing this  
20 step. Equation 1 shows steam reforming of the decomposition products and monomers as  
21 general expression; Equation 2 shows the steam reforming of acetic acid as an example.



1 In addition, another type of reforming is the decarboxylation of carboxylic acids. Equation 3  
 2 shows the general form of decarboxylation reaction<sup>37</sup>, Equation 4 and 5 show examples of  
 3 decarboxylation of formic acid and acetic acid<sup>38</sup>.



7 At low temperature, faster gasification of carbon and oxygen than hydrogen indicates the  
 8 dominance of decarboxylation of acids with more than two carbons and thermal decomposition  
 9 reactions producing carbondioxide. In contrast, at higher temperature, sharp increase in HGE  
 10 indicates the decomposition of monomers to lighter intermediates (such as formic acid and  
 11 acetic acid) followed by decarboxylation of these light compounds, generating also hydrogen  
 12 or methane gases.



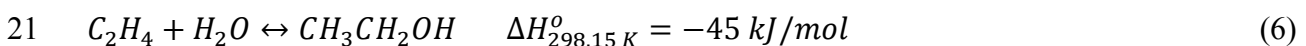
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Figure 4. Possible route of degradation of fructose in supercritical water

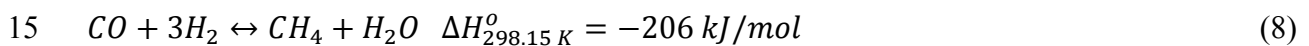
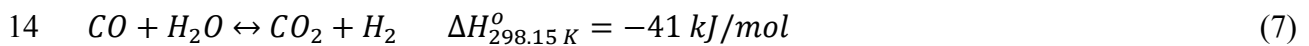
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16 Figure 4 illustrates the decomposition route of fructose. The ethylene formation from fructose  
 17 was reported in previous studies<sup>19</sup>; however, this study demonstrates a corrected route with an  
 18 additional reaction step of ethane formation. Hydrogenation of ethylene is an exothermic  
 19 reaction, with the standard-state reaction enthalpy of  $-136.3 \text{ kJ mol}^{-1}$ ,<sup>37</sup>. In addition, ethylene  
 20 can also react with steam to produce ethanol as shown in Equation 6.



1 As reported in this study, the concentration of ethane is larger than that of ethylene and the  
2 difference increases with temperature. Ethylene is reported as one of the ultimate degradation  
3 products of sucrose and glucose<sup>19</sup>; ethane formation in SCWG is usually missing in literature.  
4 In other words, ethylene will appear after (in order of formation) fructose or glucose,  
5 glyceraldehyde and glycolaldehyde, pyruvaldehyde, lactic acid, acrylic acid as also shown in  
6 Figure 4. The addition of water molecules on C-O bond generates carboxylic acids; then, further  
7 decomposition (decarboxylation reactions) generates carbon dioxide. For instance, the  
8 decomposition of acrylic acid generates carbon dioxide and ethylene. However, the results in  
9 this study imply that ethylene undergoes hydrogenation to form ethane. This trend is confirmed  
10 to be more significant at higher temperatures, considering the increasing trend of ethane and  
11 very low amount of ethylene in the gas product.

12 The main equilibrium reactions among gas species are water-gas-shift (WGS) and methanation  
13 reactions, as shown in Equation 7 and Equation 8, respectively.



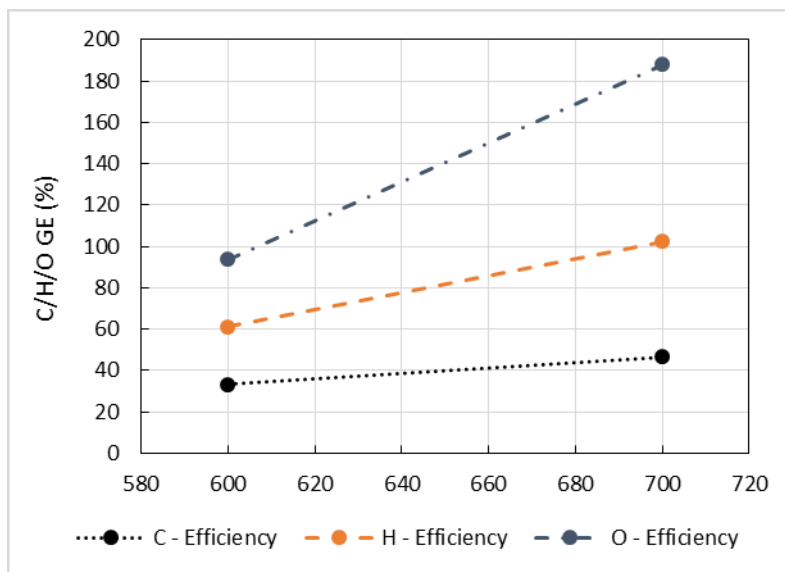
16 The yield and fraction of carbon monoxide reaches near zero at 700°C as shown in Figure 3.  
17 WGS reaction is very slow compared to the thermal decomposition of cellulose and gasification  
18 reactions of intermediates. Picou et al.<sup>33</sup> determined the parameters for the kinetics of the  
19 forward reaction, Equation 7, under excess water as first-order reaction with respect to carbon  
20 monoxide and Yakaboylu et al.<sup>34</sup> listed the parameters of reaction kinetics of thermal  
21 decomposition steps determined in the literature. The pre-exponential factor of WGS reaction  
22 is much lower than hydrolysis reactions and decomposition of monomers; only the  
23 decomposition of guaiacol (decomposition product of lignin) is slower. The decrease in  
24 equilibrium constant of WGS reaction with temperature does not shift the reaction towards  
25 carbon monoxide production due to excess water in the system; instead, the rate of WGS



1 reaction becomes influential. Considering the sharp increase in hydrogen yield and fraction, it  
2 can be concluded that water-gas-shift reaction rate becomes fast enough to give an influence at  
3 700°C. Furthermore, methane yield and fraction are very low at 500°C and increase with  
4 temperature, which implies promoted methanation reaction at over 500°C. However, methane  
5 yield and fraction increase slightly from 600°C to 700°C: this can also result from increase  
6 gasification efficiency, especially HGE increases very sharply with temperature.

