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Thermochemical conversion of agricultural wastes applying different reforming temperatures

João Santos^a, Miloud Ouadi^a, Hessam Jahangiri^{a*}, Andreas Hornung^{abc}

^a University of Birmingham, School of Chemical Engineering, Edgbaston, Birmingham, B15 2TT, UK.

^b Fraunhofer UMSICHT, Fraunhofer Institute for Environmental, Safety and Energy Technology, An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany.

^c Friedrich-Alexander University Erlangen-Nuremberg, Schlossplatz 4, 91054 Erlangen, Germany.

ABSTRACT

Lignocellulosic biomass is the most abundant renewable resource existing, and presently it is considered as a promising feedstock for the synthesis of green chemicals and biofuels for reducing transportation emissions and dependence on fossil fuels.

In this research, a TCR (thermo-catalytic reforming) reactor is used to transform lignocellulosic biomass into high quality bio-oils, biochar and syngas.

Sugarcane bagasse (SB) and oat hulls (OH) were processed in the TCR (2 kg/h) at 450 °C in the intermediate pyrolysis reactor (kept constant) and varying reforming temperature between 500-700 °C. This paper studies the conversion potential of SB and OH into sustainable bioproducts at different reforming temperatures.

TCR oils contained the highest calorific value of 34.9 MJ/kg from SB and 35.0 MJ/kg from OH at 700 °C which makes the bio-oil suitable to be applied as fuel for engines when compared to bio-oils produced from other pyrolysis technologies.

SB and OH pyrolysis gas at 700 °C contained higher H₂ yield 30.9 vol% and 31.6 vol%, respectively. The highest gas caloric values of SB and OH were 18.4 MJ/kg and 18.8 MJ/kg at the same reforming temperatures, respectively. Overall, the TCR results of SB and OH are promising for waste conversion into sustainable fuels.

Keywords: Thermo-catalytic reforming; pyrolysis; biofuels; 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 flow diagram; TGA, thermo gravimetric analysis; TCD, thermal conductivity detector; TAN, total acid number; GC-MS, gas chromatography mass spectrometry; HDO, hydro-deoxygenation.

* Corresponding author: Dr Hessam Jahangiri

Email address: h.jahangiri@bham.ac.uk

1. INTRODUCTION

Biofuels are considered one of the most efficient routes for reducing transportation emissions and dependence on fossil fuels [1, 2]. Among many possibilities of biofuel production and supply, fuels from biomass are interesting because they can potentially lead to significantly reduced CO₂ emissions and additionally this option reduces the amount of biogenic wastes and residues entering

landfill and incinerators [3, 4]. Additionally, the use of agricultural waste such as sugarcane bagasse (SB) and oat hulls (OH) is advantageous for the biofuels sector because it does not compete with food production and land use to grow energy crops [5]. Lignocellulosic biomass is the most abundant renewable resource existing and it contains a rich source in carbon. Presently, it is considered a promising feedstock for the production of sustainable fuels for the future [6].

Currently, SB after juice extraction is getting more popular for ecological and economic reasons owing to its high availability, low cost and applicability in different industrial areas such as biofuels, paper pulp and biochemicals [7, 8]. SB is mainly used for the generation of heat and power through combustion in boilers located in sugar mills for onsite consumption [9]. Nevertheless, this scenario is not energy efficient (only 26%), causes waste management issues at the plant and the ashes produced during the process are responsible for health hazards [10]. As an alternative, due to its high calorific value, SB can be used for biofuel production via thermochemical technologies making this residue a valuable raw material for pyrolysis processes [10]. In addition, SB is also utilised in more than forty applications such as animal feed, treatment of cancer (important and strong antioxidants from the acids compounds of lignin), boards and the production of sugar, pulp, furfural, paper and ethanol [8, 9].

Nowadays, OH is essentially used for combustion to generate energy due to its calorific value of 16 MJ/kg or for the production of high-value cellulose components [11]. This agricultural residue also presents a reasonable nutritive value and is used in the animal and human food industry [12]. In addition, there are some studies on the application of OH for ethanol production via chemical hydrolysis [13]. It is relevant to highlight the value of this waste in terms of local and annual availability and to explore its potential in the biofuels production market [11].

