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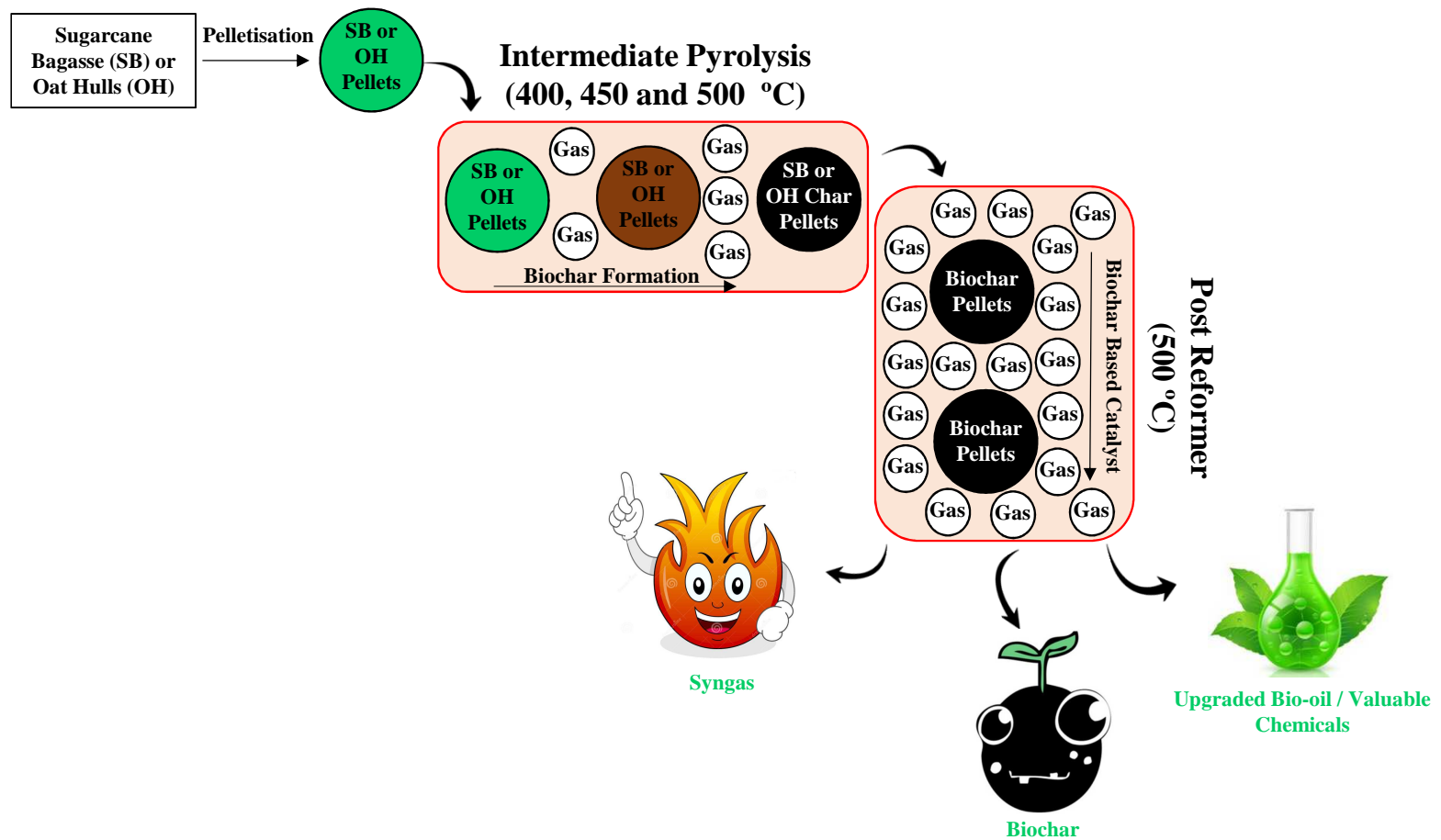
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Valorisation of lignocellulosic biomass investigating different pyrolysis temperatures

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ABSTRACT

Presently, sugarcane bagasse (SB) and oat hulls (OH) have a distinctive potential as a renewable source of biomass, due to its global availability, which is advantageous for producing liquid and gaseous fuels by thermochemical processes. Thermo-Catalytic Reforming (TCR) is a pyrolysis based technology for generating energy vectors (char, bio-oil and syngas) from biomass wastes. This work aims to study the conversion of SB and OH into fuels, using TCR in a 2 kg/h continuous pilot-scale reactor at different pyrolysis temperatures. The pyrolysis temperatures were studied at 400, 450 and 500 °C, while the subsequent reforming temperature remained constant at 500 °C. The bio-oil contained the highest calorific value of 33.4 and 33.5 MJ/kg for SB and OH, respectively at 500 °C pyrolysis temperature, which represented a notable increase compared to the raw material calorific value of SB and OH (16.4 and 16.0 MJ/kg, respectively), this was the result of deoxygenation reactions occurring. Furthermore, the increment of the pyrolysis temperature improved the water content, total acid number (TAN), viscosity and density of the bio-oil. The syngas and the biochar properties did not change significantly with the increase of the pyrolysis temperature. In order to use TCR bio-oil as an engine fuel, it is necessary to carry out some upgrading treatments; or blend it with fossil fuels if it is to be used as a transportation fuel. Overall, TCR is a promising future route for the valorisation of lignocellulosic residues to produce energy vectors.

Keywords: Thermo-Catalytic Reforming; pyrolysis; biofuel; sugarcane bagasse; oat hulls.

Abbreviations: TCR, Thermo-Catalytic Reforming; SB, sugarcane bagasse; OH, oat hulls; CHP, combined heat and power; HHV, higher heating value; PFD, process path flow diagram; TGA, thermo-gravimetric analysis; TCD, thermal conductivity detector; TAN, total acid number; GC-MS, gas chromatography-mass spectrometry.

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1. INTRODUCTION

Concerns over energy demand and security, together with the impact of CO₂ emissions from fossil fuel usage, contributing towards climate change are driving the need to find alternative and sustainable low carbon energy sources [1, 2]. Lignocellulosic agricultural waste is considered one of the most available and cheap green resources for the bioenergy sector and biofuels production [3]. Current methods to

49 exploit biomass, like extraction of pure cellulose or combustion to generate electricity,
50 are harmful to the environment and not attractive for the industry [4]. In this regard,
51 thermochemical processes (pyrolysis and gasification) are becoming popular in
52 converting biomass into valuable products [5].

53 Sugarcane is the most prominent farming harvest on the earth and the main
54 residue formed (bagasse) results from the milling of the sugarcane to extract its juice for
55 ethanol or sugar production [6]. Sugarcane bagasse (SB) is a raw material available
56 worldwide generated in 115 countries (such as USA, India, Australia, Brazil and others)
57 and its production is more significant and more efficient in tropical and sub-tropical
58 climates [7]. SB components are dispersed in a lamella structure, and their composition
59 is around 40-50% cellulose, 20-30% hemicellulose, 20-25% lignin and 1.5-3% ash [6].
60 The SB cellulose contains amorphous and crystalline components which need to be
61 submitted to physical and thermochemical treatments to have access to the
62 polysaccharides elements [8]. Milling is a suitable example of a physical process to
63 raise the particle surface area of the SB. Thermochemical treatments such as acid
64 reagents, ammonia, steam explosion and alkaline hydroxide have been described to
65 convert SB crystalline components into polysaccharide elements [9-11].