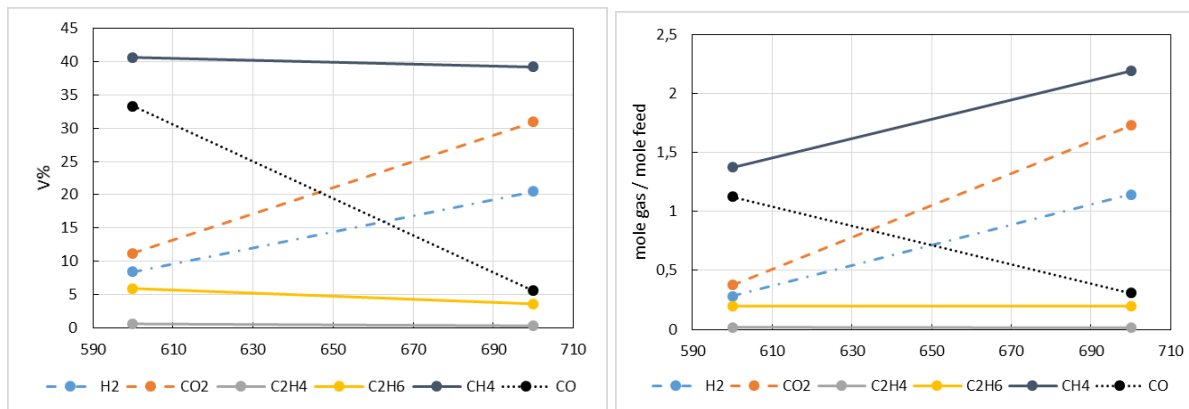
### 7 *SCWG of Isoeugenol*

8 In this study, isoeugenol has been tested as a model compound of lignin in the absence of other  
9 constituents of black liquor. Due to very low CGE at 500°C in sucrose results, isoeugenol is  
10 tested at higher temperatures, 600 and 700°C.



11  
12 Figure x. Carbon, hydrogen and oxygen gasification efficiency (add maybe hot gas efficiency)  
13 Figure x shows gasification efficiencies of carbon, hydrogen and oxygen at 600 and 700 °C.  
14 Gasification efficiencies increase with temperature. CGE increases slightly whereas sharper  
15 increase is observed for hydrogen and oxygen. CGE is relatively low: only around 45 % is  
16 reached at 700°C. Nevertheless, despite very low CGE compared to sucrose results, HGE and  
17 OGE are close to that in sucrose at 600°C and increase with temperature. Furthermore, since

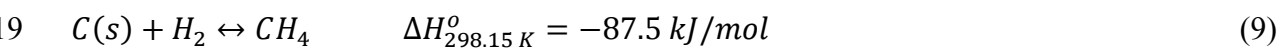
1 isoegenol has very low O/C ratio compared to sucrose, participation of water to reactions  
 2 increases OGE more dramatically.



3  
 4 Figure x+1. Left: Volume percentage of components in gas products. Right: Gas product  
 5 molar yields with respect to isoegenol in feed

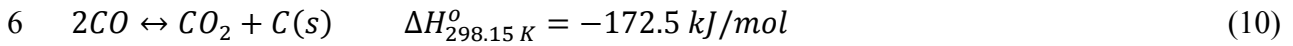
6 Figure x+1 illustrates the fractions and yields of gas species. The gas is methane-rich (around  
 7 40 %) and has high fraction of carbon monoxide as well at 600 °C. The yield and fraction of  
 8 carbon monoxide decrease with temperature; however, significant amount of carbon monoxide  
 9 remains in the gas product at 700 °C. The yields of methane, hydrogen and carbon dioxide  
 10 increase with temperature. The fractions of carbon dioxide and hydrogen increase so sharply  
 11 that methane fraction remains constant. In addition, ethane has significant fraction as well,  
 12 higher than sucrose results.

13 Thermal decomposition of lignin generates phenolic compounds (such as guaiacol, p-coumaryl  
 14 alcohol, coniferyl alcohol, sinapyl alcohol, catechol and phenol) and aromatic hydrocarbons  
 15 (such as benzene, toluene, naphthalene and their derivatives)<sup>24,xx</sup>. Dealkylation of these aromatic  
 16 and phenolic derivatives could play an important role in the formation of methane in high  
 17 amount and significant amount of ethane and ethylene (which also generates ethane through  
 18 hydrogenation). In addition, due to char formation, methane can be generated by the reaction:

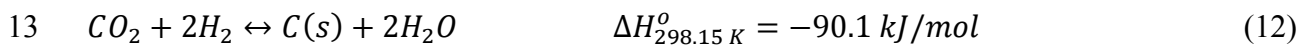
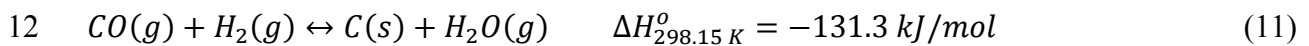


20

1 Char and tar formation occurs in SCWG in the presence of lignin through pyrolysis of lignin  
 2 and re-polymerization of phenolic or aromatic intermediates<sup>xx</sup>. Yong and Matsumura<sup>24</sup>  
 3 obtained high yield of char when investigating the kinetics of lignin decomposition under SCW.  
 4 In addition, the disproportionation of CO, also known as the Boudouard-Bell reaction, could  
 5 also be taken into consideration<sup>41</sup>:



