

# Effect of Temperature on the Catalytic Performance of Dolomite for H<sub>2</sub> Production by Steam Reforming of a Bio-oil/ethanol Mixture

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The catalytic performance of dolomite for the steam reforming of a raw bio-oil/bio-ethanol mixture (80/20 mass ratio) was studied in the 400-700 °C range. Blank runs (without dolomite) under the same operating conditions were also performed in order to differentiate the catalytic performance of dolomite from the thermal effect. Below 500 °C, dolomite mainly promotes inter-conversion reactions between the bio-oil oxygenates, contributing to a noticeable increase in the amount of ketones and phenols, whereas the ethanol conversion is low, once dolomite is saturated with CO<sub>2</sub>, and a H<sub>2</sub> yield below 10 % is obtained. Above 600 °C, dolomite is active for reforming reactions of ethanol and bio-oil oxygenates, and almost steady values of ethanol conversion (100 %), bio-oil conversion (~83 %) and H<sub>2</sub> yield (~45 %) are obtained at 700 °C throughout 4 h. Cracking reactions of oxygenates are enhanced with the increase in temperature, which involves the formation of gaseous by-products (mainly CH<sub>4</sub>, with lower amounts of CO and hydrocarbons). The CO<sub>2</sub> capture at 600 °C shifts the WGS and reforming reactions, providing high ethanol and bio-oil conversion (100 % and 90 %, respectively) and H<sub>2</sub> yield (40 %) at zero time on stream, but these reaction indices rapidly decrease when dolomite is saturated.

## 1. Introduction

The steam reforming of bio-oil is an interesting route for the sustainable production of hydrogen, whose current demand is growing due to its interest as a fuel and petrochemical raw material. Bio-oil production by pyrolysis of biomass can be performed with simple and highly developed technologies (Meier et al. 2013), and its catalytic steam reforming avoids the costly dehydration steps required for other valorization strategies. However, the raw bio-oil tends to re-polymerize and form a carbonaceous solid (pyrolytic lignin) which creates plugging problems in the reaction system and also affects the catalyst deactivation. The co-feeding of ethanol with raw bio-oil is interesting because it can be sustainably obtained by hydrolysis-fermentation of lignocellulosic biomass, it stabilizes the raw bio-oil during the storage and it also increases the H/C ratio of the feed (thus decreasing the pyrolytic lignin deposition). In addition, the joint valorization of oxygenated compounds derived from different types of biomass (i.e., bio-oil and bio-ethanol) is an interesting route for the development of bio-refinery concept (Sultana and Kumar, 2011). Nickel-based catalysts have been widely used in the literature for reforming raw bio-oil (Remiro et al., 2013a), bio-oil aqueous fraction (Medrano et al., 2011) and ethanol (Vicente et al., 2009a,b) due to the high C-C bond-breaking activity and the relatively low cost. Al<sub>2</sub>O<sub>3</sub>-based supports are often used in reforming catalysts because of their mechanical and chemical resistance (Roy et al., 2012). Although high H<sub>2</sub> yields can be achieved, quite rapid catalyst deactivation (both by coke and by sintering) has been observed under the operating conditions studied (Seyedeyn-Azad et al., 2011). Improvements in H<sub>2</sub> yield have been reported by using dolomite both as: i) *in situ* CO<sub>2</sub> sorbent in the SR of the aqueous fraction of bio-oil (Remiro et al., 2013b), and ii) low-cost catalyst for the pre-reforming of bio-oil in a two-stage fixed bed reactor system (Wu et al., 2008). Moreover, the use of a two-step system (thermal step + catalytic

step) is efficient for attenuating catalyst deactivation by coke in catalytic processes for bio-oil upgrading (Gayubo et al., 2010).

This paper studies the catalytic performance of dolomite for the steam reforming of a raw bio-oil/bio-ethanol mixture (80/20 mass ratio). The effect of temperature (in the 400-700 °C range) on the bio-oil and ethanol conversion and on the composition of the product stream and hydrogen yield is analyzed.