66 Currently, oat is one of the most produced cereals in the world, and its hulls
67 (residue from oat milling process) have unique potential as a renewable source of
68 biomass due to its global and annual availability. Oat hulls (OH) can be a promising
69 feedstock to produce liquid and gaseous fuels through thermochemical processes
70 (pyrolysis and gasification) [12]. The composition of OH is cellulose (35-45%),
71 hemicellulose (32-35%) and lignin (17-20%) and the hull represents between 20% and
72 35% of the entire grain weight [13]. One of its advantages is the low ash content
73 (between 4.5% and 5.2%) and the homogenous morphologic and particle size that does
74 not need to be milled when treated [13].

75 Pyrolysis processes are categorised into slow, intermediate and fast [14, 15].
76 Each implements different heating rates, temperatures and vapour/solid residence times
77 to the feedstock. However, a standard parameter is that heating of the feedstock always
78 occurs under starved or oxygen-free atmospheres. Every type of pyrolysis process
79 produces the same products (bio-oil, biochar and syngas), which are highly variable
80 depending on the pyrolysis technique applied [16]. Slow pyrolysis involves low heating
81 rates, long solid residence times and the main product is char. Fast pyrolysis applies
82 high heating rates, short vapour residence times and yields higher quantities of liquids
83 (up to 75 wt% on a dry basis) [16]. Intermediate pyrolysis occurs at temperatures
84 between 400 to 500 °C, solid heating rates (minutes/°C), solid residence times (minutes),
85 with a short vapour residence time (seconds) and produces relatively equal yields of all
86 products, solids, liquids and gases [17]. Slow and intermediate pyrolysis is the most
87 suitable techniques to produce biochar, but intermediate pyrolysis offers shorter solid
88 residence times [18].

89 Moreover, slow pyrolysis is a process mostly used for char formation, and it is
90 rarely seen to produce a reasonable yield of bio-oil (mainly tars formed) or to be
91 associated with combustion to generate heat and power [19]. The most relevant
92 variation between fast and intermediate technologies is the solid residence times,
93 causing a different heat transfer to the biomass. It leads to better control of the chemical
94 reactions and a lower thermal cracking of the bio-components, resulting in less tar
95 formation and general optimisation of the products formed [5]. Pyrolysis oil from the
96 intermediate process contains less viscosity, tars and ashes (lower contamination level)
97 leading to phase separation (organic and aqueous phases) and it is easier to separate the
98 organic phase from the aqueous phase, in comparison with fast pyrolysis where little

99 phase separation occurs [19, 20]. Depending on the feedstock and process parameters
100 applied, intermediate pyrolysis can yield energy vectors with improved physical and
101 chemical properties [17]. The intermediate process is capable of converting large
102 materials (chips, pellets and briquettes) and also fine particles down to dust (from
103 shredding, grinding and chopping) with higher moisture contents when compared to
104 other pyrolysis technologies [18]. Intermediate pyrolysis can process a varied range of
105 materials such as industrial residues, sewage sludge, organic waste, algae, digestate,
106 forest residues, grass, de-inking sludge and agricultural waste [21, 22].

107 Thermo-Catalytic Reforming (TCR) technology is a combination of intermediate
108 pyrolysis and post catalytic treatment (reforming). It was developed and implemented
109 by Fraunhofer UMSICHT, and it belongs to a bio-battery model used to provide energy
110 from renewable materials [17]. This process contains intermediate pyrolysis section
111 (biochar is being made by heating the biomass in the absence of oxygen) and reforming
112 section (biochar is collected which was formed from the pyrolysis section). In the
113 reforming section, the catalytic cracking of pyrolysis vapours using biochar as a catalyst
114 takes place at high temperatures between 500 to 700 °C to promote the formation of
115 synthesis gas and organic vapours which when condensed yield bio-oil with superior
116 physicochemical properties [23-25]. The gas exiting the reactor is partially condensed,
117 generating three different products: an organic bio-oil (6-11%), an aqueous phase (21-
118 35%) and a syngas fraction (27-44%).

119 The overall goal of this work was to study lignocellulosic biomass conversion
120 into upgraded fuels, using TCR technology. However, a comparison of different
121 pyrolysis temperatures of SB and OH has never been investigated in the TCR
122 technology. In this research, we report the impact of different pyrolysis temperatures
123 (400, 450 and 500 °C) at constant reforming temperature (500 °C) which are proposed to
124 convert SB and OH into bio-oil, syngas and biochar using a laboratory-scale TCR
125 reactor (2 kg/h).

127 2. MATERIALS AND METHODS

128 2.1 Raw Materials

129 SB (6 wt% moisture content) used in the TCR experiment was supplied from
130 Cosan Biomassa S/A (Brazil) and OH (14 wt% moisture content) was provided by
131 Miller Ltd (UK). Both feedstocks were received with a moisture content <15 wt%.
132 Therefore, no drying was required before the thermal conversion. Pelletisation was
133 performed to ensure consistency homogeneity of the raw SB and OH throughout the
134 TCR process remained the same and to facilitate with the transport of the material
135 through the reactor. Pelletisation was done using a KKP 300 F (22 kWe) motorised
136 pelletiser with a total capacity of 300 kg/h throughput (pellets formed were 6 mm
137 diameter by 23 mm length). Prior to pelletising, the feedstock was analysed in order to
138 determine the proximate, ultimate compositions and higher heating value (HHV).

140 2.2 TCR Experimental Procedure

141 The TCR bench-scale reactor was constructed, installed and commissioned at the
142 laboratory of Fraunhofer UMSICHT Institute, Germany with a capacity to process up to
143 2 kg/h of biomass. The process flow diagram (PFD) of the TCR technology is shown in
144 **Figure 1.**