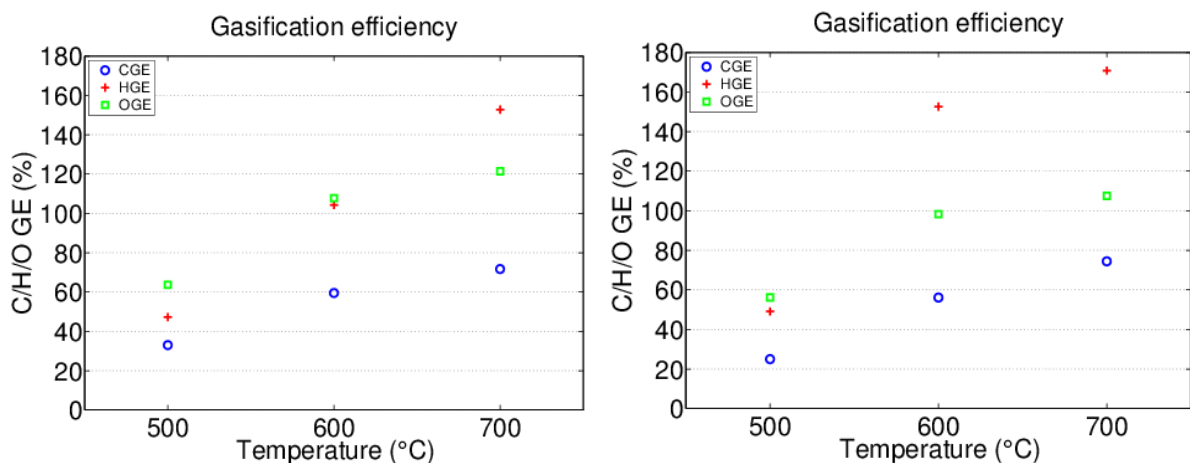
7 The disproportionation of carbon monoxide is seldom taken into account in SCWG studies; this  
 8 reaction presents a higher value for the equilibrium constant in the temperatures between 400°C  
 9 and 500°C. The equilibrium described above is considered to be shifted on the left side (CO  
 10 formation) for temperatures above 680°C<sup>28</sup>. Additional reactions producing coke and char are  
 11 the coke gasification reactions<sup>13,42</sup>:

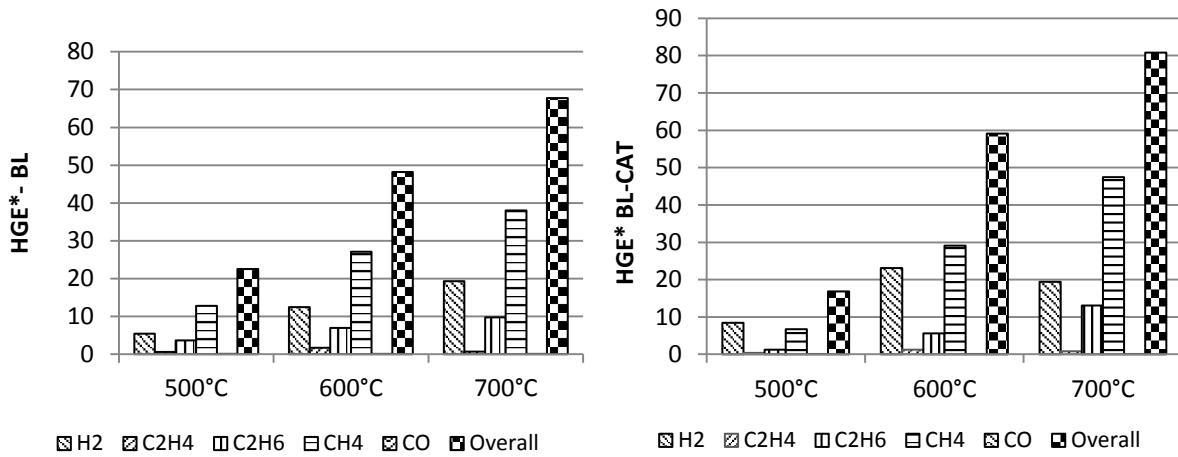


14 Considering that WGS reaction is fast enough at 700 °C, significant carbon monoxide fraction  
 15 could result from steam reforming and gasification of char and coke.

### 16 SCWG Black Liquor

17 SCWG of black liquor is tested to investigate the impact of temperature and catalyst on process  
 18 efficiency and yield. Figure 5 shows the HGE\* and gasification efficiencies in syngas.





1

2 Figure 5. Gasification efficiency and HGE\* - Left: SCWG of black liquor in the stainless steel  
 3 reactor, Right: SCWG of black liquor in the INCONEL 625 reactor.