## 2. Experimental

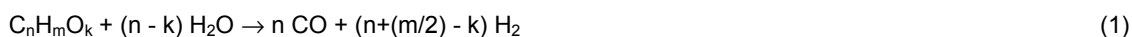
### 2.1 Feed and dolomite characteristics

The raw bio-oil was obtained by flash pyrolysis of pine sawdust in a semi-industrial plant located in *Ikerlan-IK4* technology centre (Alava, Spain), with a biomass feeding capacity of 25 kg/h. The molecular formula of this bio-oil ( $C_{3.5}H_{6.1}O_{3.3}$ ) was estimated from its elemental composition (Leco CHN-932 analyzer and ultra-microbalance Sartorius M2P). The raw bio-oil was stabilized by adding ethanol for obtaining a bio-oil/EtOH feed with 80/20 mass ratio (water-free basis). The dolomite (58 wt %  $CaCO_3$  and 36 wt %  $MgCO_3$ ) was provided by Calciner S.A. (Tolosa, Spain), and it was calcined at 850 °C for 5 h.

### 2.2 Reaction equipment, operating conditions and reaction indices

The kinetic runs were performed in a U-shaped tube (S-316 stainless steel, 5/8" i.d.), with the pyrolytic lignin being deposited in the inlet side due to the repolymerization that undergo certain bio-oil compounds during the thermal treatment of the feed. The fixed bed of calcined dolomite is located in the outlet side. The bio-oil/ethanol mixture was fed as droplets entrained by the carrier flow (He) at a feeding rate of 0.1 ml/min and additional water (0.3 mL/min) was fed in order to fix a S/C ratio  $\approx 6$ , enough to achieve high bio-oil conversion and  $H_2$  yield, without exorbitant energy cost (Remiro et al., 2013a). The analysis of the products stream was carried out by gas chromatography ( $\mu$ GC) and the liquid obtained after condensation of the stream was analyzed by GC/MS. The steam reforming (SR) conditions were: temperature, 400 - 700 °C; reaction time, 4 h; S/C = 6; space-time,  $0.27 \text{ g}_{\text{dolomite}} \text{ h} / \text{g}_{\text{bio-oil+EtOH}}$ .

The steam reforming of bio-oil proceeds according to Eq (1) followed by the water-gas-shift reaction (WGS), Eq (2), and ethanol reforming reaction is expressed by Eq (3). Other reactions, such as thermal decomposition, methanation/methane reforming and dolomite carbonation may also occur.



The conversion of bio-oil and ethanol in the mixture are individually calculated from their molar flowrates at the inlet and outlet (un-reacted bio-oil or ethanol) of the catalytic reactor, according to:

$$X_i = \frac{F_{i,inlet} - F_{i,outlet}}{F_{i,inlet}} \quad (4)$$

The  $H_2$  yield is calculated as a percentage of the stoichiometric potential of the feed, Eq (5), and the yield of other products ( $CO$ ,  $CO_2$ ,  $CH_4$  and hydrocarbons  $C_2$ - $C_4$ ) is quantified by Eq (6):

$$Y_{H_2} = \frac{\text{molar flow of } H_2 \text{ obtained}}{\left( \frac{2n + m/2 - k}{n} x F_{\text{bio-oil,inlet}} + 3 x F_{\text{EtOH,inlet}} \right)} x 100 \quad (5)$$

$$Y_i = \frac{\text{molar flow of } i \text{ (CO, CO}_2, \text{CH}_4, \text{HCs) obtained}}{(F_{\text{bio-oil,inlet}} + F_{\text{EtOH,inlet}})} x 100 \quad (6)$$

## 3. Results and discussion

### 3.1 Effect of temperature on the thermal decomposition of the feed (blank runs)

Prior to the study of the dolomite catalytic performance, blank runs (by using inert CSi, instead of dolomite) were carried out in order to analyze the effect that the thermal treatment of the feed has on its composition. The overall composition of the product stream obtained after the thermal treatment at different temperatures is shown in Table 1. Table 2 shows the composition on a water free basis of the liquid products (analyzed by GC/MS) and the composition of the raw bio-oil/ethanol feed is also shown for comparison. It should be noted that the ethanol content of the feed is slightly higher than the amount added to the raw bio-oil because a fraction of the raw bio-oil ( $\approx 30$  wt %, composed of heavy oxygenates with molecular weight higher than 320 g/mol) is unable to be identified by GC-MS (Mohan et al., 2006).

It can be observed that the amount of gases (Table 1) increases exponentially with temperature, with the major compounds being CO and CO<sub>2</sub> coming from decarbonylation/decarboxylation reactions. The cracking/decomposition reactions that form H<sub>2</sub>, CH<sub>4</sub> and light hydrocarbons (mainly ethene) are significant above 600 °C and the amount of water (coming from the feed and from dehydration reactions) slightly decreases with temperature. On the other hand, a significant increase with temperature of phenols (mainly phenol and 3-methylphenol), acetone, acetic acid and acetaldehyde can be noted (Table 2). Ethanol and levoglucosan decrease due to the thermal cracking, which is significant above 600 °C.

