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Cost-effective upgrading of biomass pyrolysis oil using activated dolomite as a basic catalyst

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ABSTRACT

This study deals with a continuous process on a calcined dolomite operating at atmospheric pressure and by co-feeding water for cost-effective upgrading of raw bio-oil at 400 ºC and 500 ºC. The distribution of carbon in the feed to the product fractions (gas and upgraded bio-oil) and to the dolomite (as CO_2 captured and coke) was investigated with time on stream, as well as the evolution of the gas and the upgraded bio-oil composition. Acids and high-molecular weight phenols were completely removed from the raw bio-oil for 0.5 h time on stream, with the upgraded bio-oil being mainly composed of ketones (acetone, 2-butanone and cyclopentanones). Chromatographic analyses of the reaction products were combined with analysis of the dolomite characteristics by thermogravimetry and X-ray diffraction. The results are explained on the basis of possible reaction mechanisms on the dolomite basic sites (CaO, $Ca(OH)_2$ and MgO) and the extent of dolomite carbonation with adsorbed CO_2. The composition of the upgraded bio-oil is suitable for subsequent catalytic valorization for obtaining fuels and chemicals, and in particular for the production of hydrogen by steam reforming.

KEYWORDS: raw bio-oil, upgrading, basic catalyst, dolomite, ketonization

1. INTRODUCTION

Pyrolysis oil (bio-oil) is a complex mixture of oxygenated compounds and water that can be produced by fast pyrolysis of lignocellulosic biomass. This liquid product is very attractive for the sustainable production of automotive fuels, H_2 and chemicals through several thermo-chemical and catalytic processes [1, 2]. Furthermore, high yield of bio-oil can be obtained from biomass by means of simple, energy-efficient, and environmentally friendly pyrolysis technologies, which have reached a high level of development [3]. However, storage, handle and conversion of raw bio-oil are hindered by its complex composition and poor properties (high oxygen content, thermal instability, acidity, corrosivity and low viscosity). Particularly, certain compounds (mainly phenols and acids) cause operational problems and catalyst deactivation in raw bio-oil valorization processes (e.g. cracking, hydrotreating and steam reforming) due to re-polymerisation and other undesirable reactions [4-7].

Consequently, many strategies have been addressed for converting the raw bio-oil into a high-quality and stable oil, whose further catalytic processing would be more feasible [8, 9]. These methods include: esterification, aldol condensation, ketonization, *in situ* catalytic cracking, and mild hydrodeoxygenation [2]. In this regard, a great variety of catalysts and reaction systems have been assessed on the basis of yield/purity of target products, reaction conditions severity, catalyst deactivation, feed-to-catalyst ratio, and catalyst cost [2, 9, 10]. The results point to the need for directing future research toward capital cost reduction by developing new catalysts and processes, eliminating operation units, decreasing reactor temperature and/or pressure, and finding sustainable sources for H_2 supply, etc. [10, 11]. Accordingly, the raw bio-oil conditioning by means of low-cost alternatives which employ cheap catalysts, waste products and/or naturally available elements [12, 13] is attracting increasing attention.

The catalytic pyrolysis of biomass using *in situ* CaO-based materials in the 450-500 ^{o}C range has been reported to improve the bio-oil quality by reducing its acidity and increasing the heating value [14, 15]. Stefanidis et al. [16] have evaluated the use of MgO as a sustainable and low-cost alternative to HZSM-5 zeolite, and stated that acid content in the bio-oil was reduced via ketonization and aldol condensation reactions on the MgO basic sites.

Dolomitic rock is a naturally abundant and low-toxic calcium and magnesium carbonate ($CaMg(CO_3)_2$) that may contain impurities of Fe_2O_3. It has been extensively used as a catalyst in biomass gasification processes for reducing the tar formation by cracking and reforming the high-molecular-weight compounds. Thus, yield and quality of the syngas produced are improved [17-21]. Furthermore, the CaO and MgO basic sites of calcined dolomite are effective for deoxygenating the bio-oil produced by biomass pyrolysis, enhancing the cracking of heavy organics into lighter fractions so that more desirable compounds are formed [14, 22-24]. Specifically, carboxylic acids are converted into ketones *via* ketonization reactions, whereas the lignin derived oligomers are converted into less-oxygenated phenols and aromatics. Consequently, the resulting bio-

oil has lower acidity, higher calorific value and improved stability, and therefore, a greater potential for utilization and/or downstream upgrading.

The feasibility of raw bio-oil valorization requires production of value-added bio-oils with high content of target products. Given the high concentration of carboxylic acids (mainly acetic acid) in raw bio-oil, ketonization emerges as an attractive alternative for decreasing the oxygen content, while maximizing the content of ketones in bio-oil. Vapor-phase ketonization of carboxylic acids over a wide variety of metal oxides (e.g., TiO_2, ZrO_2, SiO_2, Al_2O_3, MnO_2, CeO_2, $CeZrO_x$) has attracted extensive attention [9, 25, 26]. However, most of the studies have focused on the conversion of pure oxygenates (bio-oil model compounds), and there are few studies that approach ketonization of oxygenates mixture (simulated bio-oil) and raw bio-oil [27-30]. Therefore, information regarding the interactions of acids with other raw bio-oil compounds is scarce.

The capability of calcined dolomite for removing carboxylic acids (mainly acetic and formic) from bio-oil at low temperature ($\leq$ 500 ºC) has been reported in a previous study on the steam reforming (SR) of a bio-oil/ethanol mixture [31]. These acids and other reactive compounds (e.g., levoglucosan, aldehydes, phenols), which cause catalyst deactivation and constraint the viability of the SR process, are converted into less-oxygenated compounds (mainly ketones and alkyl-phenols) through ketonization, esterification, demethylation, and dehydration reactions. The prevailing reactions are strongly influenced by the operating conditions (temperature and time on stream) with ketonization being enhanced below 600 ºC.

The purpose of this paper is to assess the feasibility of a continuous catalytic upgrading of raw bio-oil using dolomite in a low-cost reaction system (atmospheric pressure, temperatures $\leq$ 500 ºC, and without external H_2 supply). Additional water was co-fed with the raw bio-oil for enhancing ketonization activity of the dolomite by promoting the formation of a $Ca(OH)_2$ strong basic phase. Suitable operating conditions of this original alternative are established for conditioning the raw bio-oil composition by removing undesirable compounds (carboxylic acids and phenols). The composition of the upgraded bio-oil (with high concentration of ketones) enables its subsequent further valorization (e.g., by steam reforming).

2. EXPERIMENTAL

2.1. Bio-oil

The raw bio-oil, provided by *BTG Bioliquids BV* (the Netherlands), was produced by flash pyrolysis of pine sawdust in an industrial plant with 5 t/h capacity and a conical rotary reactor. The elemental composition was analyzed using a *Leco CHN-932* analyzer and ultra-microbalance *Sartorious M2P*, and the water content was determined by Karl Fischer titration (*KF-Titrino Plus 870*). The contents of carbon (C), hydrogen (H), oxygen (O) and water in the raw bio-oil were 55.4 %, 6.2 %, 38.4 % and 26 wt%, respectively.

The chemical composition was analyzed using a *Shimadzu QP2010S* gas chromatography/mass spectrometer (GC/MS) provided with a BPX-5 column (50 m x

0.22 mm x 0.25 μm) and mass selective detector. The bio-oil compounds were grouped into families: acids, ketones, esters, furanes and furanones, alcohols, aldehydes, ethers, anhydrosugars, and phenols. Identification of compounds was accomplished by matching the mass spectra with those from *NIST 147* and *NIST 27* data libraries. Direct quantification of the bio-oil components by the usual calibrated peak area procedure could not be feasibly carried out from GCMS data due to the complexity of these compounds. Therefore, semi-quantitative method based on the chromatographic area percentage was used to determine the relative proportion of each compound. It should be pointed out that GC/MS technique has limited capability for detecting heavy oligomeric compounds with molecular weight greater than 320 g/mol [32].

2.2. Characterization of natural, calcined and deactivated dolomite

The dolomite used in this work was produced and supplied by *Calcinor S.A.* (Cantabria, Spain). It is a natural solid resource usually intended for agriculture, construction industry, and manufacturing refractory bricks. After being dried at 110 ºC for 12 h, the as-received natural dolomite was calcined at 850 °C for 5 h to transform it into active CaO/MgO phases. Thermal decomposition behavior of natural dolomite was analyzed using *TA Instruments Q5000 IR* thermobalance by heating the sample at 5 °C/min up to 800 °C under a N_2 atmosphere (10 ml/min). The temperature was held at 800 ºC for 10 min and then it was raised up to 900 °C and held for 10 min more.