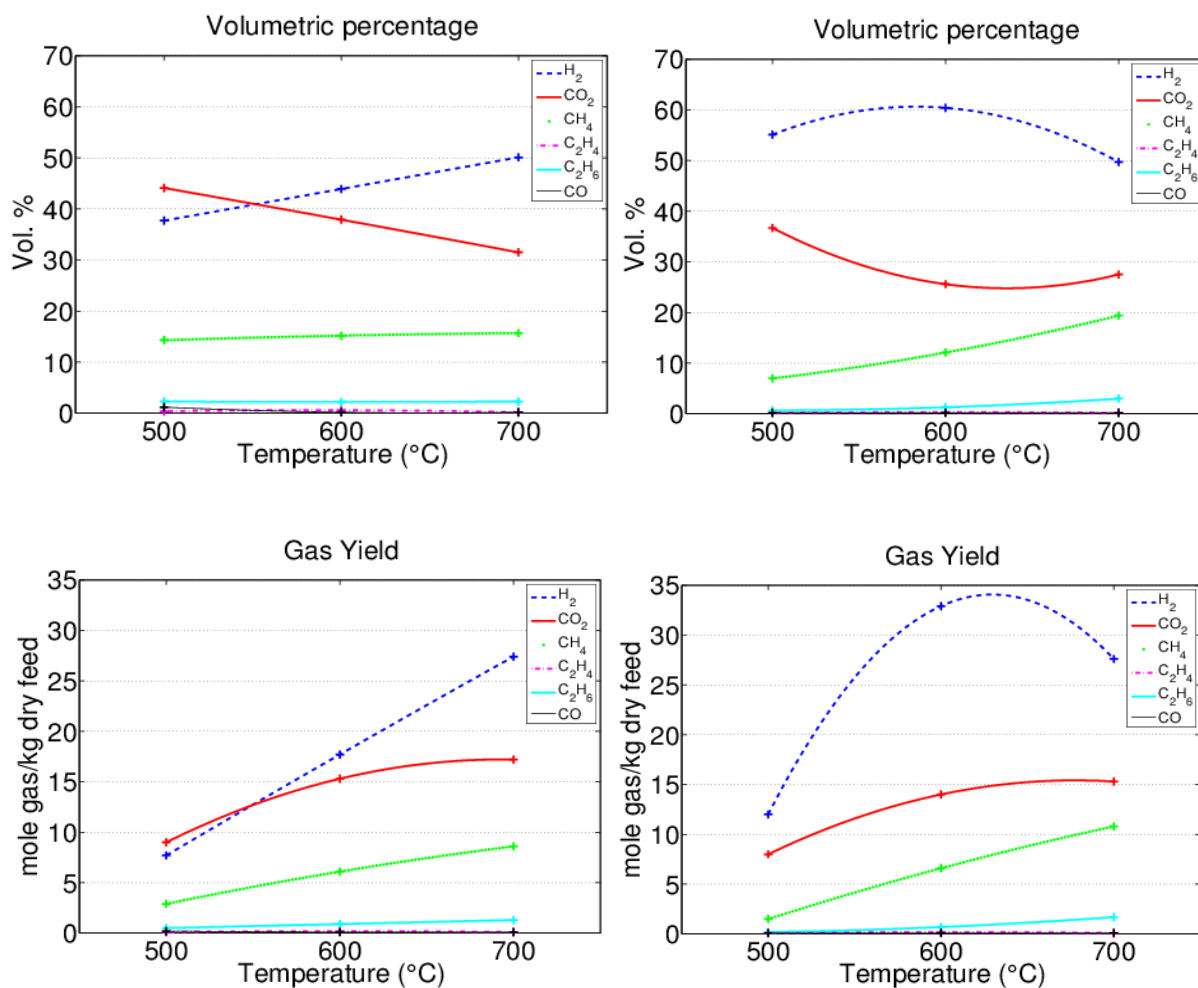
4

5 Values of the HGE\* for black liquor have been calculated considering a dry basis. In both  
 6 reactors, elemental gasification efficiencies and HGE\* increase with temperature. Methane and  
 7 hydrogen have major impact on energy recoveries as well as ethane having significant effect.  
 8 HGE reach much higher values in INCONEL 625 reactor than stainless steel at 600°C and  
 9 700°C. Consequently, HGE\* is higher in INCONEL 625 reactor except at 500°C even though  
 10 CGE values are quite close.

11

12

13



1

2

3 Figure 6. Volume percentage of gas products and gas yield – Left: SCWG of black liquor in  
 4 the stainless steel 316 reactor, Right: SCWG of black liquor in the INCONEL 625 reactor

5

6 Figure 6 reports the volume percentage of gas products and the gas yields for SCWG of BL in  
 7 stainless steel 316 and Inconel 625 reactors. As it can be seen from Figure 6, the yields of all  
 8 gases increase with temperature in case of stainless steel reactor, except for carbon monoxide  
 9 and ethylene which have very low amounts in both reactors and at all temperature conditions.  
 10 Similarly, yields increase with temperature in the case of INCONEL 625 reactor; however,  
 11 hydrogen yield decreases after 600°C. In addition, in both cases, carbon dioxide yield increases  
 12 very slightly after 600 °C. Similar to the sucrose results, ethane yield is higher than ethylene  
 13 yield and the difference increases with temperature. The molar fraction of hydrogen, methane  
 14 and ethane increase whereas fraction of carbon dioxide decreases with temperature in case of

1 stainless steel reactor, similarly to the sucrose results. This result is consistent with the previous  
2 studies conducted on important biomass components such as lignin and cellulose<sup>39</sup>. Sulphur  
3 ~~compounds were not detected in gas phase for our conditions.~~  
4 The lignocellulosic biomass has less oxygen content than sucrose due to lignin content.  
5 Therefore, promoted gasification reactions with temperature cause sharper increase in hydrogen  
6 generation than carbon dioxide generation, which can also be seen from gas yields and fractions  
7 in Figure 6. Thus, black liquor gasification in stainless steel reactor results in higher energy  
8 recovery than sucrose in the same reactor even though CGE values are close. This can be  
9 observed through the gas composition as well. SCWG of black liquor produces hydrogen-rich  
10 syngas and methane has also high proportion; in contrast; carbon dioxide has the largest fraction  
11 in the syngas from SCWG of sucrose.

