



Heriot-Watt University
Research Gateway

Catalytic cracking of Etek lignin with zirconia supported metal-oxides for alkyl and alkoxy phenols recovery

Citation for published version:

Hendry, A, Åhlén, M, Fernandes, T, Cheung, O & Sanna, A 2020, 'Catalytic cracking of Etek lignin with zirconia supported metal-oxides for alkyl and alkoxy phenols recovery', *Bioresource Technology*, vol. 317, 124008. <https://doi.org/10.1016/j.biortech.2020.124008>

Digital Object Identifier (DOI):

[10.1016/j.biortech.2020.124008](https://doi.org/10.1016/j.biortech.2020.124008)

Link:

[Link to publication record in Heriot-Watt Research Portal](#)

Document Version:

Peer reviewed version

Published In:

Bioresource Technology

Publisher Rights Statement:

© 2020 Elsevier Ltd.

General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

1 Catalytic cracking of Etek lignin with zirconia supported metal-oxides 2 for alkyl and alkoxy phenols recovery

3 *Abbie Hendry[†], Michelle Åhlén[§], Tony Fernandes^{†, ‡}, Ocean Cheung[§], Aimaro Sanna^{* †}*

4 [†] Advanced Biofuels Lab, Institute of Mechanical, Process and Energy Engineering, School of Engineering
5 and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK

6 [§] Nanotechnology and Functional Materials Division, Department of Materials Science and Engineering,
7 The Ångström Laboratory, Uppsala University, Uppsala, 534 751 21, Sweden

8 [‡] Polytech Montpellier, Département MAT, Place Eugène Bataillon, 34095 Montpellier, CEDEX 5, France

9

10 Abstract

11 Alkyl and alkoxy phenols are desirable products from the catalytic depolymerisation of lignin. In this work,
12 ex-situ catalytic pyrolysis of Etek lignin in presence of Na, Ce, NiCe, MgCe, Fe and FePd on ZrO₂ was
13 studied. The largest combined yield of monomeric phenolics and alkylphenols was produced by Na/ZrO₂
14 catalysts. A parametric study of the most promising Na/ZrO₂ then resulted in using a catalyst:lignin ratio of
15 3:1 at 500°C as the best option, enhancing at 17.5 wt% the recovery of total phenolics including 6 wt%
16 alkyl phenols, which is equivalent to 27.8 wt% and 9.5 wt% of the starting lignin in Etek lignin waste. The
17 study of the catalyst basicity indicates that the mild basicity of Na/ZrO₂ was mostly responsible for the
18 enhanced mono phenols recovery. Due to formation of thermally stable Na₂CO₃ during pyrolysis,
19 successful Na/ZrO₂ regeneration requires temperature of 900°C or higher.

20

21 **Keywords:** Lignin; Pyrolysis; sodium zirconate; catalytic cracking; alkylphenols, basicity; ZrO₂.

22

1.0 Introduction

Lignocellulosic biomass as an energy source is considered advantageous as it is a renewable fuel, it has lower carbon emissions and can be considered to have negligible impact to global warming. Cellulose makes up the majority of lignocellulosic biomass with lignin being the second most abundant component, of which between 40 and 50 million tons per year being produced worldwide, mostly as non-commercialised waste (ILI, 2020). Lignin sources are becoming ever more readily available with developments being made in the lignocellulose to ethanol industry, on top of the lignin by-product from the paper pulp industry. Being the only renewable aromatic source in nature, lignin has a great potential for the production of renewable chemicals through the interplay of extraction, depolymerisation and upgrading steps (Schutyser et al., 2018). Prior to conversion, lignin must first be extracted from the biomass source. This can be achieved by various techniques (Woiciechowski et al., 2020). One such technique uses a solution containing sulphur dioxide and a salt of sulphuric acid to break the links between the polysaccharide molecules. If a sulphuric acid solvent is used, the separated lignin is known as lignosulphonate or hydrolytic lignin. The type of extraction used, and the type of biomass source will determine the name of the component. Dilute acid is used to hydrolyse most of the polysaccharides to produce fermentable sugars which leaves the lignin behind as a solid by-product. This type of lignin is not of high-purity and can contain some cellulosic carbohydrate polymer degradation product as well as the lignin itself (Cheng et al., 2002).

Although there are adequate utilisation techniques for converting cellulose and hemicellulose into biofuels, technologies for converting lignin are lacking. Currently, only around 5% of lignin is used in low-value commercial applications. The utilisation of lignin could prove an important step in the advancement of bio refineries, as lignin composes around 10-35% weight of the biomass (Changzhi et al., 2015). The utilisation of this component could result in bio refineries becoming more economically favourable. Lignin can be used as source of platform chemicals such as alkylphenols, which are used in a variety of industrial applications. The sustainable and economic production of catechol and other bio-based chemicals from waste lignin would lead to a dramatic increase in demand as these replace fossil-based chemicals. Holladay

49 et al. analysed the potential for utilising lignin to produce value added chemical products, and they
50 determined that the overall revenue would be increased from \$12 billion to \$35 billion if the lignin were
51 used for chemicals and transport fuels as opposed to being used as a low-grade energy source. A key issue
52 in depolymerise lignin is to maximise the recovery of monomers as building blocks for the production of
53 chemicals.

54 Thermal degradation of lignin by pyrolysis has received wide interest as a lignin depolymerisation
55 technique to produce monomers, due to its relative low cost and low complexity in comparison to other
56 techniques such as gasification (high CAPEX) and liquefaction (high costs and lignin repolymerisation)
57 (Kozliak et al., 2016). Fast pyrolysis of lignin is typically run between 400 and 600°C and yields below 20
58 wt% monomers, although few studies report monomer yields of 27 wt% at 650°C from kraft lignin (Zheng
59 et al., 2013).

60 Pyrolysis can be undertaken with or without a catalyst. In 2010, fast pyrolysis of highly pure and low purity
61 lignin was performed by fourteen laboratories (Nowakowski et al., 2010). The study showed that pure
62 lignin cannot be effectively pyrolysed in bubbling fluidised bed reactors, due to its tendency to
63 agglomerate, while Etek lignin (with a high carbohydrate content) was successfully pyrolysed by Py-GC-MS,
64 resulting in about 51.6 area% guaiacols, 3.8 area% phenol and 39.5 area% carbohydrates at 600°C.

65 In catalytic fast pyrolysis, a catalyst, either physically mixed with the biomass (in situ) or placed after the
66 pyrolysis reactor (ex situ) is used. In most cases, catalytic depolymerisation was found to outperform non-
67 catalysed depolymerisation in terms of monomer yield, which illustrates the benefits gained from
68 implementing catalytic technology. Catalysts such as zeolites have been an area of interest as these can
69 promote the conversion to desirable products such as phenols. Catalysts with acidic sites have previously
70 been researched, and it has been concluded that strong acid sites in zeolite catalysts cause dehydration,
71 decarboxylation, dealkylation, cracking and isomerisation reactions which predominantly result in the
72 formation of aromatic components. Ma et al. proposed a potential reaction pathway for the fast pyrolysis
73 of lignin, where stabilisation of lignin into phenol alkoxy and aromatics were obtained using respectively
74 silicalite and ZSM-5 (Ma et al., 2012).

75 One main problem faced with using acid zeolites is the formation of coke or char on the active sites which
76 quickly deactivate the catalyst and the large content of cancerogenic PAH. In particular, the presence of
77 phenols, especially those derived from p-hydroxyphenyl units of lignin can tightly bound with zeolite acidic
78 site (Mullen and Boateng, 2010). Therefore, alternative catalysts for efficient lignin depolymerisation are
79 desired.

80 Recently, metal oxides have been studied for catalytic pyrolysis of lignin and wood, thanks to their acidity,
81 basicity, surface area or valence. Zhang et al. studied the pyrolysis on poplar wood in presence of Ce, Co,
82 Cr, Cu, Fe, Mn, Ni, Ti and V oxides (Zhang et al., 2019). All metal oxides increased the bio-oil and phenolics
83 yield and reduced coke formation (excluding V, Mn, Cu and Co) compared to the blank test. Zhang et al.
84 (2018) have investigated the use of several metal oxides including Al_2O_3 , SiO_2 and MgO in order to identify
85 trends between the acidity and basicity of the catalysts and the pyrolysis products. The study was carried
86 out on poplar, cellulose and lignin. The results showed that more basic catalysts lead to the formation of
87 gaseous products such as CO , CH_4 and CO_2 . In contrast, the acidic oxides such as Al_2O_3 increased the
88 formation of tar, carboxylic acids, aldehydes, furans and phenolics (Zhang et al., 2019).