The *TA Instruments Q5000 IR* thermobalance was also coupled to a mass spectrometer *Thermostar Balzers Instrument* for monitoring the signal corresponding to CO_2, with the aim of quantifying the amount of CO_2 adsorbed and coke deposited on the deactivated dolomite after each experiment. For this purpose, a "calcination-combustion" method was developed: i) heating from 50 ºC to 750 ºC at 5 ºC/min under inert atmosphere (10 ml/min N_2) in order to decompose $CaCO_3$ into CaO thus releasing the adsorbed CO_2 (calcination stage); ii) cooling the sample again to 50 ºC; and iii) heating from 50 ºC up to 800 ºC at 5 ºC/min under oxidizing atmosphere (60 ml/min air) in order to burn the coke deposited (combustion stage).

Crystalline phases of natural, calcined and deactivated dolomite samples were analyzed by a *D8 Advance* X-ray diffractometer (XRD). The XRD patterns were obtained over $10° \leq 2\theta \leq 80°$ using Cu kα radiation (40 kV, 40 mA). From the band intensity on the XRD analysis of the calcined dolomite, a composition of 32 % CaO and 67 % MgO was estimated. Surface areas of dolomite samples were measured by the Brunauer-Emmett-Teller (BET) N_2 adsorption method at -196 ºC using a *Micromeritics ASAP 2020* instrument.

H_2 temperature-programmed reduction (TPR) was performed on a *Micromeritics AutoChem II 2920* to analyze the reducibility of the Fe-metal species. The dolomite sample was firstly degassed at 200 ºC and subsequently heated under reducing atmosphere (10 % vol. H_2-He) from 50 ºC to 900 ºC at 5 ºC/min. The total amount of Fe impurities on the calcined dolomite (1074 μg/g) was measured by ICP-MS.

2.3. Reaction equipment and operating conditions

Schematic diagram of the reaction equipment used for the raw bio-oil upgrading experiments is shown in Fig. 1. The reactor consisted of a U-shaped stainless steel tube (1.6 cm inner diameter and 15 cm length) which was externally heated by an electric furnace. The 15 cm of pre-heating section (inlet side) allowed volatilization of the bio-oil prior to the catalytic section (outlet side), where the calcined dolomite was held by quartz wool above and below the bed. The carbonaceous solid, called pyrolytic lignin (PL) [33], was formed by re-polymerization of bio-oil compounds inside the pre-heater section. The resulting volatile stream passed through the dolomite bed. The controlled deposition of pyrolytic lignin prior to the catalytic bed minimizes the operating problems and attenuates catalyst deactivation. The reactor configuration enables continuous operation and separate collection of gas, liquid (upgraded oil) and solid (PL) reaction products. The relevance of this continuous upgrading alternative also lies in the possibility of accurately measuring the evolution with time on stream of products yield/selectivity, and hence the catalyst deactivation.

FIGURE 1

The raw bio-oil was fed as droplets (injected using a pump *Harvard Apparatus 22)* that were carried by an inert He gas flow. Prior to each upgrading experiment, the as-received natural dolomite was sieved at 90-150 μm range. Then it was activated by calcination at 850 ºC for 5 h for obtaining CaO and MgO as active basic species. Additional water was fed (*307 Gilson* pump) in order to have a steam-to-carbon ratio of around 3. The experiments were carried out by feeding the raw bio-oil for 4 h at 400 ºC and 500 ºC with a space-time of 2.8 $g_{dolomite}h/g_{bio\text{-}oil}$.

2.4. Reaction products characterization

The volatile products stream was analyzed by on-line gas chromatograph (*Agilent Micro GC490*) provided with four analytical modules: i) 5A MS column for quantifying H_2, CO, and CH_4; ii) PPQ column for light oxygenates (C_2-C_4), CO_2 and H_2O; iii) CPSil column for C_{5+} hydrocarbons; iv) Stabilwax column for C_{2+} oxygenated compounds. Furthermore, the volatile stream was sent to a condensation system (Peltier cell at 0 ºC) and separated into condensable and non-condensable fractions (Fig. 1). The condensable fraction was obtained as a heterogeneous liquid with two different phases (aqueous and organic) that could be separated by decantation. The composition of the liquid collected throughout reaction (upgraded bio-oil) was analyzed by GC/MS (*Shimadzu QP2010S* device). The elemental analysis of the solid product deposited in the pre-heater section (pyrolytic lignin) was performed in a *EuroVector EA3000* Elemental Analyzer (CHNS).

2.5. Quantification of product yields

The relative carbon yield in the gas, liquid and solid (PL) product was quantified on the basis of the carbon fed in the raw bio-oil, by using the carbon mass balances (overall carbon closure above 95 %) and according to the following equations:

$$\text{Gas yield}\,(\text{C}\,\%) = \frac{\text{F}_{\text{Gas}}}{\text{F}_{\text{bio}-\text{oil}}}\,\text{x}\,100 \quad (1)$$

$$\text{Liquid yield}\,(\text{C}\%) = \frac{\text{F}_{\text{Liq}}}{\text{F}_{\text{bio}-\text{oil}}}\,\text{x}\,100 \quad (2)$$

$$\text{PL yield}\,(\text{C}\,\%) = \frac{\text{m}_{\text{PL}}}{\text{F}_{\text{bio}-\text{oil}}}\,\text{x}\,100 \quad (3)$$

where $F_{bio\text{-}oil}$, F_{gas}, and F_{liq} is the carbon mass-flow (mg C/min) in the raw bio-oil, the gas, and the liquid product, respectively. The m_{PL} term is the rate of carbon deposition in the pyrolytic lignin (mg C/min), assuming linear deposition throughout reaction. The carbon yield in dolomite quantified the amount of the C fed in the raw bio-oil that was captured by the dolomite (resulting in $CaCO_3$ formation by CO_2 adsorption) and it was estimated by difference:

$$\text{C}_{\text{dolomite}}\,(\text{C}\,\%) = 100 - \text{Gas yield} - \text{Liquid yield} - \text{Solid yield} \quad (4)$$

Reporting the results in terms of carbon yield of individual products allows for tracking the fate of the carbon fed in the raw bio-oil. Recently, Saraeian et al. [34] emphasized the relevance of calculating the product yields in terms of overall mass and/or relative to the carbon in the feed for recognizing effective systems, strategies and catalysts for bio-oil upgrading. This would allow comparing small-scale and large-scale studies, as well as studies using different catalysts.

3. RESULTS AND DISCUSSION

3.1. Activation of dolomite by calcination

The thermogravimetric TG (weight loss, %) and DTG (derivative weight loss, %/min) profiles resulting from thermal decomposition of the natural dolomite are depicted in Fig. 2. It is observed that decomposition of this dolomite takes place in the 570–800 °C range, which is ascribed to direct transformation into the corresponding Ca and Mg oxides Eq. (5). The results indicate that the highest weight loss during the thermal decomposition occurs at 770 °C (single peak in DTG profile), and there is no weight loss above 800 °C.

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2\,CO_2 \quad (5)$$

FIGURE 2

The X-ray diffraction pattern of the as-received dolomite is compared with that of activated dolomite in Fig. 3a. These results reveal a different crystalline structure of the natural and the calcined dolomite. The XRD of natural dolomite shows intense peaks at 2θ = 30.9°/33.6°/35.4°/37.4º which correspond to $CaMg(CO_3)_2$, and peaks at 2θ = 41.2°/50.6°/51.1° corresponding to calcium peroxide (CaO_2). Less intense peaks at 2θ =

70.6°/72.9° corresponding to $CaCO_3$ are also detected. Accordingly, the natural dolomite is mainly composed of $CaMg(CO_3)_2$, and low amounts of CaO_2 and $CaCO_3$. The XRD pattern of activated dolomite shows the diffraction peaks ascribed to the presence of CaO (2θ = 32.5°/37.6°/54.1º/67.6°) and MgO (2θ = 43.2°/74.9°). Peaks corresponding to $CaMg(CO_3)_2$ are not detected.

Although a suitable calcination temperature for converting $CaCO_3$ into CaO is usually around 800 ºC, it depends on the $CaCO_3$ source. For example, the $CaCO_3$ in oyster shells is transformed into CaO at 700 ºC, whereas for eggshell and clamshell this transformation occurs at 800 ºC, and for lime mud (industrial waste from pulp and paper mills) the calcination temperature is around 1000 ºC [15]. The TG/DTG and XRD results indicate that 850 °C is a suitable calcination temperature for activating the dolomite used in this work.