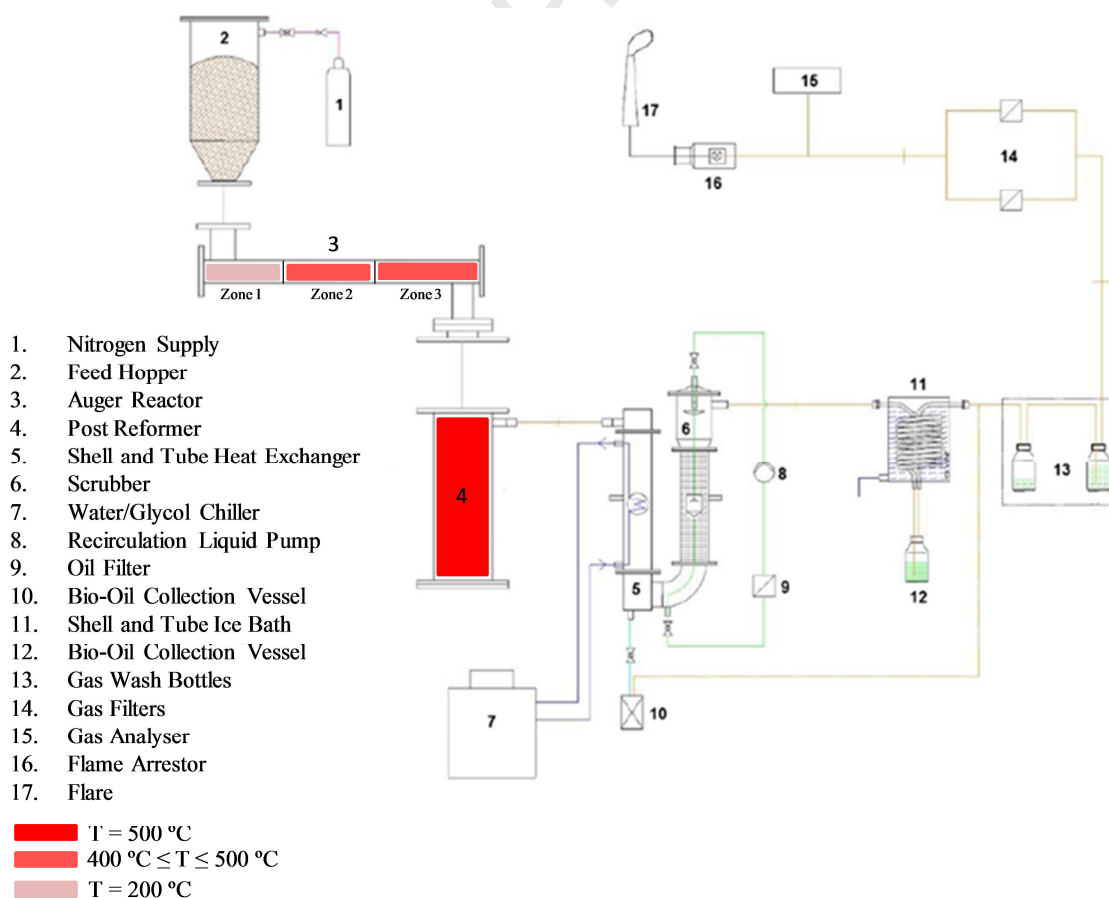
145 Before the experiment, the auger screw reactor was gradually heated for 80
146 minutes to 200 °C in heating zone 1 (to evaporate light volatile compounds) and
147 between 400 and 500 °C in the second and third zones (for intermediate pyrolysis
148 reactions) this occurred before the introduction of feedstock into the post reformer. In

149 the post reformer stage, the temperatures remained constant at 500 °C. During the
 150 heating process, the rotating screws were also turned on, and the speeds of the inner and
 151 outer screws were 4 rpm and 1.25 rpm, respectively.

152 Once the TCR had reached steady-state temperature, the first screw in the auger reactor
 153 was stopped, and the sealed hopper was opened to feed the plant with 3.5 kg of
 154 pelletised biomass (SB or OH). Then, the feed hopper was closed, and the unit was
 155 flushed with N₂ again to decrease the oxygen below to 0.5%. When the N₂ flow was
 156 stopped, the first screw in the auger reactor was turned on initiating the introduction of
 157 biomass into the TCR unit at a rate of up to 1.4 kg/h. The solid residence time was
 158 estimated to be between 5 and 10 minutes.

159 The post reformer collected the produced char from the previous step. In the post
 160 reformer, the catalytic effect which is caused by the reactions between the biochar and
 161 the pyrolysis vapours converts the non-condensable gases into a syngas rich in H₂ or
 162 CH₄ and condensable gases into upgraded bio-oil. During the reforming process, the
 163 condensable organic vapours were upgraded using biochar as a catalyst, enhancing their
 164 chemical and physical fuel properties.

165 Subsequently, upgraded organic vapours were quenched at -5 °C in the
 166 condensing unit to guarantee a complete separation between the pyrolysis liquid and the
 167 gas fraction. The bio-oil formed was collected and stored every thirty minutes in an
 168 external vessel. Then, the remaining non-condensable vapours passed through the
 169 filtration unit for aerosols, fine particles and other contaminants removal. The cleaned
 170 gas was directly measured and analysed via an online gas analyser/calorimeter.
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Figure 1. TCR (2 kg/h) process path flow diagram (PFD) [23].

2.3 Proximate Analysis

176 Total moisture content was determined by drying the sample at 105 ± 3 °C in a
177 muffle furnace (Philips K5 94) with an inert atmosphere for 3 h. The percentage of
178 moisture was calculated based on the amount of mass loss, according to ASTM E1756-
179 08. The ash content was measured using the same muffle furnace at 575 ± 25 °C, in
180 which the ash content was determined by the calculation from the mass of the residue
181 remaining after the sample was heated in the air under rigidly controlled conditions of
182 time (according to ASTM E1755-01). Volatiles and fixed carbon were determined by
183 thermo-gravimetric analysis (TGA) technique (NETZSCH TG 209 F1 IRIS).
184 Approximately 15 mg of dried feedstock was inserted into a crucible and pyrolysed
185 under an inert atmosphere of nitrogen at a flow rate of 60 ml/min, to a maximum
186 temperature of 900 ± 10 °C, with a heating rate of 10 °C/min and holding time of 15
187 minutes (according to BS EN 15148:2009).

188 189 *2.4 Ultimate Analysis*

190 Prepared samples were sent to an external laboratory (MEDAC Ltd) for CHNS
191 analysis (with oxygen determined by difference). The CHN analysis was carried out
192 according to ASTM E777 and ASTM E778. The sulphur content was measured
193 according to ASTM E775. The original analytical method (using the Thermo FlashEA®
194 1112 Elemental Analyser) was based on the complete and instantaneous oxidation of
195 the sample by “flash combustion” which converts all organic and inorganic substances
196 into combustion products. The resulting combustion gases passed through a reduction
197 furnace and were swept into the chromatographic column (CHNS/NCS separation
198 column, 2 m, 6x5 mm PTFE) by the carrier gas (He). The combustion gases were
199 separated and detected by a thermal conductivity detector (automatic EAGER300™),
200 which gave an output signal proportional to the concentration of the individual
201 components of the mixture.

202 203 *2.5 HHV*

204 The HHV (MJ/kg) was determined using the unified correlation for fuels
205 developed by Channiwala et al. [26]. The C, H, S, O, N and A are carbon weight
206 fraction, hydrogen, sulphur, oxygen, nitrogen and ash, respectively:

$$207 \text{HHV (MJ/kg)} = 0.3491 (\text{C}) + 1.1783 (\text{H}) + 0.1005 (\text{S}) - 0.1034 (\text{O}) - 0.0151 (\text{N}) -$$
$$208 0.0211 (\text{A}). \quad \text{(Equation 1)}$$

209 210 211 *2.6 Products Characterisation*

212 After the experiment, the produced liquid was separated by gravity (using a
213 separating funnel) into two phases with different densities: an organic oil phase at the
214 top and an aqueous phase at the bottom. Then, the pyrolysis liquid was analysed to
215 determine the chemical and physical properties. Biochar and syngas were also
216 characterised.
217

218 219 *2.6.1 Oil and char ultimate analyses*

220 Pyrolysis liquid and char samples were analysed externally at MEDAC Ltd,
221 applying the same method as in section 2.4 for the determination of the elemental
222 compositions (C, H, N, O and S). Furthermore, the oxygen was determined by the
223 difference ($100 - \sum (\text{CHNS} + \text{ash})$).
224

225 *2.6.2 Oil and char ash contents*

226 The ash content of the oil was calculated in accordance with ASTM D482. The
227 carbonaceous solid samples produced from the carbon residue test were combusted in a
228 muffle furnace at 775 °C. The remaining ash was cooled at room temperature and
229 weighed, then expressed as a mass percentage of the original oil sample. The ash of the
230 char was determined in a muffle furnace at 575 °C, described in section 2.3 according to
231 ASTM E1755-01.