89 Pd, Ru and Ce supported on TiO_2 and ZrO_2 were tested for catalytic pyrolysis of poplar wood (Lu et al.,
90 2010). Phenol production increased from 25.6 % to 37.2 % when using palladium and cerium as opposed
91 to the bare support. Zhan et al. (2017) worked on lignin pyrolysis with TiO_2 , ZrO_2 and $\text{Mg}(\text{Al})\text{O}_2$. The use of
92 ZrO_2 led to the largest bio-oil yield and phenolics. Kumar et al. (2020) showed that the oxidative
93 depolymerization of prot and alkali lignin in the presence of cobalt impregnated ZrO_2 catalysts at 140°C
94 selectively produced (67 area%) guaiacol monomers. These studies suggest ZrO_2 is a good support for
95 lignin depolymerisation.

96 Alkali metals (Li, Na, K and Cs) exerted notable enhancing effects on char yield and promoted the
97 conversion of the alkenyl side chains on volatile aromatics to light oxygenates, which has been attributed
98 to them being able to alter dissociation of the internal linkage of lignin and promote decarboxylation and
99 decarbonylation reactions and remove unsaturated alkyl side chain (Wang et al., 2018). However, no

100 study has focused on the catalytic cracking of lignin using Na_2ZrO_3 and Ni, Ce, Mg, Fe and Pd on ZrO_2
101 catalysts.

102 Therefore, the aim of this work was to screening metal the abovementioned metal doped zirconia catalysts
103 on the product distribution of Etek lignin after undergoing ex-situ catalytic pyrolysis and then run a
104 parametric study with the most performing catalyst to evaluate how the effect of temperature,
105 lignin:catalyst ratio, catalyst basicity and cyclic thermal regeneration affects the composition of the bio-oil.

106 2.0 Materials and Methods

107 2.1 Materials

108 The ETEK lignin was procured from Sweden as residue from ethanol production by a 2-stage weak acid
109 hydrolysis of softwood (Nowakowski et al., 2010). This lignin was not a high-purity product but contained
110 carbohydrate polymer degradation products (41% cellulose) as well as lignin (59%) as calculated by peak
111 integration of ^{13}C -NMR using the integration tool in Origin. To obtain the waste lignin composition, the
112 NMR peaks have been assigned to lignin and cellulose, deconvoluted and integrated in Origin to give a
113 semiquantitative percent assessment of the lignin and cellulose content. The lignin was provided in large
114 agglomerates and had to be ground down to a fine powder ($<500\ \mu\text{m}$) prior to beginning the experiments.

115 Na_2ZrO_3 was synthesized mixing by pestle & mortar Na_2CO_3 (99.6% purity, Sigma-Aldrich) and ZrO_2 (99.0%
116 purity, Sigma-Aldrich) in a 1.5:1 molar ratio and then calcining the mixture at 900°C for 4 hours in air. ZrO_2
117 support for Fe/ZrO_2 and PdFe/ZrO_2 was instead prepared by dropwise addition of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ (Aldrich,
118 99.5%) to water (100 ml). After addition, the suspension was aged 20 hours at 90°C , dried in an oven at
119 110°C for 15 h and subsequently calcined in flowing air (30 mL/min) at 500°C for 3 h. Different molar
120 ratios were then synthesized for the parametric study as reported later. Commercial zirconia nanopowder
121 was purchased from Sigma-Aldrich. Ce/ZrO_2 , NiCe/ZrO_2 and MgCe/ZrO_2 with metals content in both mono-
122 and bi-metallic catalysts of 5 wt% (with the exclusion of Pd for which 1 wt% was used) were prepared by
123 incipient wet impregnation method with $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ PdCl_2 and
124 $\text{FeN}_3\text{O}_9\cdot 9\text{H}_2\text{O}$ (all from Sigma Aldrich) as precursors. As an example, the Ce/ZrO_2 catalyst preparation was

125 carried out by stirring mixture of cerium (III) nitrate solution and ZrO₂ support at 300 rpm for 3h at 80°C
126 and then dried at 110°C for 24h. The dried Ce(NO₃)₂/ZrO₂ was calcined in air at 600°C (500°C for Fe/ZrO₂
127 and PdFe/ZrO₂) for 3h to obtain 5%Ce/ZrO₂ to achieve well dispersion (Aysu and Sanna, 2015).

128 2.2 Experimental Method

129 The set-up used for the experiments consisted in an ex-situ fixed bed reactor (1-inch SS316 tubular
130 reactor) was used in the experiments, consisting of a downflow layered configuration with SS316 mesh
131 and mineral wool separating the biomass from the catalyst layers. The screened catalysts were the
132 following: ZrO₂, Ce/ZrO₂, NiCe/ZrO₂, MgCe/ZrO₂, Na/ZrO₂, PdFe/ZrO₂ and Fe/ZrO₂.

133 The mass ratio of lignin to catalyst used in the catalysts screening was 1:0.5 (2g:1g) and the reaction was
134 undertaken at a temperature of 500°C. The reactor itself was placed inside a furnace making sure the
135 lignin and catalyst were placed at the centre of the tubular furnace. A condensation system with 2
136 Dreschel bottles was placed in an ice bucket in order to condense the reaction products. Nitrogen was
137 passed through the reactor at 50 ml/min during the pyrolysis reaction. Once the equipment was air-tight
138 and nitrogen was witnessed to be passing through the equipment by observing gas bubbles in a water
139 trap, the furnace was turned on to bring the reactor up to temperature at a rate of 100°C/min. Once the
140 furnace reached the reaction temperature of 500 °C, it was held at this temperature for around ten
141 minutes before being allowed to cool. The gaseous products were not collected during this experiment.
142 After that, the char/coke and the catalyst were removed from the tubular reactor and weighted prior to
143 being sent for analysis. The mass of the condenser bottles was assessed before and after the experiment.
144 Therefore, after any cleaning had taken place, the bottles were left in an oven overnight prior to
145 completing another experiment to allow them to dry out completely and then stored in a fridge for further
146 analysis. Selected pyrolysis experiments (Ce/ZrO₂, NiCe/ZrO₂, Na/ZrO₂ (at 500°C, 600°C and 1:3 L:C ratio)
147 were run in triplicates resulting in an error ≤ 2wt%.

148 The mass of the condenser bottles was then taken again in order to obtain the mass and yield of oil
149 produced from the lignin. The bio-oil collected was removed from the Dreschel bottles using 20 ml
150 acetone.

151 Using the mass of oil collected in the Dreschel bottles, the yield of oil could then be calculated using the
152 following equation:

$$153 \quad \text{Yield of Oil} = \frac{\text{Mass of Oil Produced}}{\text{Mass of Lignin Reactant}} \times 100 \quad (\text{Eq.1})$$

154 Same was done for the char/ash collected after the experiments:

$$155 \quad \text{Yield of char, ash} = \frac{\text{Mass of char, ash Pleft in the reactor}}{\text{Mass of Lignin Reactant}} \times 100 \quad (\text{Eq.2})$$

156 Deducting both from the total yield allowed the gas yield to be determined.

157 The parametric study in presence of Na/ZrO₂ was carried out using the set-up and method described
158 above. The studied parameters were the lignin:catalyst weight ratio (1:0.5, 1:1 and 1:3), the Na:Zr molar
159 ratio used to synthesised the Na/ZrO₂ catalyst (0.7:1, 1:1 1.5:1) and temperature (400, 500, 600°C).

160 The regeneration of the catalyst for the deactivation study was carried out in a muffle furnace at 700°C for
161 four hours in presence of air. Initially, a trial for the regeneration at 700 °C for different holding times (1, 2,
162 and 4 hrs) were carried out, from which 4 hours regeneration was selected due to the regenerated catalyst
163 after 1 and 2 h being grey/black, indicating a non-completed elimination of the coke. It is also important to
164 indicate that the mass of lignin and catalyst used in the deactivation tests were not the same in each
165 experiment, since it was not possible to recover the totality of the catalyst after the pyrolysis and lower
166 quantities had to be used in the following two experiments and the initial Etek lignin mass was 3 times
167 larger than the one used in the parametric study. This could have partially affected the results. Pyrolysis
168 parameters used for the deactivation study were same as described above.