The reducibility of the metal species contained in the activated dolomite was qualitatively characterized by TPR (Fig. 3b), showing a single broad reduction peak in the 500-650 ºC range. According to Di Felice et al. [19], this peak may be ascribed to the $MgFe_2O_4 \rightarrow Fe_3O_4\text{-}Fe_{3-x}Mg_xO_4$ transition. This means that the Fe^{3+} contained in activated dolomite is susceptible to reduction into $Fe^{2.5+}$ (Fe_3O_4) when it is subjected to a reductive atmosphere.

FIGURE 3

The crystal size of CaO and MgO were determined by applying the Scherrer equation to the CaO peak (2θ = 37.6°) and the MgO peak (2θ = 43.2°), resulting in average particle sizes of 85 nm and 47 nm, respectively, which reveal the nanocrystalline nature of these phases. High calcination temperatures induce the Mg surface segregation, resulting in MgO nanocrystals dispersed over CaO particles [35].

Morphology of the activated dolomite is significantly different than that of natural dolomite, thus revealing that CO_2 release during the thermal decomposition of $CaMg(CO_3)_2$ (leading to CaO and MgO formation) modifies not only the chemical composition but also the physical properties. Consequently, the activated dolomite has many orderly pores on the surface which form a more porous structure, resulting in a higher surface area (S_{BET} = 12.2 $m^2\ g^{-1}$) than that of natural dolomite (S_{BET} = 1.7 $m^2\ g^{-1}$).

3.2. Catalytic performance of activated dolomite

Given the complexity of the raw bio-oil constituent molecules (mainly levoglucosan, acids, ketones and phenolics), they may react on the dolomite catalyst *via* several reactions (decarbonylation, decarboxylation, cracking, reforming, ketonization, condensation, dehydrocyclization/aromatization, polymerization, etc), which depend on the nature of the active sites and on the reaction conditions. Although the capability of activated dolomite for capturing CO_2 by carbonation is clear [36], the main goal of this section is to delve into the dolomite catalytic behavior at low reaction temperatures (≤ 500 ºC). For this purpose, the distribution and composition of the products are analyzed

in detail. Besides, a thorough discussion on the role that the dolomite basic sites have on its catalytic behavior is presented below.

3.2.1. Distribution of product yields

Fig. 4 shows the evolution with time on stream of the relative C yield in solid (pyrolytic lignin), liquid (upgraded bio-oil) and gas (Eqs. (1)-(3)) for a reaction temperature of 400 ºC (Graph a) and 500 ºC (Graph b). The yield denoted as "C in dolomite" quantifies the amount of carbon coming from the raw bio-oil which is "captured" (as adsorbed CO_2 to form $CaCO_3$ and as coke).

According to these results, liquid and solid are the majority products at 400 ºC (Fig. 4a) and the distribution of product yields changes notably by raising the temperature up to 500 ºC. The gas yield increases, the liquid yield slightly decreases, whereas the deposition of pyrolytic lignin is significantly attenuated. Besides, the C yield in the dolomite is higher at 500 ºC, which suggests enhancement of bio-oil decarboxylation reactions leading to the formation of CO_2, which is subsequently absorbed by the dolomite.

FIGURE 4

The different stages discerned in the evolution of the relative C yields (Fig. 4) are mainly attributed to the extent of the dolomite carbonation. For both temperatures, the C-yield in dolomite is highest at zero time on stream, owing to the greatest carbonation activity of the fresh dolomite. Besides, the initial C-yield in dolomite is higher at 500 ºC (Fig. 4b) compared with 400 ºC (Fig. 4a), which is explained by the greater extent of the bio-oil decarboxylation and ketonization reactions at this temperature. Consequently, a higher amount of C in the feed is converted into CO_2 that is captured by the dolomite. The carbonation of dolomite lasts approximately 2.3 h at 400 °C (Fig. 4a) and 2.7 h at 500 °C (Fig. 4b). At 400 ºC, the CO_2 capture capability of the dolomite progressively decreases, leading to a higher C yield in the gas product. At 500 °C, the gas yield remains practically steady for 1.8 h, after which there is a sharp increase indicating saturation of CO_2 capture capability. After complete carbonation of the dolomite, the gas and liquid yields remain almost steady until the end of the experiment. For both temperatures, the C-yield in the solid product (pyrolytic lignin, Fig. 1) is constant because a linear deposition was assumed throughout each reaction.

In order to properly explain the distribution of products (Fig. 4) and their composition (discussed in the following sections), different reactions must be taken into account in the catalytic activity of dolomite. In addition to CaO and MgO, the hydration of CaO leading to the formation of $Ca(OH)_2$ [37, 38] occurs during the bio-oil upgrading experiments (Eq. (7)). Given its exothermic nature, this reaction is more favored at 400 ºC than at 500 ºC. It should be pointed out that this fact was experimentally evidenced by a sudden temperature increase (≈ 50 ºC) at the beginning of the experiment at 400 ºC. The high basicity of the $Ca(OH)_2$ is likely to have an important role in dolomite activity for bio-oil oxygenates conversion.

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s) \qquad \Delta H°_{298K} = -177 \text{ kJ mol}^{-1} \qquad (6)$$

$$CaO(s) + H_2O(g) \leftrightarrow Ca(OH)_2(s) \qquad \Delta H°_{298K} = -106 \text{ kJ mol}^{-1} \qquad (7)$$

$$Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O \qquad \Delta H°_{298K} = -71 \text{ kJ mol}^{-1} \qquad (8)$$

Both CaO and the $Ca(OH)_2$ formed (which is also active for CO_2 capture, Eq. (8)) deactivate during the experiments due to carbonation reaction. The relationship between Eq. (6) and Eq. (7) also suggests that the progressive CaO carbonation involves the $Ca(OH)_2$ disappearance.

Owing to the dolomite activity for bio-oil steam reforming [31, 39], both the oxygenates reforming, Eq. (9), and the water-gas-shift (WGS) reaction, Eq. (10), should also be considered, although they contribute to a moderate extent in the temperature range studied (400-500 ºC). Considering the dolomite activity for cracking tar and long-chain hydrocarbons in biomass pyrolysis and gasification processes [18-21], the cracking reactions involving bio-oil oxygenates should be also taken into account. These reactions lead to the formation of CO, CO_2, CH_4, H_2 and light hydrocarbons. The CO_2 formation in steam reforming and cracking reactions would contribute to the extent of the CaO and $Ca(OH)_2$ carbonation (Eq. (6) and Eq. (8), respectively).

$$C_nH_mO_k + (2n-k)\, H_2O \rightarrow n\, CO_2 + (2n+m/2-k)\, H_2 \qquad (9)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H°_{298} = -41 \text{ kJ/mol} \qquad (10)$$

The afore-shown results evidence that the catalytic behavior of activated dolomite is significantly affected by the reaction temperature. The continuous reaction system allows analyzing the evolution with time on stream of the gas and liquid products composition. This provides useful information on the influence that the dolomite deactivation (by carbonatation and coke deposition) has on its catalytic behavior, and allows to ascertain the prevailing reaction pathways. In the following sections, the composition of the gas product and the upgraded bio-oil are thoroughly analyzed and related with the catalytic behavior of the dolomite.

3.2.2. Gas product composition

The evolution with time on stream of the gas product composition (mol %) is shown in Fig. 5 at 400 ºC (graph a) and 500 ºC (graph b). The results reveal that CO_2 is effectively captured for more than 1.5 h at both temperatures, as well as a noticeable change in gas composition after dolomite saturation at 500 ºC, due to the sharp increase in CO_2 concentration (Fig. 5b).

FIGURE 5

Owing to the effective capture of CO_2 at 400ºC, the gas produced is initially composed of 75 % H_2 and lower concentrations of CO (10 %), CH_4 (10 %), and C_2-C_4 hydrocarbons (5 %). Then, the H_2 concentration decreases significantly throughout the carbonation period (≈ 1.5 h) and the CO, CH_4 and HCs concentration increase up to 40 %, 20 %, and 10 %, respectively. This evolution on the gas composition is caused by the lower extent

of oxygenates reforming and WGS reaction (Eqs. (8)-(9)), as they are selectively deactivated thus promoting cracking reactions leading to CH_4 and HCs formation. Indeed, the significant content of CH_4 and C_2-C_4 hydrocarbons is consistent with the reported cracking activity of dolomite in biomass catalytic pyrolysis and tar elimination processes [14, 21, 23]. The CO_2 concentration remains at negligible levels throughout the carbonation period, and then it increases until complete dolomite saturation (≈ 2.5 h).