232 2.6.3 HHV

233 The HHV of the bio-oil and char was determined using the unified correlation
234 for fuels as described in section 2.5.

235

236 2.6.4 Water content

237 The water content of the bio-oil was determined using a Mettler Toledo V30
238 compact volumetric Karl Fischer titration in accordance with ASTM E203-01. The
239 result was corrected to the weight percent of the total sample.

240

241 2.6.5 Total acid number (TAN)

242 The TAN of the oil was determined with a Mettler Toledo V20 compact titrator
243 using the potentiometric titration method in accordance with ASTM D664. The oil
244 sample was dissolved in a 50/50 toluene and isopropanol solution and titrated
245 potentiometrically with 0.1 N alcoholic potassium hydroxide using a combination
246 electrode. Readings were automatically plotted against the volume of the titrating KOH
247 solution used until the titration endpoint was achieved.

248

249 2.6.6 Viscosity

250 Viscosity was determined with a Cannon–Fenske Routine glass capillary
251 viscometer (ASTM D445). Throughout the analysis, the viscometer was setting at 40 °C
252 allowing passage of a specific pyrolysis oil quantity over the capillary. The final
253 viscosity is the multiplication of the oil travelling time (registered before) and the
254 viscometer constant.

255

256 2.6.7 Density

257 The pyrolysis oil density was measured at 22 °C using a glass hydrometer in the
258 range (0.8–1.0 g/cm³), according to ASTM D1298.

259

260 2.6.8 Gas chromatography-mass spectrometry (liquid-GC-MS)

261 The bio-oil sample was analysed with GC-MS apparatus equipped with a polar
262 chromatographic column. The polar analysis was performed with a 7820A Agilent HP
263 gas chromatograph connected to a 5977E Agilent HP quadrupole mass spectrometer (EI
264 70 eV, at a frequency of 1.55 scan/s within the 29-300 *m/z* range). Analytes were
265 separated by a nitroterephthalic acid-modified polyethylene glycol DB-FFAP (30 m,
266 0.25 mm ID, 0.2 µm film thickness) column using helium as a carrier gas with the
267 following thermal program: 50 °C with a hold for 5 minutes; then ramping up with a
268 heating rate of 10 °C/min until 250 °C; followed by column cleaning at 250 °C for 10
269 minutes. A sample of bio-oil was dissolved in acetonitrile solution to a 1% (w/v
270 concentration), spiked with 0.1 ml internal standard solution (1000 mg/l, 2-ethyl butyric
271 acid in acetonitrile). The compounds were identified by library searches (NIST
272 libraries). The mass spectra evaluation was quantified in terms of relative abundance of
273 peak area (% is the individual peak area to the total area).

274

275 2.6.9 Gas analysis

276 The produced pyrolysis gas was frequently measured and analysed using a gas
 277 analyser MGA 12, Dr Födisch Umweltmesstechnik, according to EN 15267-3 standard
 278 test procedure. The measurement principle of the gas analyser is based on an infrared
 279 photometer (CO, CO₂ and CH₄), an electrochemical cell (O₂) and a TCD (H₂). The
 280 heating value of the gas phase was quantified using the Union Instruments CWD2005
 281 process gas analyser. The calibration of the gas analysers was performed prior to the
 282 experiments.

283 3. RESULTS AND DISCUSSION

284 3.1 Feedstock Characterisation

285 **Table 1** shows the proximate and ultimate analyses of the lignocellulosic
 286 residues (raw SB and OH). The SB characterisation values of the current work do not
 287 present a close correlation when compared to the literature [4, 6, 27, 28]. There are
 288 more than 500 sugarcane species, and their chemical composition can be slightly
 289 different [28]. Only the ash (3.1 wt%), water (5.4 wt%) and the elemental composition
 290 (44.9 wt% of carbon, 5.9 wt% of hydrogen and 45.8 wt% of oxygen) found in Varma et
 291 al. [6] study were similar to this study. Al Arni [27] investigated bagasse with moisture,
 292 ash content and HHV of 8.5, 5.9 wt% and 18.2 MJ/kg, respectively.

293 The OH characterisation values are compared with the literature results [29-31].
 294 Abedi et al. [29] reported for the same type of biomass 41.8, 6.4, 44.7 wt% and 16.8
 295 MJ/kg for C, H, O and HHV, respectively. However, the same study showed a lower
 296 level of moisture (8.5 wt.%) and a higher amount of ash (5.8 wt.%), which is a
 297 disadvantage for char production and their respective properties [32]. Zhang et al. [31]
 298 calculated the elemental composition (C, H and O) and HHV for OH obtaining 43.5,
 299 4.7, 45.9 wt% and 16.1 MJ/kg, respectively.

300
301

Table 1. Feedstock characterisation.

	SB	OH
<u>Ultimate analysis (moisture-free basis)</u>		
C (wt%)	43.7	40.6
H (wt%)	5.1	6.0
N (wt%)	0.1	1.1
S (wt%)	0.6	<0.1
O (wt%)	46.5	49.9
<u>Proximate analysis (dry basis)</u>		
Moisture (wt%)	6.0	14.8
Ash (wt%)	4.0	2.4
Fixed carbon (wt%)	17.2	26.4
Volatiles (wt%)	72.8	56.4
HHV (MJ/kg)	16.4	16.0

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3.2 Bio-liquids Analyses

Table 2 shows the chemical composition and fuel properties of the SB and OH
 bio-oils applying different pyrolysis temperatures in the reactor. The levels of nitrogen
 and sulphur (<2 wt% and <1.4 wt%, respectively) are acceptable if the purpose of the
 SB and OH bio-oils is to be burned or combusted as a fuel [33]. The sulphur and
 nitrogen contents should be about 500 and 148 ppm for diesel engine fuels [34, 35].
 Additionally, low NO_x and SO_x emissions are preferable for environmental reasons
 [33].

311 The ash content revealed was extremely low (<0.001%), which is positive for
312 engine applications as this minimises corrosion, blocking and deposition of sediments
313 during its operation [36]. Based on the ash content of all SB and OH oils, it is evident
314 that TCR technology can produce a bio-oil containing very low residues of ash which is
315 attractive as a fuel.

316 SB and OH oils present lower acidity when submitted to higher pyrolysis
317 temperatures. The total acid number (TAN) of SB and OH decreased from 32.2 to 25.8
318 mg KOH/g and from 33.5 to 24.2 mg KOH/g with increasing the pyrolysis temperature
319 from 400 to 500 °C, respectively. The acid number of this work is significantly higher in
320 comparison with diesel (0.24 mg KOH/g) [37] and biodiesel (0.8 mg KOH/g) [38].
321 However, Asadullah et al. [39] reported that fast pyrolysis of sugarcane bagasse from
322 the fixed bed reactor at temperatures of 500 °C has much higher acid content (137.35
323 mg KOH/g) in comparison with this study (25.8-32.2 mg KOH/g). These values are still
324 high for engines, but it is essential to highlight the role of TCR in producing a bio-oil
325 with lower acidity.