169 2.3 Product and Reactant Analysis

170 2.4 SEM-EDX

171 Scanning electron microscopy (SEM) images were recorded on a Zeiss Leo 1530 microscope equipped with
172 a FEG and operated at a voltage of 2.5 kV. Samples were mounted on aluminium stubs using double-sided
173 carbon tape and sputter coated with Ag/Pd using a Thermo VG Scientific Polaron SC7640 sputter coater.

174 Energy-dispersive X-ray spectroscopy (EDX) spectra and images were obtained using a Zeiss Leo 1530
175 equipped with an Oxford Instruments X-Max silicon drift detector (SDD) on non-coated samples.

176 2.5 XPS

177 X-ray photoelectron spectroscopy (XPS) spectra were obtained using a PHI Quantera II Scanning XPS
178 Microprobe instrument. Samples were sputter-cleaned using argon ions prior to analysis, where full
179 spectra as well as individual energy-resolved spectra were collected and calibrated using the C 1s peak
180 (284.8 eV) for adventitious carbon.

181 2.6 GC-MS Analysis

182 GC-MS analysis was performed using a Shimadzu GCMS QP2010 SE equipped with a Restek RXI-5HT
183 column (30 m). 50µl bio-oil were diluted in 200µl acetone and then 1µl injected at 290°C under a pressure
184 of 95.3 kPa. The oven was programmed to hold at 40°C for 10 min, ramp at 5°C/min to 200°C and hold for
185 10 min, ramp at 10°C/min to 250°C and hold for 10 min, ramp at 10°C/min to 300°C and hold for 10 min.
186 The GC-MS results were only analysed to a retention time of below 42 minutes, as this is where the peaks
187 of interest were contained within. Any time after this was made up of small quantities of components
188 leached out from the column that did not originate from the lignin. After eliminating the data unrequired
189 for analysis of the pyrolysis products, a new area percentage for each component was calculated. These
190 components were then split up into the following groups: Phenolics (including phenolic diols, catechols
191 etc); Sugar derivatives; 5 carbon rings; Acids; PAH (naphthalene etc.). Total Sum Normalization (TSN),
192 which is the simplest method for normalizing GC-MS data was used in this work. The sum normalized data
193 were multiplied by 100 and expressed in terms of their percent contribution to the total area as follow:

$$194 \text{Area}\%_c = \frac{\text{peak area}}{\text{total area chromatogram (0-42min)}} \times 100 \quad (\text{Eq.3})$$

195 where *c* stands for compound. To related the GC-MS results to the starting mass of Etek lignin, the area%
196 of each compound were converted into wt% by considering the bio-oil yield (wt%) and that ~60% of bio-oil
197 is detectable by GC-MS at 300°C (Sanna et al., 2015). To validate the above 60%, the Na/ZrO₂ bio-oil

198 produced at 500 and 600°C were heated up to 300°C in a tube furnace in pure N₂ flow (100 ml/min) at an
199 heating rate of 20°C/min and held at 300°C for 15 min. Equation 4 was used for the calculations:

$$200 \quad \textit{Weight}\%c = \textit{area}\%c \times \textit{wt}\% \textit{bio_oil} \times 60\% \quad (\textit{Eq. 4})$$

201 where *c* stands for compound.

202 2.7 CO₂-TPD Analysis

203 Temperature programmed desorption (TPD) analysis was run using a Mettler Toledo TGA2 on all the
204 catalysts tested. This test then allowed the basicity of the catalyst to be determined. Firstly, the catalyst
205 was heated in nitrogen at 50°C/min up to a final temperature of 550°C. Once this temperature was
206 reached, the catalyst was held here for 20 minutes. The temperature was then reduced down to 60°C and
207 the gas was switched from nitrogen to carbon dioxide for a further 30 minutes. Switching to CO₂ allowed
208 the gas to adsorb to the catalyst surface. The gas was then switched back to N₂ at 60°C and held for 10
209 minutes to allow any physisorbed CO₂ to be desorbed. Finally, the temperature was increased to 600°C at
210 a rate of 10°C/min. The CO₂ desorbed during this phase is the chemisorbed CO₂ which is the volume of
211 interest to determine the basicity of the catalyst.

212 2.8 TGA Analysis

213 Thermogravimetric analysis (TGA) was undertaken to determine the decomposition rates of the Etek lignin
214 with the different catalysts using a Mettler Toledo TGA2 in the presence of N₂ (100 ml/min) and a heating
215 rate of 100°C/min. The char + ash was calculated by difference by the following equation:

$$216 \quad \textit{char, ash yield} = (\textit{initial lignin wt} - \textit{volatiles wt}) \times 100 \quad (\textit{Eq. 5})$$

217 While the Etek lignin conversion was calculated by Equation 6:

$$218 \quad \textit{Conversion} = (\textit{total wt} - \textit{char, ash wt}) \times 100 \quad (\textit{Eq.6})$$

219 2.9 ¹³C NMR

220 High-resolution solid-state 50 MHz ¹³C Nuclear magnetic resonance (NMR) analysis was conducted using a
221 cross polarization pulse sequence in conjunction with magic angle spinning in a Bruker Avance 200
222 spectrometer. Tetrakis(trimethylsilyl)silane was added to the samples as an internal standard.

223 2.10 EA Analysis

224 Elemental analysis (EA) was undertaken using an Exeter CE-440 Elemental analyser. This testing
225 determined the carbon, nitrogen and hydrogen content in the samples.

226 2.11 FTIR

227 Fourier-transform infrared spectroscopy (FTIR) of the spent char and oil samples were run using a Thermo
228 Scientific Nicolet 1S5 with a 1D7 ATR attachment.

229 3.0 Results and discussion

230 3.1 Catalysts characterisation

231 3.1.1 CO₂-TPD

232 The basicity calculated from the chemisorbed CO₂ for all catalysts resulted in PdFe/ZrO₂ (0.19 mmol CO₂/g)
233 and Fe/ZrO₂ (0.16 mmol CO₂/g) having the highest basicity compared to Na/ZrO₂ (0.09 mmol CO₂/g) and
234 MgCe/ZrO₂ (0.06 mmol CO₂/g) and the remnant catalysts (<0.04 mmol CO₂/g). A highly basic catalyst
235 would suggest that oligomers may be bound to the catalyst for longer leading to the polymerisation of
236 lignin oligomers. This would result in a high yield of char. Referring forward to Section 3.2.2, the iron
237 doped catalysts resulted among the high range of char and coke yields as expected from the TPD results.
238 The sodium doped catalyst has a basicity only half of that of PdFe/ZrO₂ and the other catalysts even milder
239 basicity. However, it has to be noted that Na/ZrO₂ typically release CO₂ at temperature higher than 750°C,
240 denoting basic sites of high strength, which are not accounted in the here described CO₂-TPD analysis
241 (Munro et al., 2020).

242 3.1.2 SEM-EDX

243 Scanning electron microscopy (SEM) images for the fresh and spent Na/ZrO₂ sample at different
244 magnifications showed that the morphology of the materials consists of irregular agglomerates with a size
245 between 30 and 40 μm of polygonal particles with a size between 3 and 10 μm. No sign of sintering is
246 evident when comparing the SEM from the fresh and spent catalyst. Both agglomeration, and large
247 particle sizes are the consequence of the sintering process that are associated with the exposure of the
248 material to the high temperature employed during its synthesis. Despite the particle morphology after
249 pyrolysis process was almost similar to that of the fresh Na/ZrO₂, small crystallites of about 30-60 nm could
250 be seen upon zooming-in of the SEM image, which could potentially belong to Na₂CO₃ formed during the
251 pyrolysis.

252 The EDS of the fresh and spent Na/ZrO₂ was performed to evaluate increased presence of carbon on the
253 surface of the spent catalyst. Despite showing an increase of the C peak (29% of Na peak) vs Na peak for
254 the spent catalyst compared to the fresh one (20%), this is not enough to confirm presence of carbonates.
255 SEM images of the bare ZrO₂ and the metal doped zirconia catalysts suggest presence of monoclinic ZrO₂
256 phase (Chintapartya et al., 2015). Smaller particles (20-50 nm) are noticeable for the Fe and FePd doped
257 ZrO₂ compare to the other catalysts (100-200 nm), due to the different synthesis method used.