Although the initial H_2 concentration in the gas obtained at 500 ºC is lower (55 %), the H_2 yield is higher due to the greater extent of oxygenates reforming and cracking reactions at this temperature, which lead to a higher total gas yield (Fig. 4). In the first hour of reaction, the H_2 concentration decreases from 55 % to 40 %, the CO increases from 20 % to 40 %, and the CH_4 and HCs concentration remain almost steady. The CO_2 concentration is negligible for 2 h and it becomes significant after dolomite saturation by carbonation, increasing sharply until a steady value. Consequently, the concentration of H_2, CO, CH_4 and HCs decrease in the gas product.

3.2.3. Liquid product composition

The distribution of primary and trace compounds in the upgraded bio-oil collected throughout each experiment is shown in Table 1 (400 ºC) and Table 2 (500 ºC). The composition of the raw bio-oil and the liquid collected in experiments without dolomite (thermal treatment) are also shown in order to discern the catalytic effect. For both temperatures, the thermal treatment of raw bio-oil produces a bio-oil with acetic acid, acetol (1-hydroxy-2-propanone) and levoglucosan as majority compounds. It should be noted that this treated bio-oil has lower concentration of phenols but greater content of acids compared with the raw bio-oil

TABLE 1

TABLE 2

The results evidence that acids are completely removed, and phenols are partially converted when activated dolomite is used as upgrading catalyst. Other attractive feature of the upgraded bio-oil collected after short reaction time (0.5 h) is its high content of ketones, mainly acetone (26 % at 400 ºC and 37 % at 500 ºC), 2-butanone (11-19 %) and cyclopentanones (17-30 %). This result suggests that the dolomite has great activity for ketonization of bio-oil oxygenates, through pathways similar to those proposed using a wide variety of catalysts for upgrading pyrolysis oils [27, 29, 30, 40]. Also noteworthy is the presence of 7.3 % of aliphatic hydrocarbons (composed of linear C_6-C_{12} alkenes and C_8 cycloalkenes) in the upgraded bio-oil obtained at 500 ºC.

Furthermore, the oxygenated phenols (i.e., guaiacols, catechols and heavy poly-substituted phenols) are completely eliminated from the raw bio-oil, with only phenol and alkyl-phenols being detected in the upgraded oil obtained throughout 0.5 h on stream. Several authors have reported the CaO activity for cracking aromatic ring side chains during catalytic pyrolysis of biomass at 450-600 ºC [14, 41, 42]. The decrease in acids concentration is key to improve the bio-oil stability and reduce its corrosivity. It is also

desirable to decrease the high molecular weight phenols, given their tendency to polymerize and deactivate the catalyst in processes of bio-oil conversion into hydrocarbons [4, 5] and bio-oil steam reforming [6, 7]. Furthermore, the conversion of guaiacols (e.g. 2-methoxyphenol) and other oxygenated phenols (e.g. 4-hydroxy-3-methoxy-benzaldehyde) into alkyl-phenols contributes to decreasing the total oxygen content in the bio-oil.

The results in Table 1 and Table 2 show an increasing content of acids and phenols with time on stream (especially after dolomite saturation when CaO and $Ca(OH)_2$ are fully carbonated to $CaCO_3$), as well as a decreasing concentration of ketones. Although the alkyl-phenols still remain as majority compounds, the content of guaiacols and catechols become significant after 4 h reaction. This result is consistent with preliminary remarks on dolomite activity [31], and confirms that guaiacol demethylation/dehydration pathway is enhanced as dolomite deactivates. This may also contribute to the high concentration of CH_4 observed in gas product (Fig. 5).

The aforementioned results reveal that the raw bio-oil upgrading with activated dolomite takes place through different reaction pathways, due to the different catalytic role of CaO, MgO and $Ca(OH)_2$ basic oxides, and the acid $CaCO_3$ resulting from carbonatation. The prevailing reaction pathways under the operating conditions used (low temperature $\leq$ 500 ºC and high water content) will be proposed and discussed in Section 3.3.

3.2.4. Characteristics of deactivated dolomite

The X-ray diffraction analysis of fresh catalyst (activated dolomite) is compared with those corresponding to dolomite after reaction at 400 ºC and 500 ºC (Fig. 6). The XRD patterns reveal that fresh dolomite is composed of CaO and MgO. The presence of CaO is not detected in any of the deactivated dolomite samples, which are mainly composed of $CaCO_3$ and MgO. These results evidence that all the CaO contained in dolomite is carbonated to $CaCO_3$ during the experiments, whereas the Mg remains in oxide phase (MgO).

The presence of residual $Ca(OH)_2$ (2θ = 18.3/34.2) is detected both in the dolomite deactivated at 500 ºC ($\approx$ 5 %) and at 400 ºC ($\approx$ 1 %), which can be explained by the thermodynamics of the $Ca(OH)_2$ carbonation (Eq. 8). Given the exothermic nature of this reaction, $Ca(OH)_2$ carbonation is more favored at 400 ºC than at 500 ºC. Furthermore, the absence of $MgCO_3$ confirms the fact that the MgO contained in dolomite does not contribute to the carbonatation reaction under the operating conditions studied [14].

As discussed in Section 3.2.1, the C "retained" in the deactivated dolomite (C-yield shown in Fig. 4) includes the CO_2 adsorbed (to form $CaCO_3$) and the coke deposited. Fig. 7 depicts the weight loss and the CO_2 signal recorded during the calcination-combustion TG analysis (described in Section 2.2), which allows to discern between the C coming from carbonation and that corresponding to the coke. The first peak is ascribed to the CO_2 captured by the dolomite, which is released during the calcination stage. The second peak corresponds to the CO_2 produced by combustion of the coke deposited. From these

results, both the amount of C adsorbed and the coke deposited on the deactivated dolomite are quantified (Table 3).

FIGURE 6

FIGURE 7

TABLE 3

3.3. Reaction pathways in raw bio-oil upgrading

The absence of acetic acid, as well as the high content of acetone in the upgraded bio-oil collected throughout 0.5 h (Table 1 and Table 2) clearly indicate the dolomite activity for acetic acid ketonization. Similarly, ketonization reactions involving other carboxylic acids may occur leading to the formation of linear ketones. It is well-established in the literature that acids can be converted through three reaction pathways: neutralization, thermal cracking and catalytic cracking. As previously reported, acids can react with CaO by neutralization reaction to form calcium carboxylate and H_2O, Eq. (10) [38, 43]. Calcium carboxylate would decompose to ketones and $CaCO_3$ at the temperature range of 400–500 ºC, Eq. (11) [44-46]:

$$2\ \text{R-COOH} + \text{CaO} \rightarrow (\text{RCOO})_2\text{Ca} + \text{H}_2\text{O} \quad (10)$$

$$(\text{RCOO})_2\text{Ca} \rightarrow \text{CaCO}_3 + \text{R-COR} \quad (11)$$

Fig. 8. shows a scheme that gathers ketonization and other possible reaction pathways involved in the raw bio-oil conversion with activated dolomite under the operating conditions used (high water content and temperatures ≤ 500 ºC). In addition to coming from carboxylic acids, acetone and 2-butanone could be also produced from acetol (1-hidroxy-2-propanone) *via* the intermediates acetic acid (which undergoes ketonization) and propanal (which undergoes carbonylation, hydrogenation, and dehydration) [27, 29]. Apparently, these are the prevailing reactions promoted by the activated dolomite, which lead to the formation of acetone and 2-butanone (the main linear ketones detected in the upgraded bio-oil). Moreover, the selectivity to linear ketones is increased by raising temperature from 400 ºC to 500 ºC.

The high content of cyclopentanone and alkyl-substituted cyclopentanones in the upgraded bio-oil produced throughout 0.5 h on stream (C5-ring ketones, Table 1 and Table 2) is an outstanding result, as they are interesting raw materials in medicine, pesticide and fragrance industries. The significant formation of cyclic ketones can be explained by the transformation of anhydrosugars (mainly levoglucosan) *via* rearrangement reactions of furfuryl type compounds (e.g., furfural) [47] (Fig. 8). It should be noted that these reactions are promoted by the high concentration of water in the reaction medium [29, 48, 49], and also by the H_2 coming from the dolomite activity for SR and WGS reactions (Eqs.(9)-(10)). Another possible pathway of forming cyclopentanone could be cyclo-ketonization of the adipic acid resulting from the catalytic

reduction of levoglucosan and other anhydrosugars [50, 51]. It should be pointed out that this reaction is promoted by the presence of $Ca(OH)_2$. Renz and Corma [52] reported a high activity of $Ca(OH)_2$ for adipic acid ketonization using a dry distillation method at 350 ºC. The formation of acetaldehyde (not detected in the raw bio-oil) suggests that this dolomite is also active for acetic acid hydrogenation to acetaldehyde, which could be attributed to the catalytic activity of the Fe impurities under a H_2-rich atmosphere [53].