Pyrolysis is the thermal degradation of biomass and it involves a group of chemical mechanisms producing radical elements. This process is endothermic requiring a heat input and it works typically with temperatures (300-800 °C) compared to gasification (800-1200 °C) [14]. After moisture removal, pyrolysis is the first stage of gasification and combustion technologies and it is generally characterised into three main groups: slow, intermediate and fast [15]. Each applies different heating rates, temperatures and vapour/solid residence times to the feedstock, however a common parameter is that heating of the feedstock always occurs in low or oxygen free atmospheres [16]. Every type of pyrolysis process produces the same energy vectors (bio-oil, biochar and syngas) which are highly variable depending on the pyrolysis technique applied. Intermediate pyrolysis requires mild temperatures (around 400 °C), moderate heating rates (200-300 °C/min), efficient cooling system for the organic vapours to minimise thermal post-degradation, solid residence times in minutes with a short vapour residence time (seconds) [17] and produces relatively equal yields of all products solids, liquids and gas. Solids, liquids and vapours from intermediate pyrolysis have interesting chemical and physical properties that can be used as energy vectors. The biochar can be used as solid fuel in gasification and combustion plants to generate heat and power [18]. It can also be an optimum soil fertiliser/conditioner (depending on feedstock), which can sequester carbon from the soil [19]. The bio-oil presents a low level of oxygen, water, tars and viscosity, being a good fuel to combust in boilers, engines and other heat/power systems [20]. After upgrading, the intermediate pyrolysis oil can be blended with fossil fuels, biodiesel, bioethanol or combinations thereof and applied as a transportation fuel in conventional engines [21]. The gas fraction contains a reasonable amount of condensable organic vapours, which offer a good calorific value to be burnt in CHP systems [19].

The TCR process includes an intermediate pyrolysis step followed by a reforming treatment, where the intermediate pyrolysis gases and liquid phase are conveyed to the post reformer. The intermediate pyrolysis stage in the TCR technology occurs in an auger reactor with temperatures from 400 to 500 °C and solid residence times between 5 and 10 minutes [22, 23]. Intermediate pyrolysis products are transported to the auger reactor downstream, where the first reforming treatment is performed between the biochar and condensable vapours, causing a catalytic effect in all products and a consequent improvement of their physical and chemical properties [24]. In the reforming step, the intermediate pyrolysis gases and solid phase (char) are conveyed to the post reformer operating in a temperature range between 500 and 700 °C. The gas exiting the reactor is partially condensed generating different products: an organic oil phase, an aqueous phase and gas fraction. The main compounds of the synthesis gas produced are hydrogen, carbon dioxide, carbon monoxide, methane and a portion of hydrocarbons [24]. The novelty of TCR technology is the utilisation of char as the catalyst for upgrading pyrolysis liquids. However, a comparison of different reforming temperatures of OH has never been investigated in the TCR technology. Furthermore, the effect of SB and OH characteristics on TCR technology have not been compared at the same experimental conditions.

In this research, we report the impact of different reforming temperatures (500 °C, 600 °C and 700 °C) which are proposed to convert SB and OH into bio-oil, syngas and biochar with superior physical and chemical properties using a laboratory scale TCR reactor (2 kg/h).

2. MATERIALS AND METHODS

2.1 Raw Materials

SB used in the TCR experiments was supplied from Cosan Biomassa S/A (Brazil). 100 kg of SB was received and its moisture content was approximately 6 wt%. The Malt Miller Ltd (UK) provided 120 kg of OH with a moisture content around 14 wt%. As both feedstocks (SB and OH) received contained a moisture content <15 wt%, no drying was required before pelletisation and thermal conversion. Pelletisation was performed using a KKP 300 F (22 kWe) motorised pelletiser with a total capacity of 300 kg/h throughput (pellets formed were 6 mm diameter by 23 mm length). Prior to pelletising, the feedstocks were analysed in order to determine the proximate, ultimate, chemical compositions and higher heating value (HHV).