258 3.1.3 XPS

259 XPS was employed to investigate the alteration of the binding energy of Zr and O at the surface. The high
260 resolution XPS spectrum of Zr 3d electron shows two peaks at 182 and 184/5 eV corresponding to 3d_{5/2}
261 and 3d_{3/2} electron of Zr⁴⁺, respectively, with no indication of metallic Zr (~178 eV) (Sinhamahapatra et al.,
262 2016). The deconvoluted high-resolution O 1s XPS spectrum suggests the presence of lattice oxygen (530.5
263 eV) and non-lattice oxygen or oxygen vacancy (~532 eV) in all the catalysts, with ZrO₂, PdFe, Fe and Ce on
264 ZrO₂ having the largest amount of oxygen vacancies, which result in surface alteration in the form of
265 defects or disorders. In the Ce, NiCe and MgCe catalysts, the Ce 3d XPS spectra were deconvoluted into
266 three peaks (882, 886 and ~900 (only in MgCe) eV) characteristics of Ce³⁺ (Thermo Scientific, 2020). In the
267 O 1s XPS spectra, the bands at around 529 and 531 eV belongs to lattice oxygen (O²⁻) and the band around

268 532 eV (in NiCe) can be associated to defect oxides (or oxygen ions with low coordination), as described
269 for the Zr 3d spectra (Deng et al., 2019). Due to the strong interference from Zr 3p signal (333 eV (3p_{3/2})
270 and 347 eV (3p_{1/2})), Pd 3d XPS signals were difficult to observed and are expected to be small in comparing
271 to the Zr 3p signals. The Pd 3d XPS spectrum of PdFe/ZrO₂ consisted of asymmetric Pd 3d_{5/2} and 3d_{3/2}
272 peaks centred at ~334/5 and 341 eV, respectively, characteristic of Pd⁰ (Tao et al., 2018). In the NiCe
273 catalyst, Ni 2p_{3/2} was found only in the oxidation state Ni²⁺ (NiO), as denoted by the bands at binding
274 energy 853 and 856 eV (Németh ET AL., 2015). Finally, the XPS of the Na 1s (1071-1071.5 eV) in Na/ZrO₂
275 can be deconvoluted in two peaks, a main peak at 1071.4 eV and a small broad peak at ~1071.8 eV, where
276 the latter could indicate low valence Na, or Na vacancies on the catalysts surface.

277 3.1.4 XRD

278 The XRD of the fresh and spent Na/ZrO₂ catalyst are consistent with Na₂ZrO₃ with diffraction peaks in
279 monoclinic (ICDD35–0770) and hexagonal (ICDD 21–1179) phases, with some minor ZrO₂ impurities in
280 monoclinic (23.7°, 28.3°, 31.5° and 50.1°) phase (Munro et al., 2020). All remnant catalysts also present
281 peaks belonging to monoclinic ZrO₂. FeO, CeO and PdO are not visible due to overlapping with ZrO₂ peaks,
282 while NiO and MgO were detected at 43°. The absence of a diffraction peak at ~25° indicates the lack of a
283 large amount of coke on the surface of the spent catalyst. In contrast to the other catalysts, the XRD of the
284 spent Na/ZrO₂ catalyst shows presence of Na₂CO₃ (2-Theta 30.1°) indicating that CO₂ resulting from the
285 lignin pyrolysis is chemisorbed in the surface of the basic Na/ZrO₂.

286 3.2 Catalysts screening

287 3.2.1 TGA and DTA Results

288 Figure 1 shows that the decomposition of 2 parts of lignin mixed with one part of the screened catalysts
289 took place in two main episodes: the first and main decomposition between 300 and 400°C, which show
290 strong link with cellulose in Etek lignin (Nowakowski et al., 2010) and a second slow event at temperature
291 higher than 400°C, linked mostly to lignin. The data obtained from the derivative thermal analysis (DTA)
292 are shown in Figure 1, while Table 1 summarises the lignin conversion and the maximum decomposition
293 rate for each catalyst and the temperature of maximum decomposition. The bare zirconia and the catalysts

294 containing ceria resulted in the Etek lignin conversion just higher than 70wt%, while Fe and Na on zirconia
295 produced respectively 4 and 6 wt% more char. The catalyst with the highest decomposition rate resulted
296 FePd/ZrO₂. The results suggest this catalyst is effective at depolymerising cellulose, whose decomposition is
297 completed at lower temperature than that of lignin. The catalyst with the lowest temperature at maximum
298 decomposition is Fe/ZrO₂, at approximately 10°C lower than the other catalysts. This suggests this catalyst
299 has a lower activation energy for decomposing cellulose as the reaction can occur at lower temperatures
300 than in presence of FePd/ZrO₂. Na/ZrO₂ instead has a decomposition peak shifted about 5°C at higher
301 temperature, which could suggest that this catalyst is more active on lignin decomposition and led to
302 cellulose decomposition in uncondensable gas and char.

303 3.2.2 Catalytic pyrolysis products distribution and bio-oil composition

304 The selected catalysts were screened for the ex-situ pyrolysis of Etek lignin. Table 2 summarises the yields
305 of oil, char and gas obtained for each catalyst. The catalyst that yielded the high percentage of bio-oil were
306 MgCe/ZrO₂ and Ce/ZrO₂, while NiCe, Fe and FePd on ZrO₂ resulted in high gas yield. Previous pyrolysis of
307 Etek lignin without catalyst in batch reactor resulted in 40 wt% bio-oil and 30 wt% char (Nowakowski et al.,
308 2010). Therefore, the presence of Mg and Ce and marginally Na, seems to be beneficial to enhance the
309 liquid product compared to Etek lignin alone. As can be noticed, char yield is constant since the
310 experiments were carried out in ex-situ configuration and the average reported.

311 Table 3 shows the relative distribution of each functional group (from GC-MS analysis) obtained from the
312 bio-oils. The most desirable products from the catalytic pyrolysis of lignin are lignin derived monomers.
313 Phenolic compounds are produced by the cleavage of ether alpha or beta-o-4 bonds and carbon to carbon
314 bonds during pyrolysis (Hanwu et al., 2014). Bare ZrO₂ resulted in an intermediate yield of phenolics
315 (mostly guaiacols) and oxygenated sugar derivatives, suggesting that the addition of different metals to
316 zirconia resulted is a very different behaviour. Zhan et al. (2017) compared ZrO₂ with TiO₂, Mg(Al)O and a
317 non-catalytic run in the pyrolysis of *Miscanthus* lignin. Among all tests, ZrO₂ resulted in a bio-oil enriched in
318 guaiacols and catechols. The combined largest total phenolics yield of 13.3 wt%, and alkylphenols (4.4
319 wt%) was obtained in presence of Na/ZrO₂. In comparison, pyrolysis of Etek lignin in absence of catalysts

320 did result in only 3-4 area% alkylphenols (17.7 area% in this work) (Nowakowski et al., 2010). Also,
321 oxidative depolymerisation of prot and alkali lignin in presence of CoZrO_2 resulted in 3% alkylphenols
322 (Kumar et al., 2020). This can be ascribed to formation of H radicals from the cellulose derived compounds
323 during the cracking of Etek lignin and the presence of the catalysts. This is supported by the relatively low
324 content in oxygenated sugar derived compounds in the bio-oil produced by Na/ZrO_2 , suggesting superior
325 cracking versus the other catalysts. The increase in alkylphenolics in presence of Na/ZrO_2 can be attributed
326 to demethylation, demethoxylation and alkyl substitution reactions (Wang et al., 2018).

327 The relative abundance of guaiacols of most of the catalysts tested was comparable to that obtained
328 pyrolyzing soda lignin at 500 °C in presence of ZSM-5 (34.2 in this work vs 32 area%) (Kumar et al., 2019).
329 ZSM-5 and mordenite also promoted aromatics formation (~13 and 33 area%), by cracking of methoxy
330 groups and hydroxy groups from guaiacols and syringols during pyrolysis of lignin. By contrast, aromatics
331 production was relatively low in presence of Na/ZrO_2 . However, the use of zeolites with lignin has the
332 drawback to result to large coke and cancerogenic PAH yield, with rapid catalyst deactivation. For example,
333 Wang et al. (2019) obtained 41.3 area% monoaromatics and 22.6 area% PAH from the pyrolysis of lignin
334 using a mixture of 1:1 red mud and ZSM5-5 (Wang et al., 2019). Moreover, about 6 area% substituted
335 cyclopentanes such as 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- were formed using Na/ZrO_2 , which
336 most-likely derived from the base-catalysed condensation of hydroxymethyl furfural via 1-hydroxyhexane-
337 2,5-dione.