FIGURE 8

The decreasing content of ketones with time on stream in parallel to the increasing content of acids suggests dolomite deactivation, which is caused both by the $CaO/Ca(OH)_2$ carbonation and by coke deposition. Indeed, the sharp increase in the content of phenols in the upgraded bio-oil obtained after ≈ 4 h on stream at 400 °C (Table 1) and after ≈ 2h at 500 °C (Table 2) can be directly related to the dolomite saturation (Fig. 4-5). This result suggests that CaO and $Ca(OH)_2$ basic oxides are the main active sites responsible for ketonization reactions, whereas the $CaCO_3$ seems to be almost inactive. As these ketonization reactions deactivate, the reactions leading to phenols formation (mainly alkyl-phenols and catechols) become significant. These reactions, which are apparently activated by the $CaCO_3$ and MgO contained in dolomite, seem to be enhanced by raising the temperature.

The results of this work are consistent with those obtained in previous studies on the *in-situ* catalytic pyrolysis of lignocellulosic biomass with calcined dolomite [23, 24], as well as on the catalytic upgrading of biomass pyrolysis vapors over CaO and MgO based catalysts using an analytical pyrolysis-gas chromatography/mass spectrometry system (Py-GC/MS) [41, 54, 55]. Ly et al. [23] state that dolomite changes the composition of the bio-oil obtained by pyrolysis of tulip tree at 450 ºC by reducing significantly the content of levoglucosan and promoting the formation of ketones (mainly cyclopentenones) and phenolic compounds. The decrease in levoglucosan is attributed to the ring-breaking reactions promoted by the Ca and Mg contained in dolomite. Lu et al. [41] compare the catalytic behavior of CaO, MgO and Fe_2O_3 and conclude that CaO decreases the levoglucosan content and fully eliminates acids, while greatly promoting the formation of linear ketones and cyclopentanones. Conversely, MgO and Fe_2O_3 result in higher formation of phenols and aromatic compounds but they are not able to reduce the acids.

It should be highlighted that ketonization of real bio-oil has been scarcely studied in the literature. A simulated bio-oil consisting of acetic acid, acetol, and furfural has been upgraded by Hakim et al. [27] in a continuous flow reactor using CeZrOx as a catalyst. Although the acetic acid content is significantly reduced, they have found that the presence of furfural decreases the ketonization activity. A more realistic study has been conducted by Mansur et al. [28] upgrading the water-soluble fraction of a bio-oil (obtained by slow pyrolysis of cedar woodchips) with zirconia-supported iron-oxides (ZrO_2–FeOx) at 350-450 ºC. Similar to our results, they report that hydroxyacetone and carboxylic acids (acetic and propionic acids) are converted into ketones (acetone and 2-

butanone). More recently, Kastner and co-workers [29, 30] have used a continuous packed bed reactor for upgrading a water extracted bio-oil over iron oxide catalysts derived from red mud. These authors also report that acetol and carboxylic acids are primarily converted into acetone and 2-butanone, with the highest yield being produced at relatively low temperatures (350-500 ºC).

CONCLUSIONS

Natural dolomite has been successfully activated and applied to raw bio-oil continuous upgrading process by means of a reaction system that enables separate collection and analysis of reaction products. This allowed studying the evolution with time on stream of the upgraded bio-oil composition. The activated dolomite is capable of removing carboxylic acids, acetol (1-hydroxy-2-propanone) and anhydrosugars (levoglucosan) from the bio-oil, whereas the formation of linear ketones (acetone and 2-butanone) and cyclopentanones i greatly increased. The heavy oxygenated phenols (e.g., guaiacols, catechols and poly-substituted phenols) are also converted into light alkyl-phenols by removing the methoxyl and hydroxyl groups.

The dolomite activity for ketonization, water-gas-shift, steam reforming and cracking reactions is attributed to its basic nature, due to the presence of CaO/MgO basic oxides and strongly basic $Ca(OH)_2$. Under the upgrading conditions used (high water content and temperatures $\leq$ 500 ºC), the basic sites of activated dolomite promote acetic acid and levoglucosan conversion *via* ketonization reactions The steam reforming and water-gas-shift reactions are enhanced by dolomite capability for CO_2 capture. As dolomite deactivates (by carbonatation of $Ca(OH)_2$ and CaO to $CaCO_3$ and by coke deposition), cracking reactions involving poly-substituted phenols that lead to the formation of alkyl-phenols become significant. After 0.5 h on stream at 400 °C, 48 % of the carbon fed in the raw bio-oil is converted into a high-quality bio-oil with low corrosive nature (negligible acid content) and high concentration of linear ketones (37 % acetone + 2-butanone) and cyclopentanones (30 %).

Consequently, the development of this cost-effective continuous process (which uses low-cost dolomite as catalyst, operates at atmospheric pressure and without external H_2 supply) is of great interest with regard to carbon efficiency, and composition of the upgraded bio-oil for its downstream valorization for producing fuels, chemicals, and particularly, H_2 by steam reforming.

Acknowledgements

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FIGURE CAPTIONS

Figure 1. Schematic diagram of the experimental equipment.

Figure 2. Thermogravimetric analysis of as-received natural dolomite.

Figure 3. Characteristics of dolomite: XRD of natural and activated dolomite (Graph a) and TPR of activated dolomite (Graph b).

Figure 4. Evolution with time on stream of carbon yields (C wt%) in dolomite, solid (pyrolytic lignin), liquid (upgraded bio-oil) and gas products. Reaction temperature: 400 ºC (Graph a) and 500 ºC (Graph b).

Figure 5. Evolution with time on stream of the gas product composition (mol %) at 400 ºC (Graph a) and 500 ºC (Graph b).

Figure 6. XRD patterns of activated dolomite (a) and dolomite deactivated after reaction at 400 ºC (b) and 500 ºC (c).

Figure 7. Calcination-combustion TG-MS analyses of dolomite deactivated after 4 h reaction at 400 ºC (a) and 500 ºC (b).

Figure 8. Proposed reaction pathways for the conversion of bio-oil majority compounds over activated dolomite under upgrading conditions of high water content (S/C= 3) and low temperature (≤ 500 ºC).