2.2 TCR Setup

The TCR bench scale reactor was constructed, installed and commissioned at the laboratory of Fraunhofer UMSICHT Institute, Germany with a capacity to process up to 2 kg/h of biomass. The entire plant works in the absence of oxygen using nitrogen supply as a purge gas and the temperature is measured through several K type thermocouples installed along the unit. The process flow diagram (PFD) of the experimental setup is shown in **Figure 1**.

The system comprises of a sealed hopper with capacity to hold a maximum of 5 kg of material, a horizontal auger screw reactor containing three different temperature zones with a length of 100 cm and a screw internal diameter of 8 cm followed by a vertical post reformer unit with 91 cm of height and 10 cm of diameter. The two reactors (auger screw and post reformer) are electrically heated and they are connected in series. The pyrolysis temperature was kept at 450 °C, while the reforming temperature varied between 500 and 700 °C. Intermediate pyrolysis is normally performed from 400 to 500 °C, however previous studies has proved 450 °C as the

temperature which can provide a better balance between the quality and quantity of the bio-oil produced. The plant was fed with 3.5 kg of pelletised SB and OH with a feeding rate of 1.4 kg/h. Before each run 500 g of biochar from previous runs were added to the reforming unit, permitting the upgradation of the organic vapours since the initial stage of the experiment.

In the condensing unit, condensable vapours from the post reformer are quenched by means of a shell and tube condenser designated scrubber within a u-tube condenser using a mixture of water and glycol from a chiller to maintain the temperature at -5 °C. Attached to the condensing unit, there is a vessel (10) to collect the bio-oil from the organic vapours condensed. Only the liquids from this vessel are analysed. Condensable vapours exiting the condenser are further quenched by means of an ice bath cooler using a vessel containing the bio-oil aqueous phase from the previous TCR runs. The aqueous phase has the function of acting as a solvent and it helps to collect the residual liquid and also to clean the vapours produced. As intermediate pyrolysis has a longer vapour residence time, it causes a better separation between the aqueous and organic phase of the pyrolysis oil.

The remaining vapours (non-condensable gases) are directed into the filtration unit composed of two wash bottles and a filter for aerosol and other contaminants capture. Then the permanent gases are directed to an online gas analyser/calorimeter for detection and gas totalisation before flaring.

All the TCR tests were made in duplicate and average values are reported.