Table 1: Effect of temperature on the composition (wt %) of the product stream (blank runs)

T, °C	400	500	600	700	800
H <sub>2</sub>	0.0	0.0	0.2	0.3	0.5
CH <sub>4</sub>	0.0	0.1	0.4	0.9	1.1
CO	0.3	0.7	2.1	3.6	3.9
CO <sub>2</sub>	1.2	1.6	1.8	3.0	4.3
C <sub>2</sub> -C <sub>4</sub> Paraffin	0.0	0.0	0.1	0.1	0.1
C <sub>2</sub> -C <sub>4</sub> Olefins	0.0	0.1	0.4	0.8	0.7
TOTAL GAS	1.6	2.6	5.1	8.8	10.6
Water	82.6	81.6	81.5	81.3	81.1
Liquid Products	15.8	15.8	13.4	9.9	8.3
TOTAL LIQUID	98.4	97.4	94.9	91.2	89.4

Table 2: Effect of temperature on the detailed composition (water-free basis) of liquid products (blank runs)

Compounds	Bio-oil / EtOH 80/20	Operating temperature, °C				
		400	500	600	700	800
HYDROCARBON	--	--	--	--	--	--
OXYGENATES	100	100	100	100	100	100
Ketones	7.7	5.9	4.7	7.3	7.5	8.4
acetone	0.7	0.0	0.0	1.5	2.4	8.4
Acids	18.0	7.8	14.0	19.5	35.8	6.6
acetic acid	13.6	3.9	11.1	17.4	33.8	6.6
Esters	3.1	2.6	4.0	1.9	2.5	--
Aldehydes	15.7	4.5	5.9	5.4	10.5	--
hydroxiacetaldehyde	12.4	--	--	--	--	--
acetaldehyde	--	0.2	1.3	3.1	10.2	--
Phenols	2.7	1.7	3.7	5.5	28.3	85.1
Phenol	0.1	0.2	0.7	2.8	10.2	64.1
3-methylphenol	0.2	0.2	0.9	1.1	7.7	20.9
Ethers	2.7	0.4	0.8	1.2	2.0	0.0
Alcohols	32.0	40.3	39.8	26.3	12.2	0.0
Ethanol	27.0	34.5	36.9	24.0	9.8	0.0
Others	18.1	36.8	27.2	32.9	0.6	0.0
Levoglucosan	14.5	35.5	26.2	32.7	0.6	0.0

### 3.2 Effect of temperature on the catalytic performance of dolomite

Table 3 shows the evolution of the product stream composition obtained in the SR with dolomite at different temperatures and the detailed composition of the liquid products is shown in Table 4. The results corresponding to the evolution with time on stream of bio-oil and ethanol conversion and the yields of H<sub>2</sub>, CO<sub>2</sub>, CO, and CH<sub>4</sub> are shown in Figures 1 and 2, respectively. In these figures, the results corresponding to the blank runs (lines) are also shown for comparison.

The catalytic capacity of dolomite is evident at 700 °C, when dolomite has a low CO<sub>2</sub> adsorption capacity (Figure 2b), and bio-oil and ethanol conversion higher than the thermal values (blank runs) are obtained (Figure 1). A significant increase in the gaseous products concentration is also observed compared to the blank runs, from 8.8 wt % (Table 1) to 17.6 wt % after 4h reaction (Table 3). The H<sub>2</sub> and CO<sub>2</sub> yields are much higher than the thermal values, which evidences the dolomite activity for oxygenates reforming. The higher concentration of CH<sub>4</sub> (Table 3) and aromatic hydrocarbons (Table 4) suggests that dolomite is also active for cracking reactions. The CO yield is significantly lower than the thermal value (Figure 2c), which reveals the catalytic activity of dolomite for the WGS reaction, which is enhanced by the CO<sub>2</sub> capture before saturation of the dolomite (Figure 2b).