FIGURES

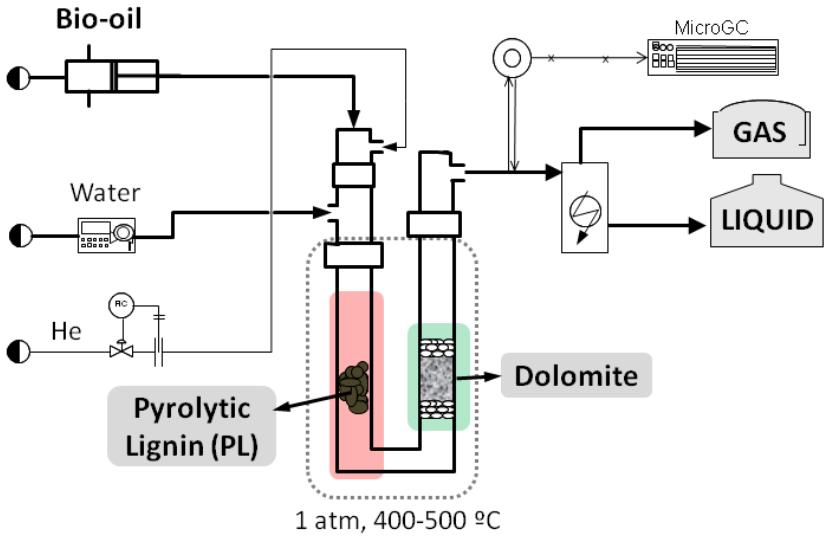


Figure 1

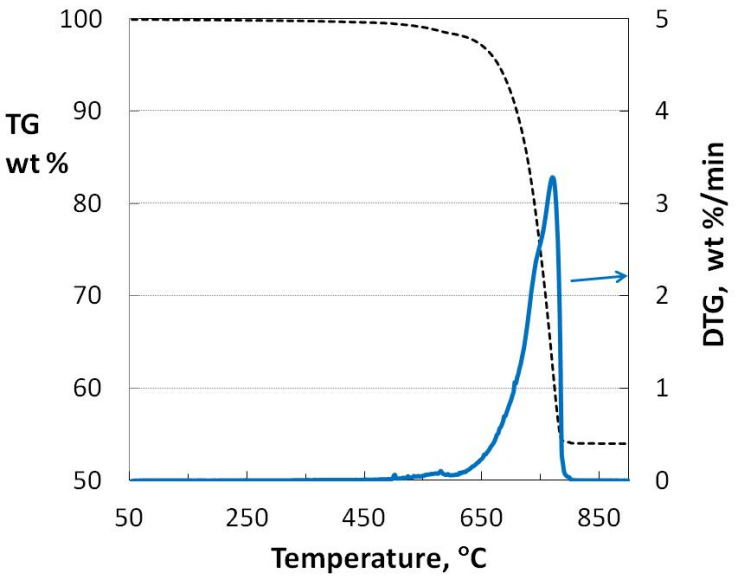
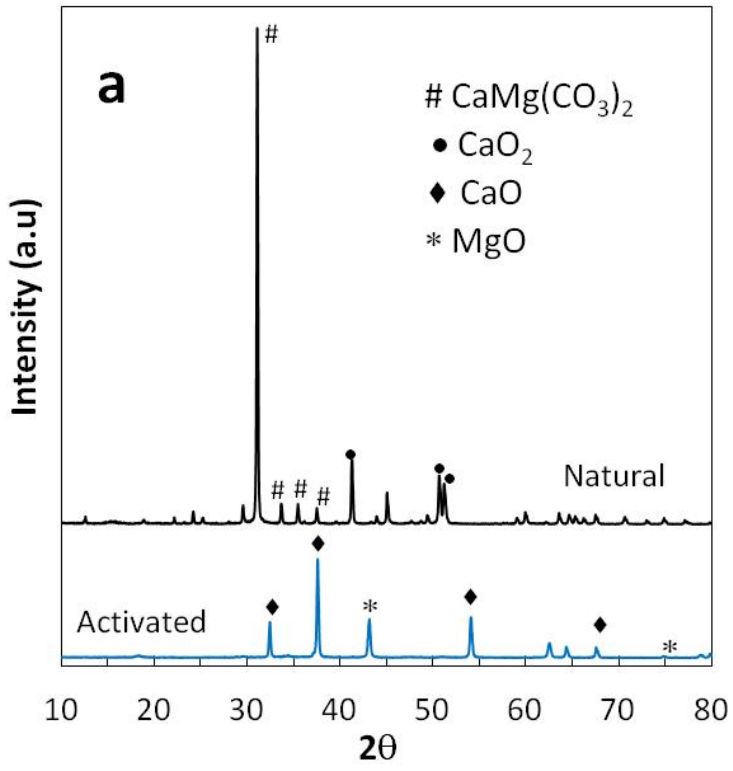


Figure 2


a
CaMg(CO3)2
● CaO2
♦ CaO
* MgO
Natural
Activated
Intensity (a.u)
2θ
10 20 30 40 50 60 70 80

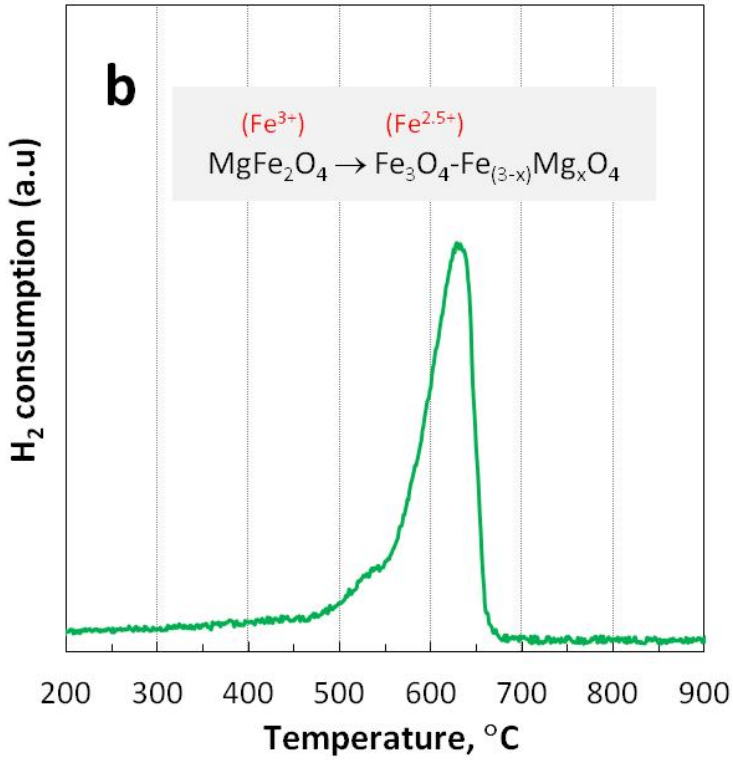

b
(Fe3+) (Fe2.5+)
MgFe2O4 → Fe3O4-Fe(3-x)MgxO4
H2 consumption (a.u)
Temperature, °C
200 300 400 500 600 700 800 900

Figure 3

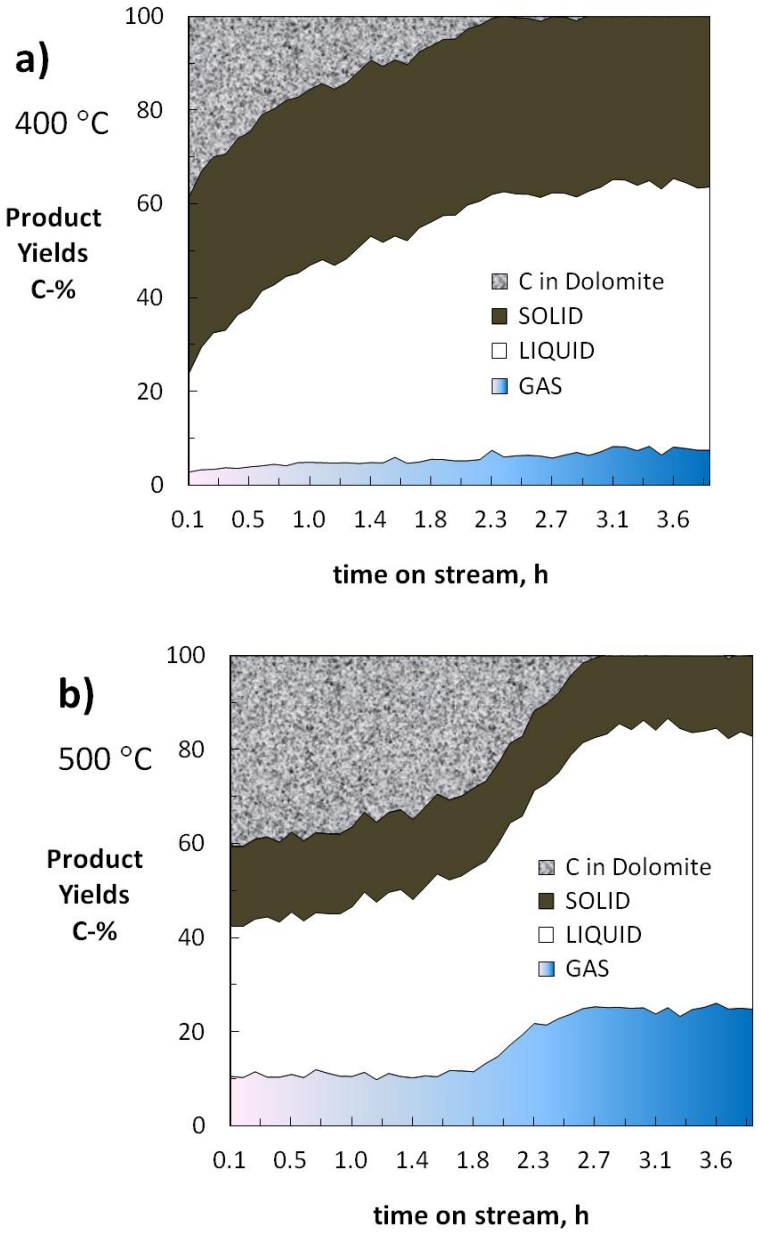

a)
400 °C
Product Yields C-%
100
80
60
40
20
0
C in Dolomite
SOLID
LIQUID
GAS
0.1 0.5 1.0 1.4 1.8 2.3 2.7 3.1 3.6
time on stream, h
b)
500 °C
Product Yields C-%
100
80
60
40
20
0
C in Dolomite
SOLID
LIQUID
GAS
0.1 0.5 1.0 1.4 1.8 2.3 2.7 3.1 3.6
time on stream, h