326 In terms of viscosity, higher pyrolysis temperatures were more effective in
327 cracking the organic vapours, thus forming lighter weight molecules and reducing the
328 viscosity of the bio-oil. The viscosity improved from 47.8 to 23.7 mm²/s for SB and
329 from 38.1 to 35.3 mm²/s for OH with increasing the pyrolysis temperatures. This is an
330 advantage to improve the fuel flow of the engine causing better combustion, despite the
331 results are still considered high for engine applications [40].

332 Higher pyrolysis temperatures were able to produce lighter chemical compounds
333 which reduced the density of the pyrolysis liquid. Lower density influences the injection
334 time and the consumption rate, which improves the engine performance [41].

335 Higher pyrolysis temperatures decreased the amount of moisture which
336 improves the HHV and the properties of the oil in terms of engine performance [22].
337 The rise in the pyrolysis temperature also helped in the promotion of dehydration
338 reactions reducing the percentage of water.

339 An increment of the pyrolysis temperature led to a bio-oil with less oxygen and
340 more carbon for both feedstocks. As a consequence, TCR bio-oil contained a better
341 HHV with higher pyrolysis temperatures. It is reasonable to conclude that higher
342 pyrolysis temperatures might stimulate more depolymerisation and thermal breaking
343 reactions of hemicellulose and cellulose resulting in a bio-oil with less oxygen, more
344 carbon and a higher calorific value [42]. Varying the pyrolysis temperature resulted in a
345 bio-oil HHV between 29.1 and 33.5 MJ/kg for both feedstocks. The bio-oil contained
346 the highest calorific value of 33.4 MJ/kg from SB and 33.5 MJ/kg from OH at 500 °C
347 pyrolysis temperature. The SB and OH experiments produced a pyrolysis oil with better
348 energy density attributed to the higher carbon and lower oxygen content.

349 Varma et al. [6] and Treedet et al. [43] converted SB through fast pyrolysis at
350 500 °C using a semi-batch and fluidised bed reactors, respectively. In both cases, the
351 HHV of the bio-oil (27.7 and 18.4 MJ/kg) was lower compared to the SB runs of the
352 present work. Treedet et al. [43] also produced SB pyrolysis oil with a higher
353 percentage of water (38.9 wt%) and higher density (1259 kg/m³) than this set of
354 experiments.

355 Results show an improvement of the bio-oil HHV when increased the pyrolysis
356 temperature. Surprisingly, Henkel et al. [44] had precisely the opposite trend processing
357 SB in an intermediate pyrolysis batch reactor. However, this study changed the
358 pyrolysis temperatures from 500 to 700 °C and not between 400 and 500 °C, which
359 might be the main cause for the decrease of the calorific value of the bio-oil. It is well

360 known that cellulose and hemicellulose depolymerisation reactions are more active
361 between 400 and 500 °C, influencing the characteristics of the pyrolysis oil [45].

362 The SB oil at 400 °C of the present work revealed better results than Ahmad et
363 al. [46] with the same biomass and experimental conditions. The difference between
364 both studies can be explained by the existence of many species of SB which might have
365 diverse chemical compositions. Ahmad et al. [46] produced a bio-oil with higher
366 oxygen content (35.2 wt%) and water (25.6 wt%), and lower carbon value (53.7 wt%)
367 and HHV (24.3 MJ/kg).

368 The heating value of TCR bio-oil from SB and OH (33.4 and 33.5 MJ/K,
369 respectively) at 500 °C pyrolysis temperature slightly different from biodiesel heating
370 value (37.10 MJ/kg) [47] and they are lower than fossil-based diesel (42 MJ/kg) [48].
371 The difference between diesel and pyrolysis oil is related to the high oxygen content of
372 biomass-derived fuels due to the presence of complex compounds such as ethers,
373 ketones, aldehydes, acids and carbolic groups [49]. The oxygen content of SB and OH
374 at 500 °C pyrolysis temperature was approximately 15 times higher than the diesel (1.0
375 wt%) [48].

376 The Van Krevelen diagram is shown in **Figure 2**, which represents the O/C and
377 H/C ratios for different technologies. The TCR results are selected at 400 °C reactor and
378 500 °C reforming temperatures which contain the highest oxygen content for SB and
379 OH bio-oils. The O/C ratios of SB and OH bio-oils were 0.32 and 0.18, respectively.
380 The H/C ratios of SB and OH bio-oils were 1.57 and 1.45, respectively. However, the
381 bio-oil from fast pyrolysis of lignocellulosic biomass has much higher values of O/C
382 (0.76) and H/C (1.72) [50] than the results from TCR of SB and OH. Moreover, the O/C
383 and H/C ratios of TCR of OH result is slightly different from hydrotreated bio-oil from
384 switchgrass [51]. Therefore, the molar ratio of O/C and H/C of SB and OH shows
385 significant improvement in bio-oil stability and performance characteristics in
386 comparison to other technologies. The TCR bio-oil of SB and OH have higher calorific
387 value, lower oxygen and viscosity contents at 500 °C pyrolysis temperature in
388 comparison with other pyrolysis temperatures (400 °C and 45 °C) in this study.

389 The aqueous phase fraction of TCR contained high oxygen content in
390 comparison with TCR bio-oil [24, 52]. The aqueous phase of sugarcane bagasse showed
391 lower oxygen content in the absence of the reforming unit in TCR process, thus
392 suggesting the probability of higher energy content in the aqueous phase fraction [46].
393 The aqueous phase of TCR contains a mixture of oxygenated compounds including
394 water, carboxylic acids, ketones, phenols, aldehydes, sugars and furans [52]. The
395 application of the aqueous phase from TCR process should be considered since the
396 aqueous phase accounts for 25-35 wt% of overall mass balance. The hydrogen content
397 can be increased by the injection of steam/aqueous phase of TCR into the process that
398 enhances water gas shift reaction [23, 53]. TCR process separated the bio-oil and the
399 aqueous phase. However, the fast pyrolysis unit produced a mixture of bio-oil and the
400 aqueous phase thus requires an external source of hydrogen to upgrade the bio-oil [54,
401 55]. Tsai et al. reported that fast pyrolysis of sugarcane bagasse at 500 °C produced
402 between 23-47 wt% of total liquids which is a mixture of both (water phase and organic
403 phase liquids) with the calorific value of 5.12 MJ/kg [56]. Furthermore, promising
404 research have studied that the bio-oil aqueous phase can be applied in a wide range of
405 applications such as composting, crop pest control, crop growth promotion, feed
406 additives, deodorising, coagulating and antifungal agents [57, 58].

407 In conclusion, the bio-oil of SB and OH from TCR process have superior
408 physical and chemical fuel properties compared to other technologies. The bio-oil can
409 be separated easily from the aqueous phase in TCR process, which is opposite of fast

410 pyrolysis bio-oil [16, 17]. The TCR crude-oil from SB and OH showed some positive
 411 aspects to be used as fuel for engines when compared to other pyrolysis technologies. It
 412 is demonstrated sufficient quality to be burned in combustors, boilers and CHP engines
 413 or similar applications [17]. In order to use the TCR bio-oil in an engine fuel, it is
 414 necessary to blend it with fossil fuels or carry out hydrotreatment upgrading. There is no
 415 need for an external source of hydrogen as it can be produced from the TCR unit and
 416 can be improved by injection of TCR aqueous phase into the system. Therefore, further
 417 study engine tests need to be done to use TCR bio-oils of SB and OH as transportation
 418 fuels.

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422 **Table 2.** SB and OH bio-oil characterisation at different pyrolysis temperatures
 423 (reforming temperature = 500 °C).