338 Ce/ZrO_2 catalyst results in a relatively high content of phenolics. In addition, this catalyst has a low
339 percentage of acids formed in the oil phase and a good recovery (8.9 wt%) of dehydrated sugars and 5-ring
340 sugars derived compounds, suggesting it is active for both cellulose and lignin depolymerisation. Despite
341 the nano-catalysts Fe/ZrO_2 and FePd/ZrO_2 where clearly not effective in depolymerise lignin into liquid
342 products (7.5-8.9 wt% phenolics), they proved to be the most efficient in the depolymerisation of the
343 cellulose fraction of the Etek lignin, with 13.5-14.1 wt% bio-oil made of levoglucosane and other sugar
344 derived molecules.

345 Small amount of PAHs was formed using MgCe/ZrO₂ and Ce/ZrO₂. Components such as naphthalenol,
346 naphthalene and tetramethyl-chroman-2-one were formed. The presence of PAHs is of interest as this
347 would suggest that condensation reactions may be taking place on the basic sites. The formation of PHAs is
348 assumed to arise from secondary reactions on the primary pyrolysis products such as char (Zhuo et al.,
349 2014). Asmadi et al. proved that the thermal decomposition of lignin through the cleavage of the alpha-
350 ether and beta-ether bonds of the lignin structure released guaiacyl-type aromatics during primary
351 pyrolysis, which then at temperature ~450°C secondary reaction can convert the former in catechols, while
352 at temperatures > 550°C monomers can condense into PAHs (Asmadi et al, 2011). Na/ZrO₂ has the
353 advantage of resulting in a large alkylphenols and very low PAH content, if compared to zeolites.

354 Lignin depolymerization over base catalysts is an excellent route to monomeric phenols, since Aryl-alkyl
355 (β-O-4) ether bonds in lignin are easier to cleave than C-C bonds in base catalysed lignin depolymerisation.
356 Moreover, base strength plays an important role on the depolymerization mechanism (Pineda and Lee,
357 2016). Figure 2 shows the relation between the total phenols and alkylphenols in the bio-oils and the
358 basicity of the catalysts. The figure suggests the presence of an inverse correlation between the basicity
359 and total phenolics and alkyl phenols formed, where the highly basic Fe/ZrO₂ and PdFe/ZrO₂ resulted in
360 the lowest yield, while the catalysts with low basicity yielded high phenolics. Na/ZrO₂ does not follow the
361 above trend, suggesting that the strength of the basic sites rather than the total basicity is beneficial to
362 maximise the depolymerisation of the lignin. This is supported by the DTA of the CO₂-TPD tests, which
363 indicate that Na/ZrO₂ differ from the rest of the catalysts having mostly mild basicity in the temperature
364 range 200-350°C instead of at ~100°C for the other catalysts.

365 3.3 Parametric study using Na/ZrO₂

366 The catalysts screening showed Na/ZrO₂ is the catalyst that offers the greatest yields in monomers and
367 alkylphenols. For this reason, the pyrolysis operating conditions and the alkalinity of Na/ZrO₂ were studied
368 to further understand its pyrolysis products' tuning. The products distribution of the parametric study is
369 shown in Table 4. Increasing the nominal temperature from 400 to 600°C resulted in a decrease of the
370 char and bio-oil yield of 16 wt% and 5 wt%, respectively. However, results in an increase of coking

371 reactions. Clearly, 400°C is not enough for the depolymerisation of the Etek lignin, while maximum bio-oil
372 yield is obtained at 500°C. A similar effect on the bio-oil yield was denoted when the catalyst:lignin weight
373 ratio was increased from 0.5:1 to 1:1 and 3:1 to the benefit of the gas yield. Increasing the catalyst amount
374 promoted cracking of condensable molecules into smaller non-condensable gas. This may be due to an
375 enhanced contact between the vaporised molecules and the active sites in the catalyst, due to the larger
376 amount of the latter. An increased alkalinity improves the oil yield but also increased the coke yield. This is
377 an agreement with Zhang et al. (2018), where basic catalysts promoted coke formation. The small variation
378 of char yield can be ascribed to experimental error. Table 4 shows the elemental composition of the chars
379 and catalysts. As expected, there is an increase in C content by increasing the pyrolysis temperature. The
380 variation of catalyst:lignin ratio and the basicity of the catalysts resulted in similar C content in chars, due
381 to the ex-situ pyrolysis configuration. The amount of coke on the spent catalysts well reflect the change of
382 temperature, where the larger lignin depolymerisation at 600°C results in the highest coke %. Coke instead
383 decreases when a 1:1 and 3:1 catalyst:lignin ratio are used, indicating that in the ex-situ fixed bed
384 configuration, an excess of biomass vs the catalyst is not efficient for a good biomass derived volatiles -
385 catalyst contact.

386 Table 5 shows the main functionalities in the bio-oils obtained in the parametric study. Increasing the
387 temperature from 400°C to 600°C drastically increased the amount of alkyl (from 2.2 to 6.7 wt%) and
388 alkoxy (from 5.0 to 9.9 wt%) phenols in the bio-oil, resulting in 17.2 wt% total phenolics. At 600°C, sugar
389 derivatives such as levoglucosan were also cracked into gas phase or condensed into coke.

390 FTIR of bio-oils were also carried out to study the variation of the main chemical functionalities. Bands at
391 2955, 2927 and 2873 cm^{-1} belong to C-H stretching of aliphatic compounds (Sharma et al., 2004; NSimba et
392 al., 2013). According to Wang et al. bands at 1669 cm^{-1} correspond to C=O stretch in unconjugated
393 ketones, carbonyl and ester groups. Their presence could indicate 5 carbon rings compounds such as
394 ketones or aliphatic ketones, carbonyl or ester. The 1598 and 1514 cm^{-1} bands are related respectively to
395 C=O stretching of conjugated ketones to aromatics rings and aromatic ring vibrations. The 1456 cm^{-1} band
396 is related to aliphatic C-H asymmetric deformations. The 1360 and 1271 cm^{-1} are respectively the syringyl
397 and guaiacyl ring symmetric stretching with C-O stretching. Similarly, the 1136 cm^{-1} band refer to C-H

398 plane deformation in guaiacyl and syringyl. The transmission band at 1036cm^{-1} is related to C-O
399 deformation of primary alcohol, in fact according to Sharma et al. between 1000 and 1100 cm^{-1} , the width
400 and the high depend on sugar derivatives amount. The 991 cm^{-1} band refers to C=C bending on mono-
401 substituted alkenes. Finally, all the bands under 920 cm^{-1} are relative to aromatic C-H bending out of plane
402 (Sharma et al., 2004; NSimba et al., 2013; Wang et al., 2014).

403 The bio-oil FTIR results are in line with GCMS results. The bands at 1271 and 1360 cm^{-1} increase according
404 to the temperature increase. Moreover, at the lowest temperature (400°C), the abundance of sugar
405 derivatives (1000 - 1100 cm^{-1}) and unconjugated ketones (1667 cm^{-1}) is higher. Increasing the temperature
406 seems to result in a larger content in furans (1514 and 1598 cm^{-1}) derived from cellulose, and aliphatic
407 compounds (1463 cm^{-1}).

408 Table 5 shows an excellent total phenolics ($17.5\text{ wt}\%$) and alkylphenols ($6.0\text{ wt}\%$) yield for the bio-oil
409 obtained with a lignin:catalyst ratio of $1:3$, which is due to the enhanced vapours-catalyst contact. Using
410 the $1:3$ ratio, the bio-oil is almost exclusively made of phenolics derived from the lignin fraction (91%) of
411 the Etek lignin. Since only $59\text{ wt}\%$ of the Etek lignin waste is made of lignin and assuming that none of the
412 phenolics derive from the cellulose fraction, this means that $27.8\text{ wt}\%$ and $9.5\text{ wt}\%$ of the starting lignin is
413 recovered respectively as phenolics and alkyl phenols, which is at the high-end of the data in literature.