12 Regarding catalytic influence, the HGE\* values are significantly higher in case of INCONEL  
13 625 reactor than stainless steel case at 600 °C and 700 °C. At 700 °C, HGE\* exceeds 80 %,  
14 which is very promising potential compared with the current status of this method. On the other  
15 hand, stainless steel reactor results in higher HGE\* than INCONEL 625 reactor at 500 °C. This  
16 is a different trend from the one reported by Chakinala et al.<sup>40</sup> and further investigations would  
17 be required to understand when actually Nickel catalysts are starting their effect on the  
18 gasification conversion and if the particular feedstock used had also an effect on this results.  
19 Furthermore, hydrogen yield decreases at 700°C in case of black liquor gasification in  
20 INCONEL 625 reactor as an exceptional trend. Meanwhile, methane yield is slightly higher  
21 and carbon dioxide yield is slightly lower than the stainless steel reactor case at 700°C.  
22 However, alkali metal salts catalyse WGS reaction producing carbon dioxide and hydrogen,  
23 and nickel catalysts facilitate steam reforming of methane at higher temperatures<sup>35</sup>. These  
24 trends implies promoted dealkylation reactions relative to decarboxylation.

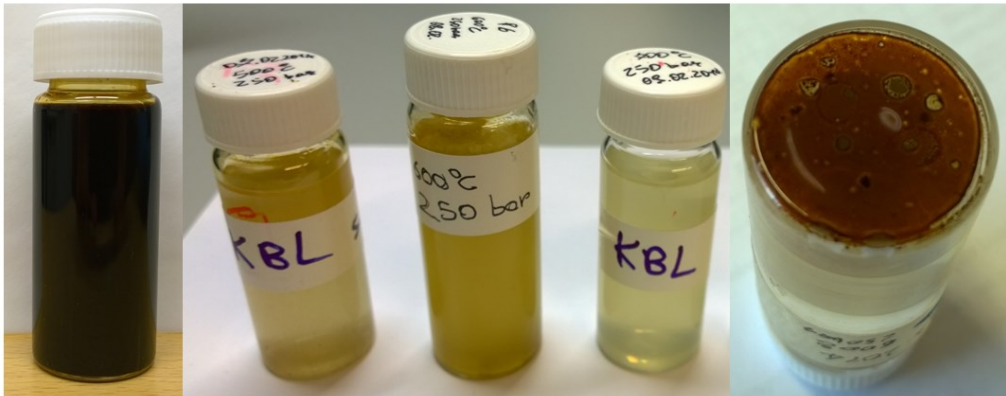
25

1 Regarding the order of gas-generating reactions, OGE has higher value than HGE at 500°C but  
2 HGE increases much sharper with temperature. This trend implies that decarboxylation of high-  
3 molecular-weight carboxylates, steam reforming and methanation reactions have more impact  
4 at 500°C: relatively more CO<sub>2</sub> production and consumption of significant part of generated H<sub>2</sub>  
5 in methanation. Considering that CO amount is very low, methanation seems to be faster than  
6 steam reforming. Nevertheless, increasing temperature promotes decarboxylation of low-  
7 molecular-weight carboxylates and results in more methane and hydrogen formation.

8 It should also be noted that black liquor has alkali content as well, such as Na; therefore,  
9 decarboxylation reactions occur as shown in Equation 14 and 15 which results in sodium  
10 carbonate. However, salt deposition can cause blocking problem in the reactor due to low  
11 solubility. For this reason, char and salt formation should be addressed when designing SCWG  
12 process. Nevertheless, these salts represent valuable products and they should be recovered; for  
13 this reason, efficient recovery of these salts can be an opportunity with SCWG.

14 Furthermore, liquid analysis provides additional information since CGE varies from about 30%  
15 to 70% for experiments conducted with both reactors, i.e. below 100 % in all cases. This can  
16 imply either incomplete decomposition of organics or carbonate content in the liquid effluent.  
17 Table 5 shows the total organic carbon and chemical oxygen demand of the liquid effluents.  
18 The results on liquid analysis indicate that the conversion of organic content is incomplete and  
19 the conversion increases with temperature. The decline in organic content becomes sharper at  
20 higher temperature. In addition, the INCONEL 625 reactor provides higher conversion at 600  
21 and 700 °C whereas the conversion in stainless steel reactor is higher at 500 °C. Liquid analysis  
22 also confirms that tar and char formation decreases with temperature. At higher temperatures,  
23 as also shown in Figure 9, the relative amount of tar compounds is evidently decreased and the  
24 lignin degradation is on the other hand increased. Figure 7 gives a visual description of the  
25 original black liquor feed as received (Kraft black liquor – KBL). The liquid products at the

1 tested temperatures and an example of tar formation at 500°C for tests conducted in the stainless  
2 steel reactor.



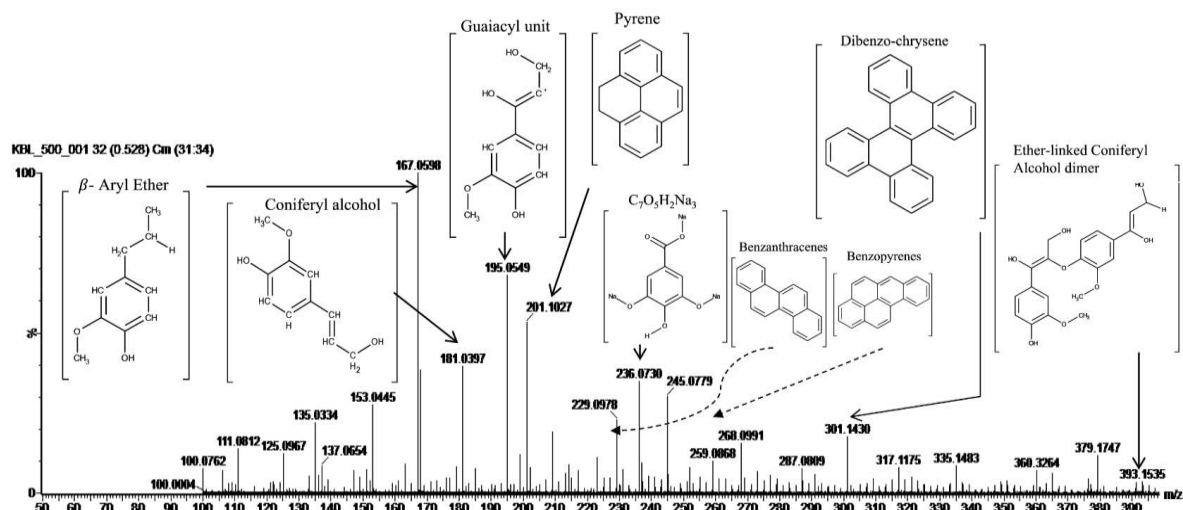
3  
4 Figure 7. Left: KBL as received. Center: Liquid product at 500°C, 600°C and 700°C (from  
5 left) at 25MPa. Right: Evidence of tar formation at 500°C and 25MPa for experiments  
6 conducted in the stainless steel reactor