Figure 4

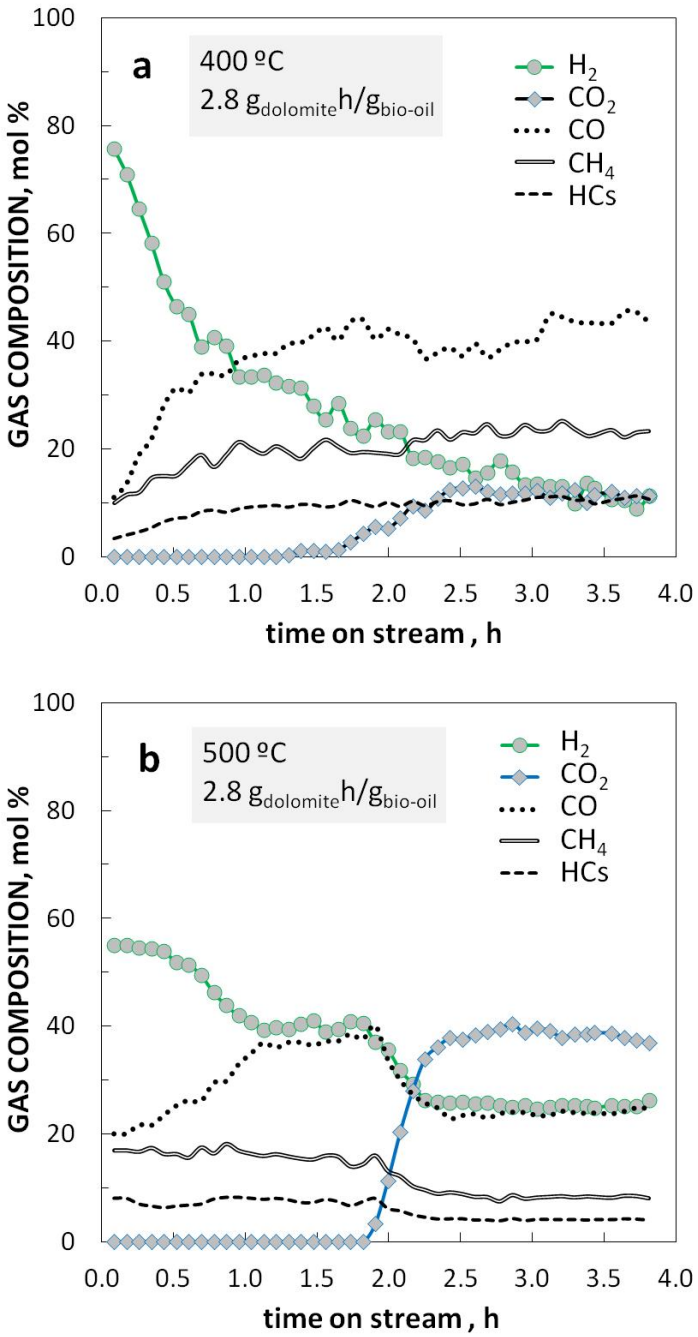

a
400 ºC
2.8 g$_{dolomite}$h/g$_{bio-oil}$
H$_2$
CO$_2$
CO
CH$_4$
HCs
GAS COMPOSITION, mol %
time on stream , h
b
500 ºC
2.8 g$_{dolomite}$h/g$_{bio-oil}$
H$_2$
CO$_2$
CO
CH$_4$
HCs
GAS COMPOSITION, mol %
time on stream , h

Figure 5

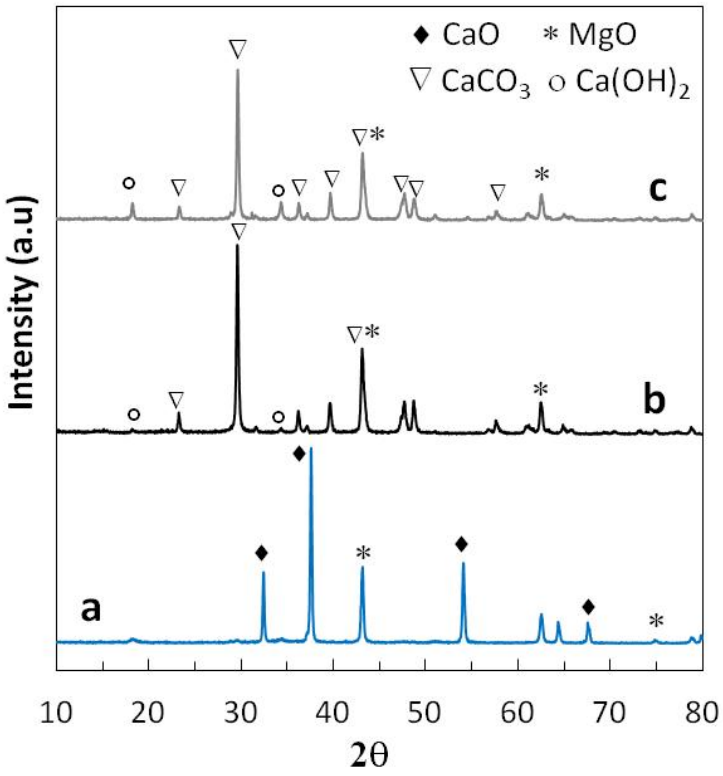


Figure 6

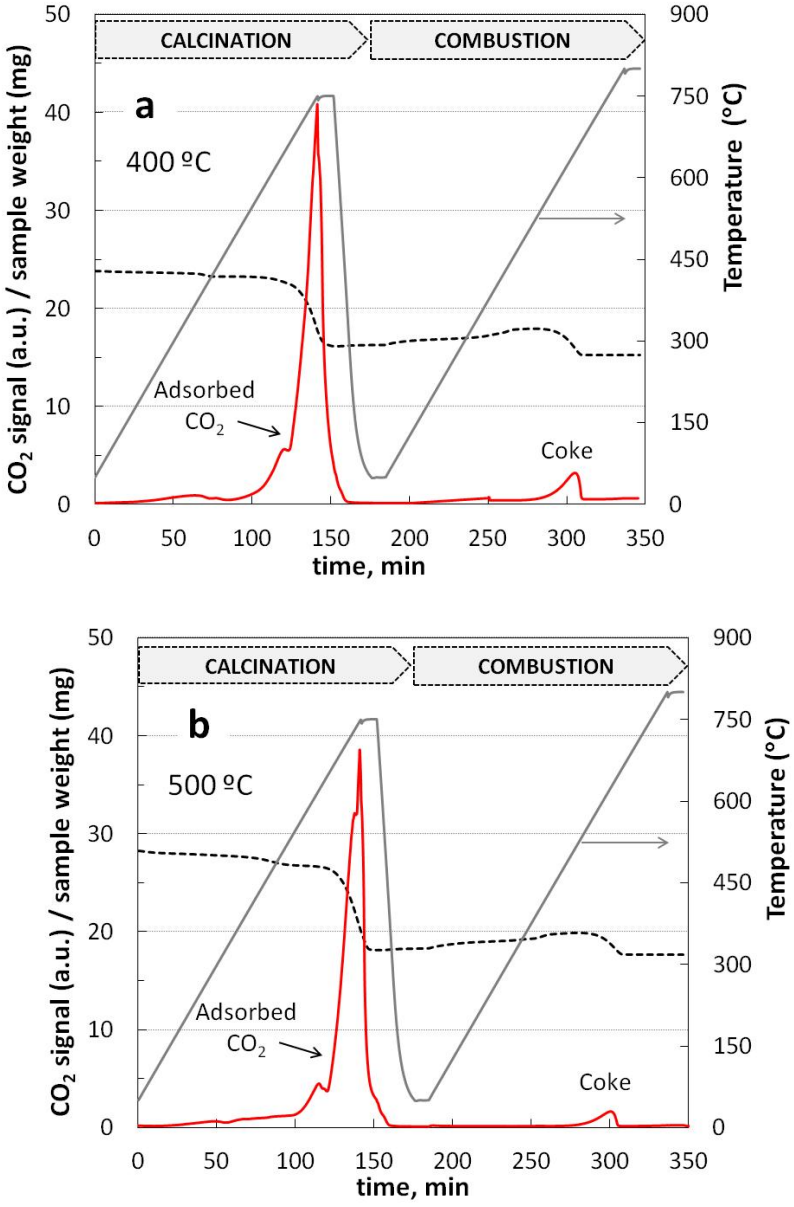

CALCINATION
COMBUSTION
a
400 ºC
Adsorbed
CO_2
Coke
CO_2 signal (a.u.) / sample weight (mg)
Temperature (°C)
time, min
b
500 ºC