414 The study of the catalyst basicity on the products distribution shows that the best phenols' yield is
415 obtained with the $1:1$ catalyst, meanings that the catalyst need to be mildly basic to be able to generate
416 mono-aromatics. The GC-MS and FTIR of the bio-oils also show that furan and aliphatics decrease when
417 alkalinity decrease, whereas sugars derivatives and ketones increase.

418 3.3.1 Catalyst deactivation study

419 The regeneration of Na/ZrO_2 was studied to evaluate its deactivation after three consecutive pyrolysis
420 experiments. Table 5 shows the %variation in bio-oils composition. The consecutive regenerations
421 decreased the bio-oil yield of about 13% and affected the bio-oil composition, with decreased overall
422 monomers yield. Phenolics, aromatics and cyclopentanes all decreased in content after 3 cycles. This is
423 corroborated by FTIR results, which shows a decrease in aromatic skeletal vibrations (1603 and 1508 cm^{-1}),

424 guaiacol ring breathing (1267 cm^{-1}) and an increase in ketones/esters/carbonyls (1703 cm^{-1}) with
425 regeneration cycles (Zhan et al, 2017). Therefore, the accumulation of recalcitrant deactivates the catalyst.

426 The elemental analysis of the regenerated catalysts (Table 4) show an increase in carbon (from 2.6 wt% to
427 3.3 and 3.6 wt% after 2 and 3 cycles) in the catalyst due to accumulation of carbon with the regeneration
428 cycles. Therefore, the regeneration was not completed suggesting that the C species required a higher
429 temperature for their decomposition.

430 The XRD of the spent Na/ZrO₂ reports the presence of Na₂CO₃ on surface, which can explain the
431 incomplete removal of C from the catalyst during regeneration, since Na₂CO₃ decomposition requires
432 temperature $>900^\circ\text{C}$ (Munro et al., 2020). This is confirmed by the XPS of the spent catalysts. The main
433 difference encountered in comparison to the fresh catalysts was that the Na/ZrO₂ was the only catalyst to
434 present a clear peak at 289 eV for C1s indicating presence of carbonate species (Na₂CO₃). The presence of
435 Na₂CO₃ on surface can be linked to the decrease in methoxy and alkyl phenols production. A previous work
436 showed that after the cleavage of the ether bonds between the lignin building units, followed by cracking
437 and reforming of the alkyl side chains of these units, phenols are released from lignin pyrolysis over a time
438 range between 374°C and 496°C . However, in the presence of 10% Na₂CO₃, the generation time of phenols
439 was postponed for about 123°C , due to the phenols generated by the secondary reaction between sodium
440 phenolate and the volatile need to higher reaction temperature (Guo et al., 2012). Therefore, the
441 deactivation of the Na/ZrO₂ can be linked to fouling due to the inefficacy of removing the inorganic C at
442 the regeneration temperature used in this study, indicating that a temperature of $\sim 900^\circ\text{C}$, as previously
443 reported, is required to decompose Na₂CO₃ and that this catalyst could have a role in enhanced sorption
444 gasification reactions.

445 4.0 Conclusion

446 The catalytic cracking of Etek lignin in presence of metal doped zirconia catalysts was
447 investigated. Na/ZrO₂ catalyst was effective for increasing both the total monomeric phenols and the
448 alkylphenols in the bio-oil compared to the other catalysts. This was considered to be caused by existence
449 of mild basic sites over Na/ZrO₂ surface. The parametric study in presence of Na/ZrO₂ has shown that a

450 temperature of 600°C and a lignin: catalyst ratio of 1:3 increase the yield of total phenolics and
451 alkylphenols respectively to 27.8 wt% and 9.5 wt%, if the fraction of lignin in starting Etek lignin is
452 accounted. The study of the regeneration of Na/ZrO₂ demonstrated that the catalyst suffers deactivation
453 after a number of reuses due to incomplete removal of carbon deposits during thermal treatment at
454 700°C. XRD, XPS and EDS analyses revealed that the carbon left on the catalyst surface is inorganic
455 carbonate (Na₂CO₃), which requires temperature > 900°C to be completely removed. In summary, Na/ZrO₂
456 represents a candidate for the catalytic depolymerisation of lignin by pyrolysis but further studies are
457 required to evaluate its long-term stability.

458 Supplementary Material

459 E-supplementary data of this work can be found in online version of the paper.

460 Acknowledgements

461 We would like to acknowledge the Swedish Research Council for Sustainable Development (FORMAS, grant
462 #2018-00651), the Åforsk Foundation (grant #19-549) are gratefully acknowledged for funding this work and
463 the CATMAT group at Ca Foscari University-Venezia (Italy) for synthesizing Fe/ZrO₂ and FePd/ZrO₂
464 nanopowders.

465 References

- 466 Asmadi M., Kawamoto H. and Saka S., 2011, Gas- and solid/liquid-phase reactions during pyrolysis of
467 softwood and hardwood lignins, *J. Anal. Appl. Pyrolysis*, 92, 2, 417-425.
- 468 Aysu T., Sanna A., 2015, Nannochloropsis algae pyrolysis with ceria-based catalysts for production of high-
469 quality bio-oils, *Bioresour. Technol.*, 194, 108-116.
- 470 Changzhi L., Xiaochen Z., Aiqin W., Huber G.W. and Zhang T., 2015, Catalytic Transformation of Lignin for
471 the Production of Chemicals and Fuels, *Chem. Rev.*, 11599-11624.
- 472 Chintapartya R., Palagiria B., Nagireddy R.R. and Reddy V.S.R.I., 2015, Effect of phase transformation on
473 optical and dielectric properties of zirconium oxide nanoparticles, *Phase Transitions*,
474 <http://dx.doi.org/10.1080/01411594.2015.1039012>.
- 475 Deng J., Li S., Xiong L., Wang J., Yuan S., Chen Y., 2019, Different thermal behavior of nanostructured CeO₂-
476 ZrO₂ based oxides with varied Ce/Zr molar ratios, *Mater. Chem. Phys.* 236, 121767.
- 477 Guo D.I., Wu S.B., Liu B., Yin X.L., Yang Q., 2012, Catalytic effects of NaOH and Na₂CO₃ additives on alkali
478 lignin pyrolysis and gasification, *Appl. Energy* 95, 22–30.
- 479 Hanwu L., Wang L., Wei Y., Zhu L. and Zhang X., 2014, Bio-based phenols and fuel production from catalytic
480 microwavepyrolysis of lignin by activated carbons, *Bioresour. Technol.*, 162, 142-147.
- 481 ILI, The International Lignin Institute, About Lignin, 2020. Available: [http://www.ili-](http://www.ili-lignin.com/aboutlignin.php)
482 [lignin.com/aboutlignin.php](http://www.ili-lignin.com/aboutlignin.php). [Accessed 30th May 2020].

483 Jiayang Cheng Y. S., 2002, Hydrolysis of lignocellulosic materials for ethanol production: a review,
484 Bioresour Technol., 83, 1-11.

485 Kozliak E., Kubatova A., Artemyeva A., Nagel E., Zhang C., Rajappagowda R. and Smirnova A., 2016, Thermal
486 Liquefaction of Lignin to Aromatics: Efficiency, Selectivity, and Product Analysis, ACS Sus. Chem. & Eng., 4,
487 5106-5122.

488 Kumar A., Kumar A., Kumar J., Bhaskar T., 2019, Catalytic pyrolysis of soda lignin over zeolites using
489 pyrolysis gas chromatography-mass spectrometry, Bioresour. Technol., 291, 121822.

490 Kumar A., Biswas, B., Bhaskar T. 2020, Effect of cobalt on titania, ceria and zirconia oxide supported
491 catalysts on the oxidative depolymerization of prot and alkali lignin, Bioresour. Technol. 299, 122589.

492 Lu Q., Zhang Y., Tang Z., Li W.-z. and Zhu X.-f., 2010, Catalytic upgrading of biomass fast pyrolysis vapours
493 with titania and zirconia/titania based catalysts, Fuel, 2096-2013.

494 Mullen C. A. and Boateng A. A., 2010, Catalytic pyrolysis-GC/MS of lignin from several sources Fuel Process
495 Technol., 91, 11, 1446-1458.