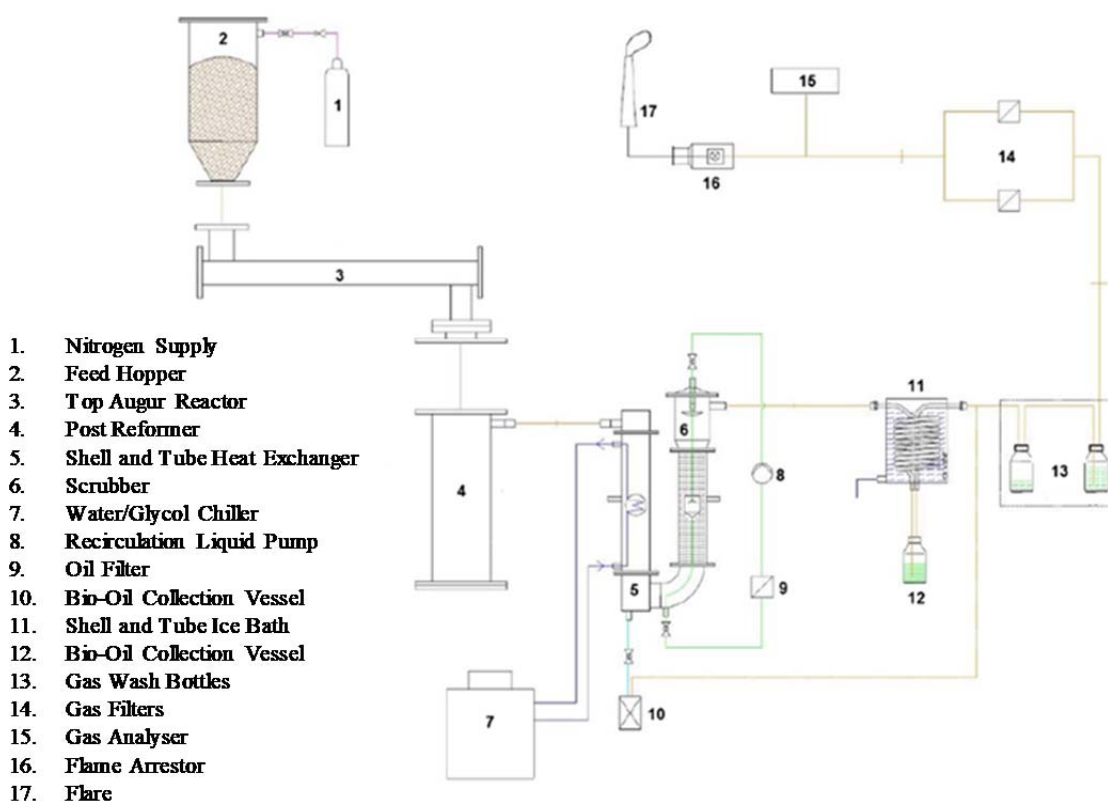


Figure 1. TCR (2 kg/h) process path flow diagram (PFD) [25].

2.3 Proximate Analysis

Total moisture content was determined by drying the sample at 105 ± 3 °C in a muffle furnace (CARBOLITE CWF1300) with an inert atmosphere for 3 h. The percentage of moisture was calculated based on the amount of mass lost (according to

ASTM E1756-08). The ash content was calculated using the same muffle furnace at 575 ± 25 °C for 5 h. The ash percentage was determined by weighting the amount of sample left in the muffle furnace after the heating process was completed (according to ASTM E1755-01). Volatiles and fixed carbon were determined by thermo gravimetric analysis (TGA) technique (NETZSCH TG 209 F1 IRIS). Approximately 15 mg of dried feedstock was put in a crucible and heated to 900 ± 10 °C (heating rate of 10 °C/min) in a nitrogen atmosphere (flow rate of 60 ml/min) and hold time for 15 min (according to BS EN 15148:2009). The fixed carbon was measured based on the amount of sample left in the crucible, while the volatiles represent the percentage of mass lost during the heating.

2.4 Ultimate Analysis

SB and OH dried samples were sent to an external accredited laboratory (Medac Ltd) to quantify the elemental content (C, H, N and S) of both feedstocks. The C, H, N analysis (with oxygen determined by difference) was carried out according to ASTM E777 and ASTM E778, and reported in wt%. The sulphur content was measured according to ASTM E775. The original analytical method (using the Thermo FlashEA[®] 1112 Elemental Analyser) was performed by complete oxidation of the solid (flash combustion), transforming all organic and inorganic compounds in combustion elements. The combustion gases produced crossed a chromatographic column using helium as the inert gas, and then the thermal conductivity detector (TCD) calculated the percentage of each element (C, H, N and S) providing an output signal to the system.

2.5 HHV

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

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

2.6 Products Characterisation

After the experiments, the bio-oil (only organic phase after separation by gravity), biochar and permanent gases were analysed to determine their chemical and physical properties. It is important to know the chemical composition of the TCR products to determine its applicability.

2.6.1 Oil and char ultimate analysis

C, H, N and S content of the SB and OH oil and char were calculated applying the same method as section 2.4 (Equation 1). Furthermore, the oxygen was determined by difference ($100 - \sum \text{CHNS} - \text{ash}$).

2.6.2 Oil and char ash content

Oil ash percentage was obtained following ASTM D482 standard. A muffle furnace at 775 °C was used to combust the carbonaceous compound obtained from carbon residue. Subsequently, the ash produced after the combustion was quantified to calculate the respective fraction of the initial bio-oil. The quantification of ash in the char was determined at 575 °C as described in section 2.3 according to ASTM E1755-01.