Figure 7

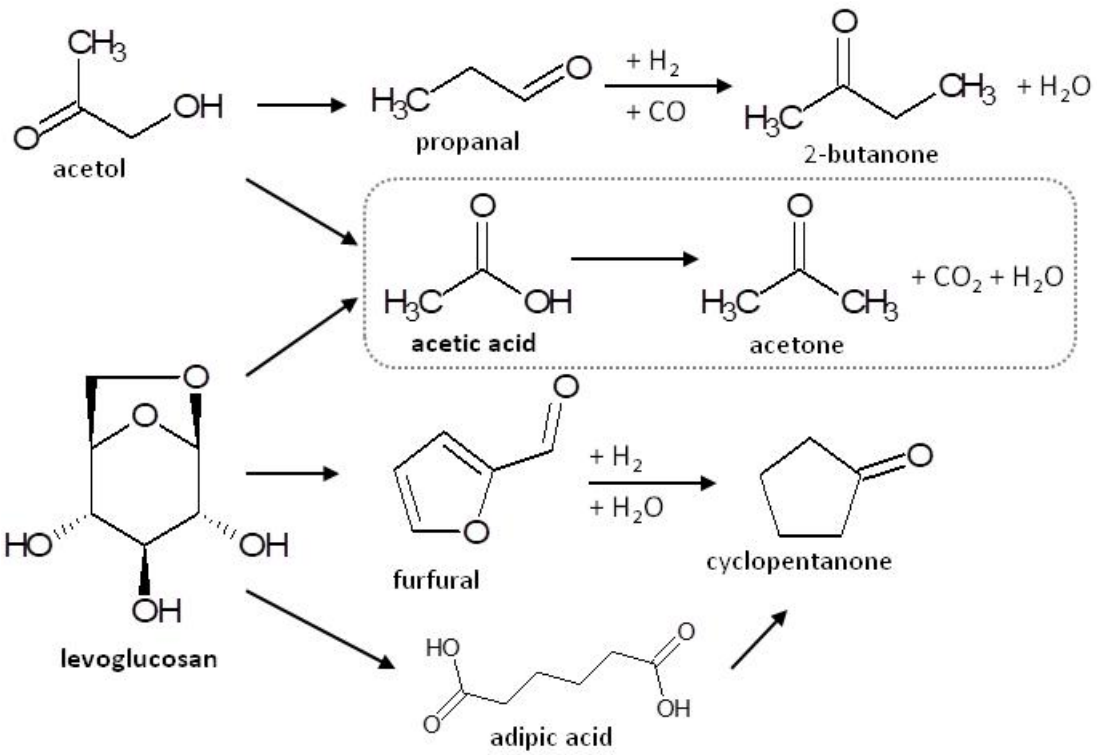

acetol
propanal
+ H2
+ CO
2-butanone
+ H2O
acetic acid
acetone
+ CO2 + H2O
levoglucosan
furfural
+ H2
+ H2O
cyclopentanone
adipic acid

Figure 8

TABLES

Table 1. Semi-quantitative composition (% area) of raw bio-oil, liquid collected without catalyst (thermal treatment at 400 ºC), and upgraded bio-oil produced throughout reaction with 2.8 $g_{dolomite}h/g_{bio\text{-}oil}$ at 400 ºC.

	RAW BIO-OIL	Thermal 400 ºC	UPGRADED BIO-OIL		
			0.5 h	2 h	4 h
ACIDS	10.0	23.1	-	0.5	3.8
(Acetic)	*(8.0)*	*(21.1)*	-	-	-
KETONES	20.4	27.1	81.1	70.5	48.1
LINEAR	*15.0*	*20.4*	*43.5*	*36.9*	*22.1*
(Acetol)	*(5.6)*	*(15.2)*	-	-	-
(Acetone)	*(5.6)*	*(2.1)*	*(26.2)*	*(20.0)*	*(10.1)*
(2-butanone)	*(0.3)*	*(1.8)*	*(10.9)*	*(9.3)*	*(4.2)*
CYCLIC	*5.4*	*6.7*	*37.5*	*33.6*	*26.0*
(C5 ring)	*(4.2)*	*(5.7)*	*(30.4)*	*(27.5)*	*(20.1)*
ESTERS	3.7	4.7	-	0.2	0.6
FURANONES	6.9	3.8	-	4.3	2.3
ALCOHOLS	4.1	4.9	7.1	10.8	5.7
ALDEHYDES	5.0	9.8	6.1	6.2	5.1
(Acetaldehyde)	-	*(0.8)*	*(2.9)*	*(3.0)*	*(2.4)*
(Furaldehydes)	*(3.8)*	*(5.2)*	-	*(0.6)*	*(0.8)*
ETHERS	1.9	-	0.8	0.6	1.3
ANHYDROSUGARS	21.4	13.6	-	-	-
(Levoglucosan)	*(14.4)*	*(11.1)*	-	-	-
PHENOLS	26.7	12.9	4.9	5.1	29.2
Alkyl-phenols	*2.8*	*0.9*	*4.9*	*4.4*	*14.3*
Guaiacols	*12.4*	*6.4*	-	*0.3*	*12.2*
Catechols	*6.4*	*3.7*	-	*0.4*	*1.5*
Siringols	*0.1*	*0.2*	-	-	-
Naphtalenols	-	-	-	-	*1.1*
Other	*4.8*	*1.7*	-	-	*0.1*
C_5-C_{12} ALIPHATICS	-	-	-	1.9	3.9

Table 2. Semi-quantitative composition (% area) of raw bio-oil, liquid collected without catalyst (thermal treatment at 500 ºC), and upgraded bio-oil produced throughout reaction with 2.8 $g_{dolomite}h/g_{bio\text{-}oil}$ at 500 ºC.

	RAW BIO-OIL	Thermal 500 ºC	UPGRADED BIO-OIL		
			0.5 h	2 h	4 h
ACIDS	10.0	28.3	-	0.8	5.5
(Acetic)	*(8.0)*	*(22.5)*	-	-	-
KETONES	20.4	28.1	83.5	64.7	43.9
LINEAR	*15.0*	*20.6*	*63.0*	*45.4*	*30.3*
(Acetol)	*(5.6)*	*(15.4)*	-	-	-
(Acetone)	*(5.6)*	*(2.2)*	*(37.1)*	*(27.0)*	*(13.4)*
(2-butanone)	*(0.3)*	*(1.6)*	*(18.6)*	*(10.8)*	*(7.6)*
CYCLIC	*5.4*	*7.5*	*20.5*	*19.3*	*13.5*
(C5 ring)	*(4.2)*	*(7.5)*	*(17.4)*	*(18.2)*	*(13.2)*
ESTERS	3.7	3.5	-	0.6	0.4
FURANONES	6.9	3.4	-	0.2	1.5
ALCOHOLS	4.1	3.1	1.1	1.5	0.8
ALDEHYDES	5.0	10.5	0.8	5.7	6.6
(Acetaldehyde)	-	*(1.4)*	-	*(4.1)*	*(3.0)*
(Furaldehydes)	*(3.8)*	*(4.3)*	*(0.3)*	*(0.7)*	*(2.1)*
ETHERS	1.9	-	-	0.6	2.4
ANHYDROSUGARS	21.4	10.0	-	-	1.0
(Levoglucosan)	*(14.4)*	*(8.1)*	-	-	-
PHENOLS	26.7	13.2	7.3	21.4	35.1
Alkyl-phenols	*2.8*	*1.3*	*7.3*	*14.9*	*17.1*
Guaiacols	*12.4*	*3.4*	-	*3.7*	*3.6*
Catechols	*6.4*	*7.5*	-	*1.9*	*12.1*
Siringols	*0.1*	-	-	-	-
Naphtalenols	-	-	-	*0.9*	*2.1*
Other	*4.8*	*1.0*	-		*0.2*
C_5-C_{12} ALIPHATICS	-	-	7.3	4.4	3.0

Table 3. Characteristics of deactivated dolomite: surface area (m^2/g), amount of carbon adsorbed ($gC/g_{dolomite}$) and coke deposited ($gC/g_{dolomite}$).

	400 ºC	500 ºC
Surface area (m^2/g)	16.8	9.7
C adsorbed ($gC/g_{dolomite}$)	0.15	0.16
Coke deposited ($gC/g_{dolomite}$)	0.12	0.08