496 Munro S., Åhlén M., Cheung O., Sanna A., 2020, Tuning Na₂ZrO₃ for fast and stable CO₂ adsorption by solid
497 state synthesis, Chem. Eng. J., 388, 124284.

498 Németh M., Schay Z., Srankó D., Károlyi J., Sáfrán G., Sajó I., Horváth A., 2015, Impregnated Ni/ZrO₂ and
499 Pt/ZrO₂ catalysts in dry reforming of methane: Activity tests in excess methane and mechanistic studies
500 with labelled ¹³CO₂, Appl. Cat. A: Gen. 504, 608–620.

501 Nowakowski D., Bridgewater A., Elliott D. and Wild P., 2010, Lignin fast pyrolysis: Results from an
502 international collaboration, J. Anal. Appl. Pyrol., 88, 53-72.

503 Nsimba R.Y., Mullen C.A., West N.M. and Boateng A.A., 2013, Structure-property characteristics of
504 pyrolytic lignin derived from fast pyrolysis of a lignin rich biomass extract, ACS Sus. Chem. & Eng., 1, 2, 260-
505 267.

506 Pineda A., Lee A.F., 2016, Heterogeneously catalyzed lignin depolymerization, Appl. Petrochem. Res., DOI
507 10.1007/s13203-016-0157-y

508 Sanna A., Vispute T.P., Huber G.W., 2015, Hydrodeoxygenation of the aqueous fraction of bio-oil with Ru/C
509 and Pt/C catalysts, Applied Catalysis B: Environmental, 165, 446-456.

510 Sharma R.K., Wooten J. B., Baliga V. L., Lin X., Chan W.G. and Hajaligol M.R., 2004, Characterization of chars
511 from pyrolysis of lignin, Fuel, 83, 11-12, 1469-1482.

512 Sinhamahapatra A., Jeon J.P., Kang J., Han B. and Yu Y.S., 2016, Oxygen-Deficient Zirconia (ZrO_{2-x}): A New
513 Material for Solar Light Absorption, Scientific Reports 6, 27218.

514 Tao H., Sun X., Back S., Han Z., Zhu Q., Robertson A.W., Ma T., Fan Q., Han B., Jung Y. and Sun Z., 2018,
515 Doping palladium with tellurium for the highly selective electrocatalytic reduction of aqueous CO₂ to CO.
516 Chem. Sci., 9, 483.

517 Thermo Scientific, 2020, XPS database. <https://xpssimplified.com/elements> [Access 20/05/2020]

518 Wang S., Li Z., Bai X., Yi W., Fu P., 2018, Influence of inherent hierarchical porous char with alkali and
519 alkaline earth metallic species on lignin pyrolysis, Bioresour. Technol., 268, 323–331.

520 Wang S., Li Z., Bai X., Yi W., Fu P., 2019, Catalytic pyrolysis of lignin in a cascade dual-catalyst system of
521 modified red mud and HZSM-5 for aromatic hydrocarbon production, Bioresour. Technol., 278, 66–72.

522 Wang S., Lin H., Ru B., Sun W., Wang Y. and Luo Z., 2014, Comparison of the pyrolytic behaviour of
523 pyrolytic lignin and milled wood lignin by using TG-FTIR analysis, J. Anal. Appl. Pyrol., 108, 78-85.

524 Wang W., Wang M., Huang J., Zhao X., Su Y., Wang Y., Li X., 2019, Formate-assisted analytical pyrolysis of
525 kraft lignin to phenols, *Bioresour. Technol.*, 278, 464–467.

526 Woiciechowski A.L., Dalmas Neto C.J., Souza Vandenberghe L.P., de Carvalho Neto D.P., Novak Sydney A.C.,
527 Junior Letti L.A., Karp S. G., Zevallos Torres L.A., Soccol C.R., 2020, Lignocellulosic biomass: Acid and
528 alkaline pretreatments and their effects on biomass recalcitrance – Conventional processing and recent
529 advances, *Bioresour. Technol.*, 304, 22848.

530 Zhan S., Chenguang W., Kang B., Xinghua Z., Chiling Y., Renjie D., Longlong M. and Changle P., 2017, Py-
531 GC/MS study of lignin pyrolysis and effect of catalysts on product distribution, *Int. J. Agr. Bio. Eng.*, 10, 5,
532 214-225.

533 Zhan S., Chenguang W., Kang B., Xinghua Z., Chiling Y., Renjie D., Longlong M., Changle P., 2017, Py-GC/MS
534 study of lignin pyrolysis and effect of catalysts on product distribution, *Int. J Agric & Biol Eng*, 10, 5, 214-
535 225.

536 Zhang C., Hu X., Guo H., Wei T., Dong D., Hu G., Hu S., Xiang J., Liu Q. and Wang Y., 2018, Pyrolysis of
537 poplar, cellulose and lignin: Effects of acidity and alkalinity of the metal oxide catalysts,” , *J. Anal. Appl.*
538 *Pyrol.*, 134, 590-605.

539 Zhang C., Zhang L., Li Q., Wang Y., Liu Q., Wei T., Dong D., Salavati S., Gholizadeh M. and Hu X., 2019,
540 Catalytic pyrolysis of poplar wood over transition metal oxides: Correlation of catalytic behaviors with
541 physiochemical properties of the oxides, *Biomass Bioenerg.*, 124, 125-141.

542 Zheng Y., Chen D. Y. and Zhu X. F., 2013, Aromatic hydrocarbon production by the online catalytic cracking
543 of lignin fast pyrolysis vapors using Mo₂N/γ-Al₂O₃, *J. Anal. Appl. Pyrol.*, 104, 514–520.

544 Zhuo H., Wu C., Onwudili J., Meng A. and Zhang Y., 2014, Polycyclic Aromatic Hydrocarbon Formation from
545 the Pyrolysis/Gasification of Lignin at Different Reaction Conditions, *Energy Fuels*, 28, 6371-6379.

546

547

548 **Figures Captions**

549

550 **Figure 1.** (a) TGA and (b) DTA of lignin pyrolysis in presence of different catalysts.

551 **Figure 2.** – Distribution of main Etek lignin derivatives vs catalysts basicity.

552

553

554

555

556

557

558

559 **Table 1.** - TGA and DTA of Etek lignin pyrolysis in presence of different catalysts.

| Catalyst | Char+Ash yield (wt%) | Conversion to volatiles (%) | Temperature at maximum decomposition rate (°C) | Maximum decomposition rate (mg/s) |
|-----------------------|-------------------------|--------------------------------|---|---|
| ZrO ₂ | 28 | 72 | 383 | 0.047 |
| Ce/ZrO ₂ | 28 | 72 | 385 | 0.045 |
| NiCe/ZrO ₂ | 28 | 72 | 384 | 0.047 |
| MgCe/ZrO ₂ | 29 | 71 | 382 | 0.045 |
| Fe/ZrO ₃ | 33 | 67 | 373 | 0.040 |
| FePd/ZrO ₂ | 31 | 69 | 383 | 0.051 |
| Na/ZrO ₂ | 35 | 65 | 388 | 0.039 |

560 * Conversion = (Weight of initial biomass – Weight of bio-char + ash) x 100

561

562

563 **Table 2.** – Mass balance of Etek lignin pyrolysis in presence of different catalysts using the ex-situ fixed bed
 564 reactor.

| wt% | ZrO₂ | NiCe/ZrO₂ | Ce/ZrO₂ | MgCe/ZrO₂ | Fe/ZrO₂ | FePd/ZrO₂ | Na/ZrO₂ |
|-----------------------|------------------------|-----------------------------|---------------------------|-----------------------------|---------------------------|-----------------------------|---------------------------|
| Bio-oil | 43 | 38 | 46 | 49 | 40 | 40 | 41 |
| Gas | 29 | 34 | 26 | 23 | 32 | 32 | 31 |
| Char+Ash | 28 | 28 | 28 | 28 | 28 | 28 | 28 |
| Conversion to | | | | | | | |
| volatiles (%)* | 72 | 72 | 72 | 72 | 72 | 72 | 72 |

565 * Conversion = (Weight of initial biomass – Weight of bio-char + ash) x 100

566

567

568

569 **Table 3.** – GC-MS analysis of bio-oil in presence of different catalysts*.