7  
8 Table 5. TOC and COD analysis for liquid products at different temperatures. INCONEL 625  
9 and stainless steel 316.

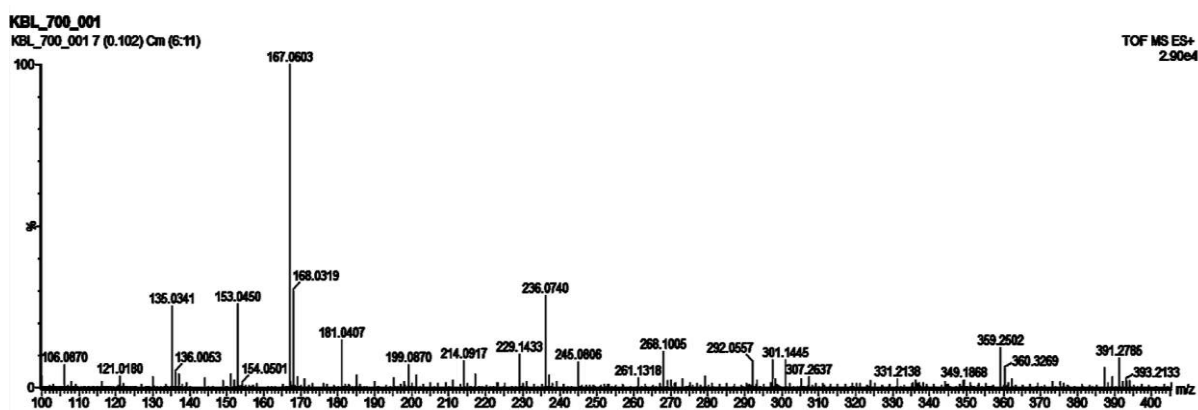
SAMPLE	DATE	NPOC	CODCr
		mg/L	mg/L
BL 25 MPa 500°C	1.3.2014	1936	7040
BL 25 MPa 600°C	2.3.2014	1310	5335
BL 25 MPa 700°C	4.3.2014	296	1279
BL 25 MPa 500°C Cat.	5.3.2014	2142	7590
BL 25 MPa 600°C Cat.	6.3.2014	1078	3989
BL 25 MPa 700°C Cat.	7.3.2014	160	762

10  
11 From MS analyses, it is possible to obtain relative information on the composition of the main  
12 elements present in the liquid products even if it has to be acknowledged that the technique  
13 gives only estimated formulas for relatively abundant compounds. Figure 8 and Figure 9  
14 demonstrate mass spectra for liquid products of SCWG of black liquor at 500°C and at 700°C  
15 in the stainless steel reactor.





1  
 2 Figure 8. MS analysis of liquid products from SCWG of BL at 500°C in stainless steel reactor

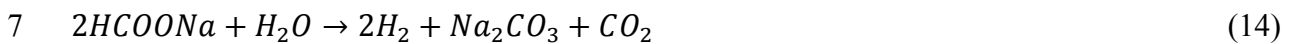


3  
 4 Figure 9. MS analysis of liquid products from SCWG of BL at 700°C in stainless steel reactor

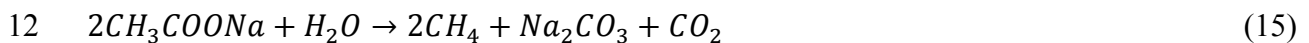
5  
 6 Lignin is the most abundant compound of black liquor and its constituents can be recognized  
 7 from the MS analysis. As a matter of fact, the most abundant compounds detected are coincident  
 8 with the principal monomers of lignin; therefore, it is possible to recognize here the guaiacyl  
 9 unit which is among the most abundant units forming lignin, besides coniferyl alcohol<sup>43</sup>.  
 10 The most abundant compound detected is addressed here to the  $\beta$ -aryl ether which also  
 11 represents one of the main types of monolignols utilized during radical-radical coupling to form  
 12 lignin<sup>43</sup>. The compound is still the most abundant at 700°C, Figure 9, while the relative  
 13 abundance of coniferyl alcohol and guaiacyl unit is much decreased at these conditions. The