Table 3: Effect of temperature on the product stream composition (wt %) obtained in the SR with dolomite. Operating conditions: S/C = 6 and space-time = 2.4 g<sub>dolomite</sub> h/g<sub>bio-oil+EtOH</sub>

T, °C	400			500			600			700		
time, h	0.5	2	4	0.5	2	4	0.5	2	4	0.5	2	4
H <sub>2</sub>	0.2	0.0	0.0	0.6	0.4	0.2	1.4	0.5	0.4	1.2	1.1	1.2
CH <sub>4</sub>	0.2	0.5	0.4	1.2	0.9	0.3	2.0	0.7	0.6	1.6	1.3	1.4
CO	0.6	0.9	0.7	0.8	1.2	0.9	1.6	2.4	2.4	0.9	1.6	2.0
CO <sub>2</sub>	0.0	0.1	0.3	0.1	0.1	3.8	1.1	4.3	4.2	9.0	10.4	11.8
C <sub>2</sub> -C <sub>4</sub> Paraffin	0.1	0.3	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1
C <sub>2</sub> -C <sub>4</sub> Olefins	0.1	0.2	0.1	0.3	0.3	0.2	0.8	0.4	0.4	1.1	1.0	1.0
TOTAL GAS	1.3	2.0	1.7	3.2	3.0	5.5	7.2	8.5	8.1	13.9	15.5	17.6
Water	82.4	84.5	89.9	86.2	86.9	83.9	91.3	85.1	85.3	83.9	82.5	80.6
Liquid products	16.3	13.5	8.4	10.6	10.0	10.5	1.5	6.5	6.6	2.2	6.5	9.7
TOTAL LIQUID	98.7	98.0	98.3	96.8	97.0	94.5	92.8	91.5	91.9	86.1	84.5	82.4

Table 4: Effect of temperature on the detailed composition (wt %) of liquid products

T, °C	400			500			600			700		
time, h	0.5	2	4	0.5	2	4	0.5	2	4	0.5	2	4
HYDROCARBON	0.3	1	3.4	0.3	0.7	0.3	0.0	0.2	0.3	9.7	4.0	3.5
Lineal	0.2	0.4	0.5	0.3	0.3	0.3	0.0	0.2	0.3	0.0	0.0	0.0
Cyclic	0.1	0.4	0.5	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Aromatic	0.0	0.2	2.4	0.0	0.0	0.0	0.0	0.0	0.0	9.7	4.0	3.5
OXYGENATES	99.7	99.0	96.6	99.7	99.3	99.7	100	99.8	99.7	90.3	96.0	96.5
Ketones	58.9	42.3	31.0	76.6	46.0	37.5	22.3	10.7	9.6	72.6	8.4	2.3
Acids	0.0	0.4	3.7	0.0	0.2	3.2	0.0	4.3	11.3	0.0	0.0	0.0
Esters	0.0	0.9	1.4	0.0	0.0	1.0	0.0	1.7	1.5	0.0	0.0	0.0
Aldehydes	0.9	5.0	7.3	0.3	2.2	8.0	0.0	13.6	11.3	0.0	0.0	0.0
Phenols	4.7	14.1	19.6	12.6	12.8	17.5	76.5	24.5	26.2	17.7	87.5	94.2
Ethers	0.0	0.3	0.2	0.2	0.1	0.4	1.2	1.0	1.0	0.0	0.0	0.0
Alcohols	35.2	36.0	33.1	10.0	37.8	32.2	0.0	44.2	38.8	0.0	0.0	0.0
Ethanol	25.6	30.6	30.7	2.9	25.8	24.6	0.0	34.0	36.9	0.0	0.0	0.0
Levoglucosan	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