Pyrolysis Temperature (°C)	SB			OH		
	400	450	500	400	450	500
<u>Ultimate analysis</u>						
C (wt%)	63.4	71.3	72.2	70.7	72.2	72.8
H (wt%)	8.3	7.1	8.6	8.6	8.2	8.3
N (wt%)	0.4	0.7	0.7	1.8	1.9	1.8
S (wt%)	0.4	0.1	0.3	1.3	0.7	0.7
O (wt%)	27.5	20.8	18.2	17.6	17.0	16.4
<u>Fuel properties</u>						
HHV (MJ/kg)	29.1	31.1	33.4	33.1	33.2	33.5
Ash (wt%)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Water (wt%)	9.9	4.7	4.2	7.8	4.8	4.4
TAN (mg KOH/g)	32.2	27.7	25.8	33.5	30.5	24.2
Viscosity (mm ² /s)	47.8	24.9	23.7	38.1	36.5	35.3
Density (kg/m ³)	1077	1062	1061	1078	1074	1072

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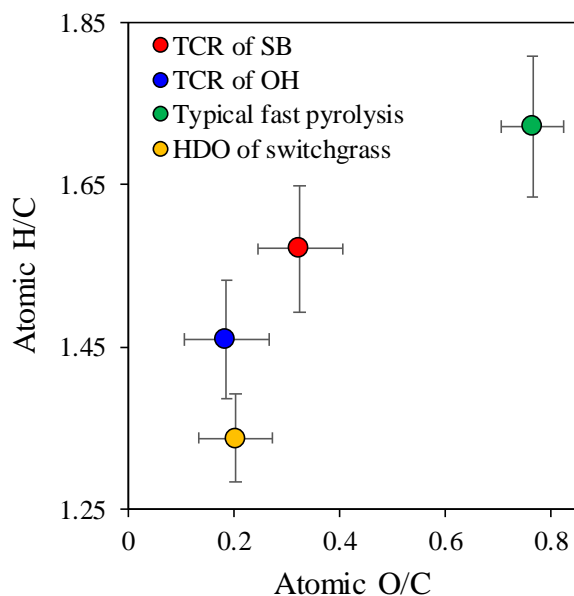


Figure 2. The Van Krevelen diagram of TCR of SB and OH bio-oil (at 400 °C reactor temperature and 500 °C reforming temperature) and fast pyrolysis bio-oil from lignocellulosic biomass [50], as well as, hydrotreated bio-oil from switchgrass [51].

3.3 GC-MS Analysis of Bio-oil

The 14 most relevant and frequent peaks were identified, as shown in **Figures S1** and **S2**. The GC-MS results are represented in **Table 3** for SB and OH bio-oil (organic fraction) at different pyrolysis temperatures. Phenols, aromatics and furans are the most common chemical compounds present in the SB and OH bio-oils. For both feedstocks, phenols represent the main group in the bio-oil, which is responsible for the high acidity found in **Table 2** [19].

Phenols and aromatics were the highest fractions of bi-oil, but furans were the less abundant compound. Furans are derived from hemicellulose, while phenols are formed from lignin, and their presence in TCR liquids showed that both fractions were thermally degraded during the process efficiently [59, 60]. When the pyrolysis temperature was at 500 °C, the benzene and toluene yields were higher in comparison with other pyrolysis temperatures. High pyrolysis temperatures have a significant effect on the stimulation of deoxygenation reactions increasing the level of aromatics present in the pyrolysis liquid [61].

Table 3. Compounds detected and identified by GC-MS of the SB and OH bio-oil at different pyrolysis temperatures (reforming temperature = 500 °C).

			SB			OH		
Pyrolysis Temperature (°C)			400	450	500	400	450	500
#	Group	Chemical compound	Conc. (%)			Conc. (%)		
1	Aromatic	Benzene	4.77	5.76	5.29	5.88	5.71	6.51
2	Aromatic	Toluene	5.63	7.06	6.99	8.38	7.98	9.61
3	Furan	Furfural	6.73	6.56	5.29	5.48	5.71	4.4
4	Furan	2-Furanmethanol	4.70	4.55	3.78	5.58	5.98	4.74

5	Aromatic	Ethylbenzene	4.71	5.00	4.11	6.28	5.42	6.31
6	Aromatic	Benzene, 1,3-dimethyl-	4.91	5.16	4.69	5.11	5.49	5.21
7	Aromatic	1,3,5,7-Cyclooctatetraene	4.95	5.66	5.49	7.58	5.98	8.21
8	Phenol	Phenol	10.33	10.26	11.79	10.28	10.48	10.31
9	Phenol	Phenol, 2-methyl-	6.83	7.46	8.09	7.68	7.78	8.01
10	Phenol	Phenol, 3-methyl-	9.83	9.76	11.49	8.98	9.48	10.21
11	Phenol	Phenol, 2,4-dimethyl-	5.43	5.46	4.79	5.00	5.88	5.41
12	Phenol	Phenol, 4-ethyl-	17.73	11.96	11.39	8.98	10.98	8.41
13	Aromatic	Naphthalene	5.21	6.25	6.49	8.38	6.18	6.31
14	Furan	Benzofuran, 2,3-dihydro-	8.24	9.10	10.32	6.41	6.95	6.35

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3.4 Gas Analysis

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The gas composition (H_2 , CH_4 , CO , CO_2 and C_xH_y) of the SB and OH experiments at different pyrolysis temperatures are shown in **Table 4**. The non-detectable volume in the syngas might be the existence of hydrocarbons like ethylene and propane not detected by the gas analyser. Applying 400 and 450 °C as pyrolysis temperature, CO_2 was the main gas in SB and OH syngas. Low pyrolysis temperatures stimulate the degradation of hemicellulose and cellulose, which is linked to the cracking of carboxyl and carbonyl compounds, increasing the formation of CO_2 [62].

When the pyrolysis temperature is raised, the volume of CO_2 decreased for the reasons mentioned previously, related to the decomposition of cellulose and hemicellulose. Methane yields were also reduced with the increment of pyrolysis temperature due to lignin deformation at different pyrolysis temperatures [45]. It is reported that lignin deformation and cracking released much more H_2 and CH_4 in comparison with cellulose and hemicellulose in a packed bed system [45]. The reason is that cellulose appeared more OH and C-O compounds and hemicellulose contained higher C=O organic compounds, while lignin had higher aromatic rings and O- CH_3 functional groups [45]. The gas analysis revealed CO to be the main compound present in both pyrolysis gases at 500 °C (32.6 and 29.5 vol% for SB and OH, respectively). The reason might be the decarbonylation and decarboxylation reactions, increasing the amount of CO [63]. SB at 450 °C and OH at 500 °C generated the syngas with better calorific values (15.9 and 17.3 MJ/kg) due to higher H_2 volume (25.7 and 23.1 vol%).

Al Arni [27] used a batch reactor to process SB at 500 °C through two pyrolysis regimes (fast and slow). For both types of fast and slow pyrolysis, the H_2 volumes (8.7 and 9.6 vol%, respectively) were approximately less than half of the TCR SB run with the same pyrolysis temperature (500 °C). The reforming unit containing biochar as a catalyst could favour deoxygenation reactions resulting in the production of H_2 and improving the HHV of the pyrolysis gas [44].