2.6.3 HHV

Channiwala et al. [26] fuels equation was used to calculate the HHV of the SB and OH oil and char:

2.6.4 Water content

Mettler Toledo V30 Compact Volumetric Karl Fischer titration was used to determine the water percentage of the SB and OH oils (ASTM E203). The value obtained of the total sample was revised to weight percent.

2.6.5 Total acid number (TAN)

ASTM D664 was the reference to calculate the oils acid number, using a Mettler Toledo V20 Compact titrator (potentiometric titration technique). The solvents toluene and isopropanol (50/50) served to dissolve the bio-oil. Thereafter a solution of KOH (0.1 N) was the reagent selected to titrate potentiometrically the bio-oil using a combination electrode.

2.6.6 Kinematic Viscosity

The kinematic viscosity of all bio-oil samples was determined with a Cannon–Fenske Routine glass capillary viscometer (ASTM D445). Throughout the analysis, the viscometer was set at 40 °C allowing passage of a specific pyrolysis oil quantity over the capillary. The viscosity final result is the multiplication of the oil travelling time (registered before) and the viscometer constant.

2.6.7 Density

The bio-oil density was measured at 22 °C using a glass hydrometer between 0.8 and 1.0 g/cm³ (ASTMD1298).

2.6.8 Gas chromatography mass spectrometry (GC-MS)

GC-MS was performed to detect the most abundant chemical compounds present in the SB and OH pyrolysis oil. Bio-oil samples were diluted in ethanol (1:10 ratio) and analysed with a gas chromatograph coupled with a mass spectrometer Shimadzu GCMS-QP2020. Chromatograph was equipped with a 30 m nonpolar, 0.25 mm inner diameter (i.d.), 0.25 µm film thickness DB-5ms (column name) and 1.5 m middle polar, 0.15 mm i.d., 0.15 µm film thickness VF17ms (column name) from Agilent. Helium with 5.0 purity was used as carrier gas in all experiments. The injection volume was set to 1 µL. The measurements were performed at a constant linear velocity (40 cm/min) of carrier gas. The temperature of the GC oven was programmed from 40 °C (3 min hold) to 320 °C (3 min hold) at 10 °C/min. The temperatures of the injector, MS-interface and MS was set to 250, 280 and 200 °C, respectively. The quadrupole MS detector was operated at a scan speed of 5000 Hz using a mass range of 35-500 m/z. Furthermore, solvent cut time was 3 min.

2.6.9 Gas analysis

The permanent gases produced were frequently analysed and measured using a gas analyser MGA 12, Dr Födisch Umweltmesstechnik according to EN 15267-3 standard test procedure. The gas analyser methodology was established on an infrared photometer (CO, CO₂ and CH₄), an electrochemical cell (O₂) and a TCD (H₂). The percentage not detected was presumed to be hydrocarbons which the levels were above of the analyser limits. The Union Instruments CWD2005 process gas analyser was used

to calculate the HHV of the gas fraction. The calibration of the gas analysers were performed prior to the experiments.

3. RESULTS AND DISCUSSION

3.1 Feedstock Characterisation

The ultimate/proximate analysis and HHV of the SB and OH pellets used in the TCR experiments are shown in **Table 1**. In general SB and OH pellets have a similar elemental composition and HHV. The HHV of SB (16.4 MJ/kg) is slightly higher compared to the OH (16.0 MJ/kg) due to its lower moisture and oxygen content and higher carbon content. However, the high calorific value of these lignocellulosic residues makes them valuable for biofuels production through thermochemical technologies [10]. Results from the ash content show a low level for SB and OH which are 4.0% and 2.4%, respectively.

Table 1. Feedstock characterisation.