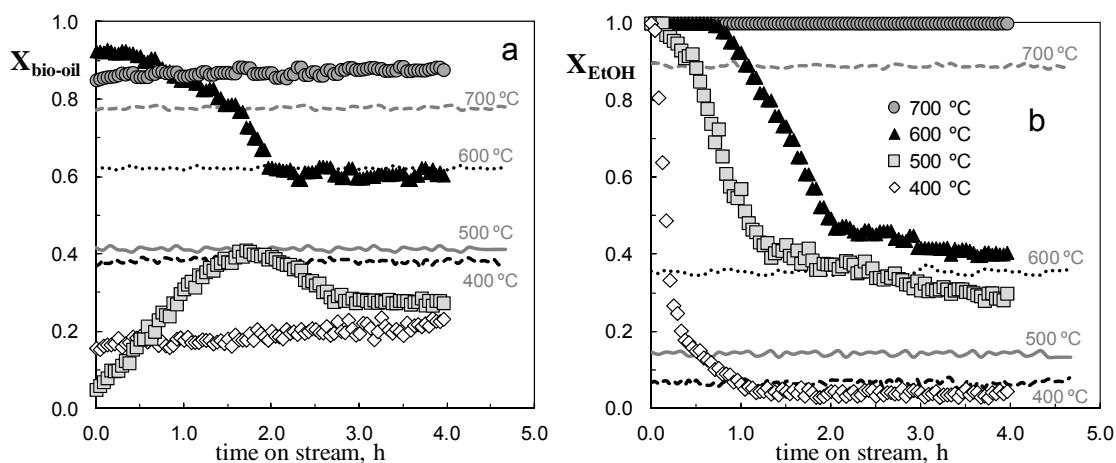


Figure 1: Effect of temperature on the evolution with time on stream of bio-oil (a) and ethanol (b) conversion in the SR of bio-oil/ethanol mixture over dolomite (points) and comparison with the results of thermal decomposition obtained in blank runs (lines)

At 600 °C, the CO<sub>2</sub> adsorption capacity of dolomite effectively displaces WGS reaction. During the CO<sub>2</sub> capture period ( $\approx$  1 h), high bio-oil and ethanol conversion (Figure 1) and a H<sub>2</sub> yield of 40 % (Figure 2a) are obtained, and there is also a remarkable formation of CH<sub>4</sub>, which decreases in parallel with the increase of CO yield, suggesting deactivation of the methanation reaction that is favored at this temperature. As the

dolomite becomes saturated ( $1 < t < 2$  h), the  $H_2$  yield and bio-oil and ethanol conversions significantly decrease. After complete saturation, the  $H_2$  and  $CO_2$  yields are still higher than those caused by the thermal effect (lines in Figure 2), thereby indicating a residual catalytic activity of dolomite for ethanol reforming (Figure 1b). The yields of  $CH_4$  and  $CO$  (higher than the thermal values) also indicate a residual dolomite activity for cracking reactions.