Ahmad et al. [46] obtained a syngas with the same HHV (13.8 MJ/kg) with similar experimental conditions (TCR of SB at 400 and 500 °C as pyrolysis and reforming temperatures). Despite **Table 4** showing a higher H_2 yield (21.5 to 12.1 vol%), the lower percentage of CH_4 (19.5 to 15.6 vol%) and CO (32.8 to 21.2 vol%) found in his work might justify the same calorific value between both studies. The different gas composition among both works may come from the use of diverse SB species with different chemical natures. The quantity of combustible gases and the HHV of these experiments are sufficient to be utilised as a fuel for production of heat and power via CHP engines.

486 **Table 4.** SB and OH permanent gas composition at different pyrolysis temperatures
 487 (reforming temperature = 500 °C).

Pyrolysis Temperature (°C)	SB			OH		
	400	450	500	400	450	500
<u>Component</u>						
H ₂ (vol%)	21.5	25.7	19.9	16.5	15.8	23.1
CH ₄ (vol%)	15.6	13.5	10.9	11.6	7.0	6.4
CO (vol%)	21.2	20.2	32.6	26.5	25.5	29.5
CO ₂ (vol%)	30.5	28.8	23.6	30.1	25.6	21.2
C _x H _y (vol%)	2.5	2.3	2.7	3.0	2.7	3.4
Non-detectable (vol%)	8.7	9.5	10.3	12.3	23.4	16.4
HHV (MJ/kg)	13.8	15.9	13.4	16.2	15.3	17.3
Density (kg/m ³)	0.90	0.89	0.98	0.91	1.2	0.85

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489 3.5 Char Analysis

490 **Table 5** indicates the ultimate analysis of the biochar, ash content and its HHV.
 491 Biochar is mainly composed of fixed carbon and ash, as mentioned before. SB biochar
 492 suffered a fluctuation in terms of carbon and energy content when the pyrolysis
 493 temperature was increased. The biochar from SB produced at 450, and 500 °C
 494 (pyrolysis and reforming temperatures) was the only one out of this context having a
 495 substantially lower carbon value and energy content compared to the rest of the trials.
 496 For OH runs, the biochar presented similar chemical composition and calorific value
 497 between different pyrolysis temperatures.

498 The SB biochar at 400 °C contains the highest calorific value (29.7 MJ/kg)
 499 attributed to the highest carbon content (79.6 wt%). Inversely, SB biochar at 450 °C is
 500 the less energetic (24.9 MJ/kg) having the lowest carbon value (70.3 wt%). Fixed
 501 carbon is the combustible compound of the pyrolysis char raising the HHV [64].
 502 Generally, for the same pyrolysis temperatures, OH char presented less ash and more
 503 carbon than the SB char leading to a better HHV. This is a result of the chemical
 504 composition of both raw feedstocks, where the OH contains more fixed carbon and less
 505 ash compared to SB (**Table 1**). The existence of ash reduces the energy content of the
 506 biochar [65].

507 The present work produced SB biochar (500 °C) with the HHV between Varma
 508 et al. [6] and Lee et al. [66] studies. The first author used fast pyrolysis to process SB at
 509 500 °C obtaining a char with lower carbon content (66.9 wt%) and subsequently lower
 510 energy density (24.3 MJ/kg). However, the second author converted SB via slow
 511 pyrolysis at 500 °C producing biochar with a higher carbon value (85.6 wt%) and HHV
 512 (32.8 MJ/kg). Slow pyrolysis involves slower heating rates and longer residence times
 513 which promotes aromatisation reactions increasing the C-C bonds and the percentage of
 514 fixed carbon in the biochar [67].

515 Henkel et al. [44] processed SB via intermediate pyrolysis (batch reactor), and
 516 the same fluctuation of the SB HHV (from **Table 5**) was observed when the pyrolysis
 517 temperature was increased. In the same study, the biochar at 500 °C demonstrated lower
 518 carbon content (71.9 wt%), and calorific value (24.3 MJ/kg) compared to the SB run for
 519 the present work at the same pyrolysis temperature. The reforming unit of the TCR

520 enables a longer residence time of the char causing cracking reactions resulting in final
521 biochar richer in fixed carbon.

522 In relation to TCR results from the literature review, Ahmad et al. [46] produced
523 SB char at 400 and 500 °C (pyrolysis and reforming temperature) with higher ash
524 content (30.5 wt%) and lower carbon value (67.9 wt%) and energy density (24.0
525 MJ/kg). The variance between these results and **Table 5** (for the same parameters)
526 might be due to the different chemical composition of the SB applied. All the biochars
527 from this section contained similar carbon value and energy content when likened to the
528 classic sub-bituminous coal (73.9% carbon and 29.05 MJ/kg energy content) [68]. The
529 only exception is the SB char produced at 450 °C. The biochar from this set of
530 experiments is energetically interesting to produce heat and power through boilers,
531 gasifiers and furnaces. Moreover, it can also be utilised as a fertiliser, activated carbon
532 and for catalytic upgrading [65, 66, 68-70].

533

534 **Table 5.** SB and OH biochar characterisation at different pyrolysis temperatures
535 (reforming temperature = 500 °C).

Pyrolysis Temperature (°C)	SB			OH		
	400	450	500	400	450	500
<u>Ultimate analysis</u>						
C (wt%)	79.6	70.3	77.1	78.2	79.3	79.0
H (wt%)	2.2	1.6	1.5	2.7	2.0	2.3
N (wt%)	0.44	0.39	0.47	1.4	1.1	1.3
S (wt%)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
O (wt%)	2.76	11.61	2.73	2.2	5.8	1.3
Ash (wt%)	15.0	16.1	18.2	15.5	11.8	16.1
HHV (MJ/kg)	29.7	24.9	28.1	29.3	29.2	29.3

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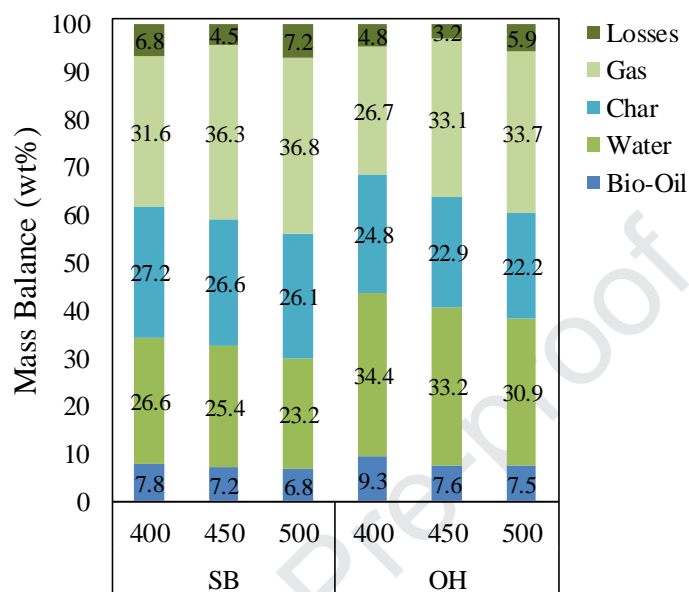
538 *3.6 Mass Balance and Energy Yield*

539 The mass balance and the energy yield for the SB and OH experiments are
540 demonstrated in **Figures 3** and **4**. When the pyrolysis temperatures were lower, the
541 production of pyrolysis liquid (bio-oil and aqueous phase/water) and biochar increased.
542 The formation of pyrolysis oil comes from the breakdown of cellulose and
543 hemicellulose at lower temperatures through devolatilisation and depolymerisation
544 reactions [45]. Biochar production is also favoured at low pyrolysis temperatures where
545 charring and cross-linking reactions occur with more intensity [71, 72]. The lowest
546 pyrolysis temperature (400 °C) resulted in the most significant yields of SB and OH bio-
547 oil and biochar.