1 relative large presence of  $\beta$ -aryl ether and guaiacyl unit is due to the type of wood used for the  
2 BL tested. As a matter of fact guaiacyl unit is the most abundant in soft wood lignin<sup>44</sup>.  
3 MS results indicate that heterocyclic compounds like tricyclic aldehydes could be present in the  
4 liquid products as well as products from cyclization of acids. Lignin represents a source of  
5 renewable aromatic chemicals and tar (commonly known as mono-, di- or tri-naphthalene)  
6 formed during gasification processes<sup>29</sup>; however, reactions pathways in black liquor are very  
7 much complicated by the presence of alkali and alkaline metals. Aromatics are difficult to be  
8 degraded and they are stable at high pressures and temperatures. From the MS spectra it is  
9 possible to recognize stable molecular ions in the range of 220 – 300 m/z at 500°C; this is the  
10 range at which tar compounds are present<sup>45</sup>. In Figure 8 are illustrated some possible tar  
11 compounds detected. Starting from the most abundant, it is possible to recognize pyrene,  
12 chrysene and dibenzo-chrysene which was indicated by Flego and co-workers<sup>46</sup> as a possible  
13 pyrolysis compound in the proximity of our peak at 301m/z.  
14 In the range between 230-280 m/z benzantracenes and benzopyrenes may be present in this  
15 range<sup>47</sup>. In this case, one possible molecular formula proposed here for the stable 236 m/z  
16 compound would be  $C_7O_5H_2Na_3$  (m/z 236.067) corresponding, to 3,4,5-trihydroxybenzoic acid  
17 or gallic acid in which one phenolic group is free without chemically bound sodium:  $-CO_2Na$   
18 plus two  $-ONa$  and one  $-OH$  groups. In hardwood-based black liquor (especially eucalyptus)  
19 the presence of gallic acid is possible, since this compound, a moiety in extractives, is one of  
20 the prominent compounds in hydrolysable tannins (e.g., gallotannins).  
21 HPLC results showed that there is none of glucose, fructose, galactose and xylose in the  
22 condensate products for all cases (for all temperatures, catalytic and non-catalytic cases).  
23 Considering that hydrolysis is faster than sugar decomposition in SCW, it can be assumed that  
24 cellulose and hemicellulose are hydrolyzed completely and the remaining organic content  
25 consists of intermediates.

1 Kraft black liquor has a significant amount of carboxylic and hydroxyl acid salts. Sodium salts  
2 of carboxylic acids represent an important part of the reactions involved during SCWG of black  
3 liquor. These salts were reported as important intermediates during the formation of H<sub>2</sub> and  
4 CH<sub>4</sub>. Sodium formate influences the conversion to hydrogen while sodium acetate leads to  
5 methane production<sup>48</sup>. The reaction of sodium formate with water at supercritical condition can  
6 be written as:



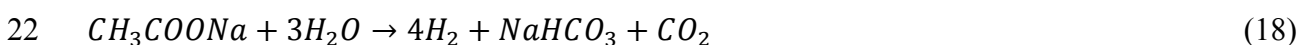
8 The reaction above is demonstrated to give increasing fractions of H<sub>2</sub> and CO<sub>2</sub> with increasing  
9 temperatures up to around 400°C; however, there is no significant change of hydrogen and  
10 carbon dioxide percentages at higher temperatures. The reaction of sodium acetate in SCW can  
11 be written as follows<sup>49</sup>:



13 More in details, the reaction of sodium acetate with water follows a molecular mechanism with  
14 two reactions steps:

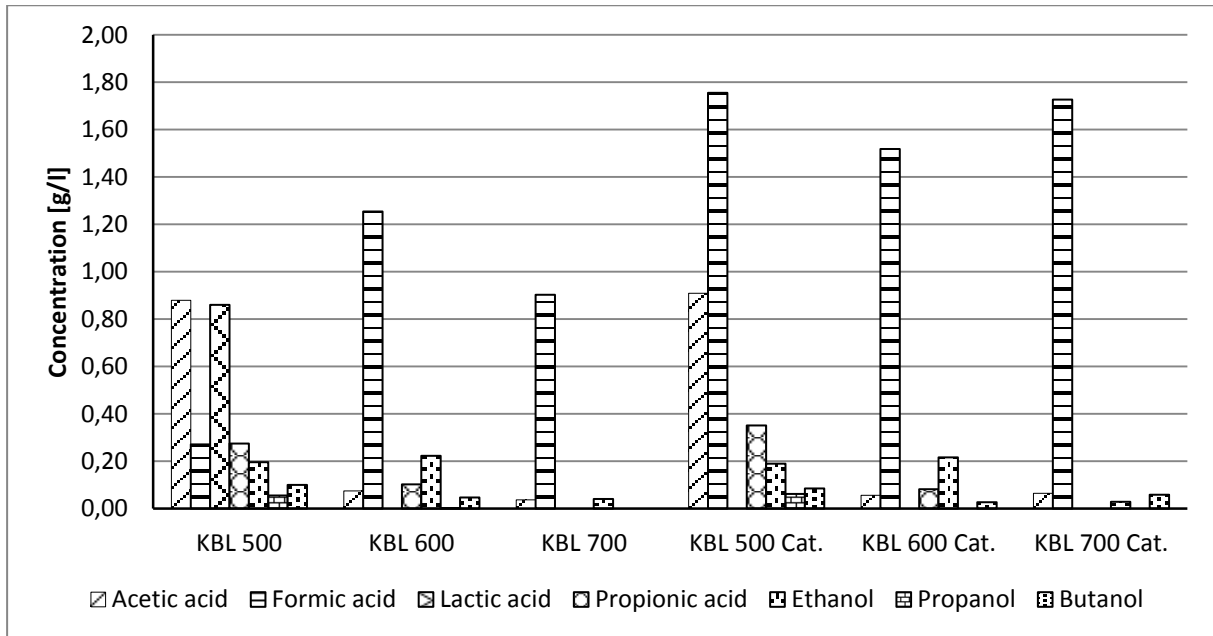


17 The first is considered to be the limiting step of reaction while the second step, Equation 17, is  
18 considered to be the fastest<sup>50</sup>. Nevertheless, Matsumura and collaborators<sup>51</sup> state that water  
19 becomes an oxidant if the temperature is increased in supercritical conditions; therefore,  
20 Onwudili et al.<sup>49</sup> concluded that there could be an increased production of hydrogen at high  
21 temperatures due to the reaction:



23 However, this would have been justified also by the fact that reactions in SCW at increased  
24 temperatures would take place under a radical mechanism.