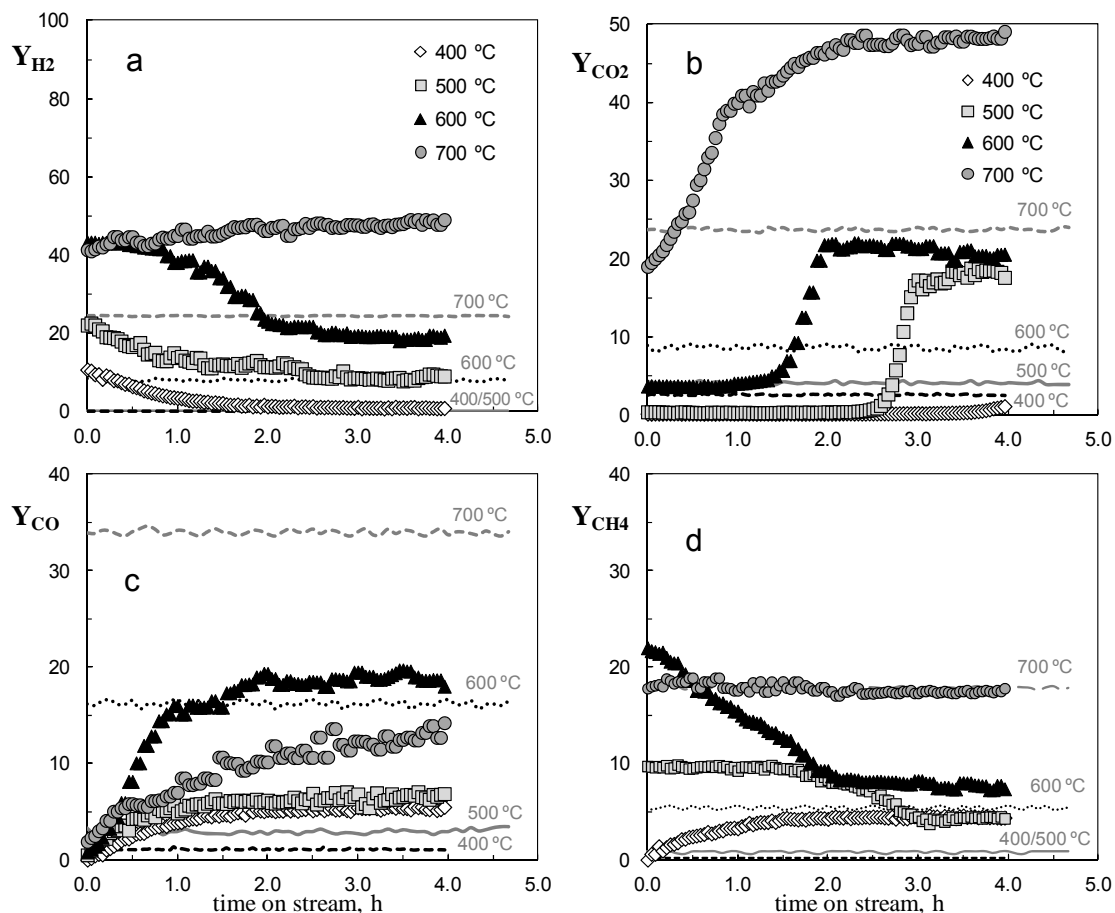


Figure 2: Effect of temperature on the evolution with time on stream of the yields of  $H_2$  (a),  $CO_2$  (b),  $CO$  (c) and  $CH_4$  (d) during the SR of the bio-oil/ethanol mixture over dolomite (points) and comparison with the results of thermal decomposition obtained in blank runs (lines)

During the  $CO_2$  capture period at  $500\text{ }^\circ\text{C}$  ( $\approx 2.5$  h), ethanol is initially fully converted but its conversion decreases rapidly with time on stream (Figure 1b) to around 40 % in 1.5 h and then there is a much more slow decrease in ethanol conversion to 30 % after 4 h (higher than 13 % obtained in the blank run). This evidences that dolomite maintains a residual activity for the ethanol reforming in spite of the noticeable deactivation at this temperature. The bio-oil conversion is initially very low and it increases with the reaction time in parallel to the decrease in ethanol conversion, always being lower than the thermal value. This unusual evolution could be explained by the formation of oxygenates (mainly acetone and acetaldehyde) from ethanol, and it suggests that dolomite promotes inter-conversion reactions between the bio-oil oxygenates (which compete with cracking reactions), with acids, esters, aldehydes and levoglucosan being converted into ketones (mainly acetone) and phenols (mainly phenol and 3-methylphenol) (Tables 2 and 4). Dolomite is not active for reforming oxygenates in bio-oil at this temperature. The initial  $H_2$  yield of 20 % gives evidence of the dolomite activity for the ethanol reforming reaction, which deactivates rapidly to a pseudo-steady state value of 10 %. After complete saturation,  $CH_4$  and  $CO$  yields are higher than those caused by the thermal effect (Figure 2), thereby indicating a residual dolomite activity for cracking reactions.

The results reveal that  $400\text{ }^\circ\text{C}$  is a too low temperature for the bio-oil/ethanol mixture reforming, despite the effective capture of  $CO_2$  (Figure 2b). Bio-oil conversion is much lower than the thermal value, ethanol conversion decreases drastically within 30 min to the thermal value and a low yield of  $H_2$  is obtained at

zero time on stream, which is negligible after 1 h reaction. At this temperature the inter-conversion reactions between the bio-oil oxygenates are favored and, as these reactions are deactivated, the decomposition/cracking reactions become significant, which leads to the formation of CO and CH<sub>4</sub> (Figure 2) and aromatic hydrocarbons (Table 4).

#### 4. Conclusions

Besides reforming and cracking reactions, dolomite also promotes inter-conversion reactions between the bio-oil oxygenates, mainly of levoglucosan, acids, esters and aldehydes, which are converted into ketones (mainly acetone) and phenols (mainly phenol and 3-methylphenol). These compounds can in turn be reformed and/or cracked to form lighter oxygenates (acetone, acetaldehyde) and hydrocarbons (mainly aromatics, probably coming from phenols). The increase in operating temperature enhances the reforming reactions of ethanol and oxygenates in the raw bio-oil with dolomite, with the highest conversion of ethanol (100 %) and bio-oil (above 83 %) and H<sub>2</sub> yield (around 45 %) being achieved at 700 °C, which remain almost steady for 4 h. The temperature increase also promotes the cracking reactions of oxygenates, which involves the formation of gaseous by-products (mainly CH<sub>4</sub>, and also CO and hydrocarbons). The CO<sub>2</sub> capture at 600 °C is effective to displace the WGS reaction and the reforming reactions, providing initially a H<sub>2</sub> yield of 40 % and high concentration CH<sub>4</sub>, along with low amounts of CO and CO<sub>2</sub>, but both ethanol and bio-oil conversions and H<sub>2</sub> yield rapidly decrease when dolomite gets saturated

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