548 At the same time, the gas fraction was maximised due to the degradation of
549 biochar into lighter compounds when submitted to higher temperatures in the pyrolysis
550 reactor. The increment of temperature also promoted other decomposition reactions
551 resulting in less bio-oil and more syngas [44]. The run of SB and OH at 500 °C
552 (pyrolysis temperature) produced the highest syngas fraction (36.8 wt% and 33.7 wt%,
553 respectively). The gas yields observed in this figure are higher for SB than OH
554 experiments due to the higher water content present in OH feedstock (**Table 1**). More

555 moisture means less gas produced, which is attributed to the higher removal of water-
556 soluble compounds present in the pyrolysis gas [73].

557 TCR technology presented a high efficiency in terms of mass balance. The
558 conversion of biomass into valuable products was between 92.8 and 96.8 wt%. In the
559 best experiment, only 3.2 wt% was losses (OH at 450 °C pyrolysis temperature). The
560 losses might be explained due to errors measuring weights, non-detectable gases by the
561 gas analyser and the remained bio-oil in the cleaning section.



562 **Figure 3.** Mass balance of SB and OH trials at different pyrolysis temperatures
563 (reforming temperature = 500 °C).
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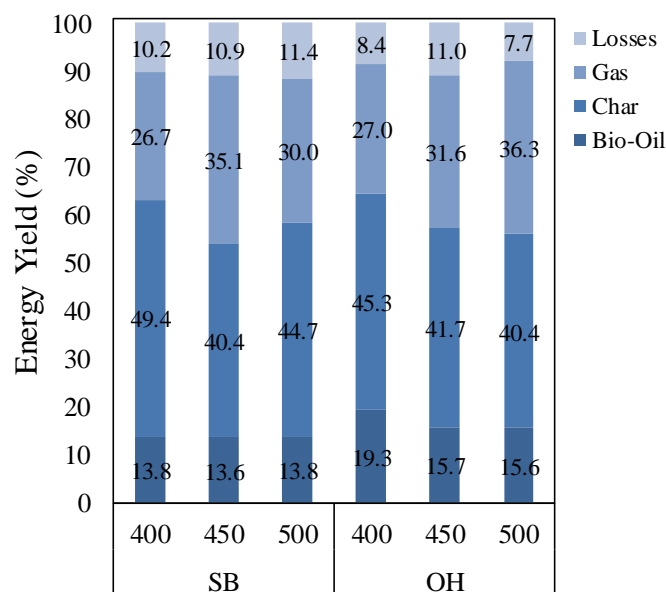
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566 It is observed that the OH energy yields for bio-oil are higher than SB for any
567 single pyrolysis temperature (**Figure 4**). This can be explained by the better energy
568 value, and higher oil production found in OH runs (**Table 2** and **Figure 3**). Biochar had
569 the highest energy fraction in all experiments. The best biochar results were achieved
570 with the lowest reforming temperatures for both biomasses, where SB and OH at 400 °C
571 obtained 49.4 and 45.3%, respectively. Despite the present runs producing more syngas
572 than char, the calorific value of biochar (24.9–29.7 MJ/kg) is significantly higher
573 compared to the pyrolysis gas (13.4–17.3 MJ/kg) which can justify the results from
574 **Figure 4**.

575 The energy losses were from 7.7 to 11.4%, where the OH trial at 500 °C was the
576 most efficient one converting 92.3% of the energy from the feedstock into TCR
577 products. In general, SB experiments presented more energy losses than OH, which can
578 be associated with more mass losses demonstrated in **Figure 3**. Furthermore, some
579 pyrolysis liquid could not be extracted from the condensing unit due to the difficulty of
580 collecting all the liquid produced. For that reason, some bio-oil energy was lost and not
581 considered for the energy yields affecting the efficiency of the process.

582 To sum up, various feedstock (wood, sewage sludge, paper sludge, de-inking
583 sludge, food/market waste and digestate) were processed through TCR plants
584 successfully, and the results have already been published [74]. The TCR produces high-
585 quality products from a wide range of biomass kinds. The energy losses can be
586 minimised by applying efficient isolation and increasing the reactor scale. The last
587 achievement is the commercial TCR system with a 300 kg/h capacity at UMSICHT,

588 which is the future work of this study [74]. TCR technology proved its efficiency in
 589 terms of mass balance and energy yield in this study.



590
 591 **Figure 4.** Energy yield of SB and OH trials at different pyrolysis temperatures
 592 (reforming temperature = 500 °C).
 593

594 4. CONCLUSIONS

595 In this study, SB and OH were successfully processed using TCR technology in
 596 a 2 kg/h continuous pilot-scale reactor. The pyrolysis liquid, char and gas fraction were
 597 produced and characterised. Increasing the pyrolysis temperature reduced the oxygen
 598 value of the bio-oil and raised its carbon content and the HHV. The total acid number
 599 (TAN) of the oils was improved from 32.2 to 25.8 mg KOH/g for SB and from 33.5 to
 600 24.2 mg KOH/g for OH with increasing the pyrolysis temperatures. The increment of
 601 pyrolysis temperature improved the viscosity from 47.8 to 23.7 mm²/s for SB and from
 602 38.1 to 35.3 mm²/s for OH. The TCR oil would require further upgradings (blending or
 603 hydrotreatment) before its application in vehicle engines. The aqueous phase of TCR
 604 liquid can be used to improve the TCR hydrogen content for the hydrotreatment
 605 process. The HHV of SB and OH biogas did not change significantly with increasing
 606 the pyrolysis temperatures. The OH biochar presented similar carbon content and
 607 calorific value, but SB biochar did not behave similarly with increasing the pyrolysis
 608 temperatures. The highest energy density of the biogas and biochar was 17.3 and 29.7
 609 MJ/Kg respectively, which indicates the potential for generation of heat and power
 610 through CHP engines. For the mass balance, the increase of pyrolysis temperature
 611 produced more syngas and less bio-oil and char. From 92.8 to 96.8 wt% of the
 612 feedstock was converted into valuable TCR products. The energy losses represented
 613 between 7.7 and 11.4% of the total energy yield and these can be minimised by
 614 applying efficient isolation and increasing the reactor scale. TCR technology proved its
 615 efficiency in terms of mass balance and energy yield in this study. Overall, TCR was
 616 shown to be a promising future route for the valorisation of lignocellulosic biomass in
 617 order to produce energy vectors.

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622

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Valorisation of lignocellulosic biomass investigating different pyrolysis temperatures

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Highlights:

- Sugarcane bagasse (SB) and oat hulls (OH) were successfully converted into valuable products (bio-liquid, syngas, and biochar) using the TCR reactor.
- The fuel properties of the TCR oil improved with the increment of the pyrolysis temperature (higher HHV and lower water, acidity, viscosity and density content).
- TCR technology proved its efficiency in terms of mass balance and energy yield.
- The chemical properties of the TCR products showed the potential to be used as energy vectors.