1 Figure 10 shows the content of some light carboxylic acids and alcohols of condensate effluent.  
 2 The concentrations of most of the compounds decrease with increasing temperature; however,  
 3 formic acid under non-catalytic case and ethanol reach the highest concentration at 600°C  
 4 whereas butanol and formic acid under the catalytic case have the lowest concentration at  
 5 600°C.



6  
 7 Figure 10. Main compounds detected in liquid products by HPLC. From left: products at 500,  
 8 600 and 700°C (stainless steel) and products from SCWG in Inconel 625 (right)

9  
 10 Regarding the environmental aspect of the liquid effluent, the organic content and nitrogen  
 11 content were analysed. Table 5 demonstrated TOC and COD analysis for our conditions while  
 12 the total nitrogen content is shown in Table 6.

13 Table 6. Total Nitrogen analysis for the given samples.

SAMPLE	DATE	TN
		mg/l
BL 25 MPa 500°C	1.3.2014	22.8
BL 25 MPa 600°C	2.3.2014	31.3
BL 25 MPa 700°C	4.3.2014	31.5
BL 25 MPa 500°C Cat.	5.3.2014	21.3
BL 25 MPa 600°C Cat.	6.3.2014	26.4

1  
2 Traditionally, the quality of treated wastewater, in terms of organic content, is defined by the  
3 measurements of parameters such as Biochemical Oxygen Demand (BOD), Chemical Oxygen  
4 Demand (COD) and Total Organic Carbon (TOC). Being the TOC a measure often used for the  
5 monitoring of industrial wastewater quality<sup>52</sup>, this study considers TOC as an analytical  
6 parameter for the determination of the organic pollution of the black liquor wastewater from  
7 the SCWG apparatus. The organic content and nitrogen analysis indicates that the black liquor  
8 wastewater generated by the SCWG apparatus is more polluted than typical domestic  
9 wastewater, especially in terms of organic content<sup>53</sup>. Thus, as expected, the SCWG operation  
10 should follow the Integrated Pollution Prevention and Control (IPPC) directive (Council  
11 Directive (EC) 2008/1/EC of 15 January 2008), which provides instruction for regulating the  
12 emissions of pollutants likely to be emitted in significant quantities to air, water or land from  
13 industrial facilities.

#### 14 **Conclusions**

15 SCWG has a promising potential as a thermo-chemical conversion route for high moisture black  
16 liquor: single phase medium and effective solvent for organics (i.e. no mass transfer limitations)  
17 as well as no energy-consuming pre-treatment required (such as drying). In addition, the  
18 conventional treatment is unfeasible for small-scale non-wood mills, for which SCWG can be  
19 the solution. Therefore, this study presents experimental results on SCWG of sucrose,  
20 isoeuganol and black liquor to investigate the impacts of temperature, catalyst and constituents  
21 on syngas and reaction mechanism ~~by means of analyses conducted on gaseous and liquid~~  
22 ~~products.~~

23 The results illustrate the promoting impact of temperature on the biomass conversion, gas yields  
24 and hot gas efficiency. Regarding the composition of syngas, the molar fraction of combustible

1 gases (except CO) increases with temperature whereas the fraction of carbon dioxide decreases,  
2 thus producing more desirable gas for energy production. Hot gas efficiency also increases with  
3 temperature due to increasing yields.

4 The comparison between black liquor and sucrose results provide important conclusions  
5 regarding the effect of constituents. Due to higher H/C and lower O/C ratios in lignocellulosic  
6 biomass, sharper increase in hydrogen occurs in SCWG of black liquor and hot gas efficiency  
7 is higher compared to sucrose gasification. Furthermore, black liquor gasification produces  
8 hydrogen-rich syngas whereas syngas from sucrose gasification is carbon dioxide-rich.

9 This study provided informative remarks about the reaction mechanism and the impact of  
10 process parameters. The hydrogenation of ethylene to form ethane resulted in an additional step  
11 to the degradation route. Ethylene also reacts with steam and produces ethanol. From the  
12 experimental data, it can be concluded that ethylene hydrogenation is much faster than ethylene  
13 formation and the reaction kinetics is improved at higher temperature. The decarboxylation of  
14 low-weight carboxylates is promoted by temperature and the gasification of intermediates  
15 represents the rate determining step. Slow rate of WGS reactions can be observed at low  
16 temperature while the reactions are influenced only at 700 °C. There is faster methanation than  
17 steam reforming in the presence of alkali metals while nickel catalyst is promoting  
18 decarboxylation of high-weight organics, methanation and steam reforming at low temperature,  
19 rather than decarboxylation of low-weight carboxylates. Furthermore the promotion of nickel  
20 catalyst on the methanation and ethylene hydrogenation is more influentially than hydrogen  
21 formation at high temperature. From the gasification efficiency results, water is demonstrated  
22 to be a reactant as well as a solvent media.

23 The process conditions of SCWG should be determined based on the usage of syngas:  
24 maximizing energy recovery if the purpose is to produce energy through gas engine or  
25 maximizing some specific species (e.g. hydrogen, methane or carbon dioxide) if the purpose is

1 further catalytic synthesis to produce biofuels and other hydrocarbons. The future aspect with  
2 respect to scientific knowledge includes obtaining more experimental data and developing  
3 accurate models to describe the process thermodynamics and reaction kinetics. From the  
4 process development viewpoint, considering slower degradation of lignocellulosic content and  
5 incomplete conversion of organics, black liquor could be pre-treated through lignin removal  
6 and/or partial wet oxidation. These alternatives could be compared in terms of economical and  
7 operational aspects.

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