| Functional group, wt% | ZrO₂ | NiCe/ZrO₂ | Ce/ZrO₂ | MgCe/ZrO₂ | Fe/ZrO₂ | FePd/ZrO₂ | Na/ZrO₂ |
|------------------------------|------------------------|-----------------------------|---------------------------|-----------------------------|---------------------------|-----------------------------|---------------------------|
| Acids | 0.3 | 1.1 | 0.5 | 1.0 | 2.3 | 0.0 | 0.4 |
| Alkyl Phenols | 1.8 | 3.1 | 3.1 | 2.0 | 0.7 | 1.7 | 4.4 |
| Aromatics | 1.5 | 0.1 | 1.0 | 0.8 | 0.0 | 0.0 | 0.3 |
| Catechols | 1.1 | 1.1 | 1.5 | 1.1 | 1.5 | 0.4 | 0.1 |
| Cyclopentanes | 0.4 | 0.7 | 1.4 | 0.5 | 0.2 | 0.2 | 1.4 |
| Furans | 1.7 | 1.9 | 1.4 | 1.7 | 0.0 | 0.0 | 0.7 |
| Guaiacols | 8.5 | 8.0 | 8.8 | 9.7 | 5.4 | 6.8 | 8.4 |
| Other | 1.6 | 0.8 | 0.8 | 5.5 | 0.7 | 1.0 | 3.4 |
| Oxygenated Sugar | | | | | | | |
| Derivatives | 7.8 | 5.0 | 7.5 | 4.2 | 13.3 | 13.9 | 4.5 |
| PAH | 0.0 | 0.1 | 0.5 | 0.7 | 0.0 | 0.0 | 0.1 |
| Phenol | 0.0 | 0.2 | 0.2 | 0.1 | 0.0 | 0.0 | 0.4 |
| Esters | 0.7 | 0.4 | 0.8 | 1.8 | 0.0 | 0.0 | 0.5 |
| Ketones | 0.3 | 0.5 | 0.2 | 0.2 | 0.0 | 0.0 | 0.1 |
| Total phenolics** | 11.5 | 12.3 | 13.5 | 12.9 | 7.5 | 8.9 | 13.2 |

570 * Lignin:catalyst ratio, 1:0.5; ** includes alkyl phenols, catechols, guaiacols and phenol

571

572

573 **Table 4.** Parametric study products distribution and EA of chars and spent catalysts.

| Parame Ter, wt% | Bio- oil | Char +Ash | Coke ** | Gas | Conver- sion | Char C% | Char H% | Char N% | Char O% | Catalyst C%*** | Catalyst H*** | Catalyst N%*** |
|--|---------------------|----------------------|--------------------|------------|-------------------------|--------------------|--------------------|--------------------|--------------------|---------------------------|--------------------------|---------------------------|
| T, 400°C* | 33.0 | 39.0 | 4.7 | 23.3 | 56.3 | 74.4 | 3.4 | 0.4 | 21.9 | 4.4 | 0.3 | 0.01 |
| T, 500°C* | 41.0 | 28.0 | 5.7 | 25.3 | 66.3 | 83.0 | 2.8 | 0.4 | 13.8 | 5.3 | 0.4 | 0.02 |
| T, 600°C* | 38.0 | 23.0 | 9.6 | 29.4 | 67.4 | 88.6 | 2.1 | 0.5 | 8.9 | 8.8 | 0.7 | 0.06 |
| Lignin: catalyst ratio, 1:0.5 | 41.0 | 28.0 | 5.7 | 25.3 | 66.3 | 83.0 | 2.8 | 0.4 | 13.8 | 5.3 | 0.4 | 0.02 |
| Lignin: catalyst ratio, 1:1 | 32.0 | 29.0 | 3.8 | 35.2 | 67.2 | 82.1 | 2.7 | 0.4 | 14.8 | 3.6 | 0.2 | 0.01 |
| Lignin: catalyst ratio, 1:3 | 32.0 | 29.0 | 3.3 | 35.7 | 67.7 | 81.4 | 2.7 | 0.5 | 15.5 | 3.1 | 0.2 | 0.01 |
| Na₂CO₃: ZrO₂ mol.ratio, 0.7:1* | 35.0 | 27.0 | 5.2 | 32.8 | 67.8 | 81.6 | 2.7 | 0.4 | 15.4 | 4.9 | 0.2 | 0.01 |
| Na₂CO₃: ZrO₂ mol.ratio, 1:1* | 36.0 | 27.0 | 6.6 | 30.4 | 66.4 | 81.5 | 2.8 | 0.4 | 15.4 | 6.2 | 0.4 | 0.03 |
| Na₂CO₃: ZrO₂ mol.ratio, 1.5:1* | 41.0 | 28.0 | 5.7 | 25.3 | 66.3 | 83.0 | 2.8 | 0.4 | 13.8 | 5.3 | 0.4 | 0.02 |
| R1 | 39.0 | 35.0 | 2.8 | 23.2 | 62.2 | 83.4 | 2.7 | 0.4 | 13.5 | 2.6 | 0.1 | 0.02 |
| R2 | 35.0 | 33.0 | 3.9 | 28.1 | 63.1 | 82.9 | 2.7 | 0.4 | 14.0 | 3.3 | 0.6 | 0.02 |
| R3 | 34.0 | 31.0 | 3.6 | 31.4 | 65.4 | 81.8 | 2.7 | 0.4 | 15.1 | 3.6 | 0.0 | 0.02 |

* Lignin:catalyst ratio, 1:0.5; ** calculated from EA of spent catalyst; *** regenerated at 700°C-2h

574

575

576

577 **Table 5.** GC-MS analysis of bio-oils from the parametric study.

| Functional group, wt% | Alkoxy-p | Alkyl-p | Phenol | Aromatics | PAH | Furans | Acids | Oxygenated sugars | Cyclopentanes | Other | Total Phenolics** |
|---|----------|---------|--------|-----------|-----|--------|-------|-------------------|---------------|-------|-------------------|
| T, 400°C* | 5.0 | 2.2 | 0.2 | 0.1 | 0.0 | 0.6 | 0.7 | 4.9 | 0.5 | 5.7 | 7.4 |
| T, 500°C* | 8.5 | 4.4 | 0.4 | 0.3 | 0.1 | 0.7 | 0.4 | 4.5 | 1.4 | 4.0 | 13.2 |
| T, 600°C* | 9.9 | 6.7 | 0.7 | 0.1 | 0.1 | 0.4 | 0.1 | 1.4 | 2.3 | 1.1 | 17.2 |
| Lignin:catalyst ratio, 1:0.5 | 8.3 | 4.3 | 0.4 | 0.3 | 0.1 | 0.7 | 0.4 | 4.4 | 1.4 | 3.9 | 12.9 |
| Lignin:catalyst ratio, 1:1 | 7.5 | 3.1 | 0.4 | 0.3 | 0.1 | 0.8 | 0.7 | 5.5 | 1.5 | 4.9 | 11.0 |
| Lignin:catalyst ratio, 1:3 | 11.4 | 6.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 0.5 | 0.7 | 17.5 |
| Na₂CO₃:ZrO₂ mol.ratio, 0.7:1* | 7.6 | 2.8 | 0.2 | 0.3 | 0.2 | 0.9 | 0.1 | 5.7 | 1.4 | 1.9 | 10.6 |
| Na₂CO₃:ZrO₂ mol.ratio, 1:1* | 5.5 | 3.4 | 0.3 | 0.2 | 0.1 | 0.6 | 0.3 | 4.7 | 1.2 | 5.2 | 9.2 |
| Na₂CO₃:ZrO₂ mol.ratio, 1.5:1* | 8.3 | 4.3 | 0.4 | 0.3 | 0.1 | 0.7 | 0.4 | 4.4 | 1.4 | 3.9 | 12.9 |
| R1 | 8.9 | 4.1 | 0.2 | 0.7 | 0.8 | 0.2 | 0.5 | 3.1 | 1.6 | 3.2 | 13.2 |
| R2 | 7.6 | 3.9 | 0.4 | 0.4 | 0.6 | 0.2 | 0.7 | 2.9 | 1.3 | 3.1 | 11.8 |
| R3 | 7.1 | 3.0 | 0.2 | 0.6 | 0.6 | 0.2 | 1.5 | 3.7 | 0.8 | 2.8 | 10.3 |

578 *Lignin:catalyst ratio, 1:0.5; ** includes Alkoxy-p, alkyl-p and Phenol

579

580

581