	SB	OH
Ultimate analysis (moisture-free basis)		
C (wt%)	43.7	40.6
H (wt%)	5.1	6.0
N (wt%)	0.1	1.1
S (wt%)	0.61	<0.1
O (wt%)	46.5	49.9
Proximate analysis (dry basis)		
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

3.2 Bio-oil Analysis

The properties of the bio-oil organic phase of SB and OH at different reforming temperatures, after separation from the aqueous phase, are shown in **Table 2**. It is observed a lower oxygen level when higher reforming temperatures are applied. A low oxygen content leads to a better calorific value and reduces the instability of the oil deaccelerating the polymerisation reactions and the ageing effect of the bio-oil [27].

Consequently, the results show an increase in carbon content and HHV when the post reformer reaches higher temperatures for both feedstocks. The HHV of SB and OH increased from 31.1 MJ/kg to 34.9 MJ/kg and from 33.0 MJ/kg to 35.0 MJ/kg, respectively. Comparing the HHV value of the bio-oil for all experiments with the original feedstock (16.4 and 16.0 MJ/kg for SB and OH, respectively), the potential of the TCR technology in valorising the energy density of biofuels per unit volume is recognised.

The present work at 500 °C (reforming temperature) obtained significantly better results in terms of HHV and water content compared to the fast pyrolysis process using the same biomass (SB) and similar pyrolysis temperatures (around 450 °C), increasing the quality for fuel applications. Pattiya et al. [28] and Islam et al. [29] produced SB fast pyrolysis oil (at 430 °C and 475 °C, respectively) containing 31.1 wt% and 39.10

wt% of oxygen and 11.7 wt% and 11.6 wt% of water with calorific value of 26.7 MJ/kg and 23.5 MJ/kg, respectively.

Fast pyrolysis leads to lower thermal cracking of the bio-components, while in intermediate pyrolysis, higher thermal cracking occurs, resulting in less tar formation and general optimisation of the process [30]. Additionally, the benefits of mixing biochar with fresh biomass were proven via intermediate pyrolysis. The effect of char recycling is the novelty of this reactor type creating an additional catalytic effect in the process. This leads to a better quality pyrolysis oil when compared to commercial bio-oils from fast pyrolysis due to oil formation with lower molecular weight (mainly aromatics such as benzene, toluene and ethylbenzene and olefins) increasing the calorific value of the bio-oil [31, 32].

Neumann et al. [17] reported the same trend when they increased only the reforming temperature through TCR technology. With the increment of temperature his work show an improvement of the bio-oil properties such as less water and oxygen, more carbon content and better HHV.

Low nitrogen and sulphur contents shown are associated with low NO_x and SO_x emissions when the pyrolysis oil is combusted. Moreover, small portions of these two compounds can minimise engine wear and corrosion due to its strong acidity level [21]. OH bio-oil contains higher sulphur content compared to SB oil which makes the OH liquid less attractive in combustion applications.

The ash content was $<0.001\%$ for all the experiments. It is crucial to have a bio-oil with a low ash composition due to the problems related to engine performance such as blocking, corrosion, deposition and erosion of the fuel line, injectors and fuel pump [33].

Concerning water content, lower reforming temperatures showed higher percentages which give lower ignition and combustion temperatures in the cylinders and subsequently lower NO_x emissions [32]. The water content of SB and OH were 4.7 (wt%) and 4.8 (wt%) at 500 °C, respectively. However, when the pyrolysis oil contains less water the energy density is higher. Thus, it is more susceptible to blend with fossil based fuels due to a better miscibility and there are less issues separating the organic phase from the aqueous one [34]. Additionally, TCR runs decreased the oxygen present in the pyrolysis oil from the initial feedstock favouring the properties and the stability for fuel applications [35].

The TAN of SB and OH oil decreased with higher reforming temperatures. The TAN of SB and OH decreased from 27.7 mg KOH/g (at 500 °C) to 15.6 mg KOH/g (at 700 °C) and from 33.0 mg KOH/g (500 °C) to 35.0 mg KOH/g (700 °C), respectively. The existence of phenolics in the oils plus the water content may justify the high acid number of the pyrolysis oil at lower reforming temperatures found in this work [25]. This can be reduced by mixing the bio-oil with biodiesel or other alkaline fuels.

The present study points to higher viscosity with lower reforming temperatures. At higher reforming temperatures the organic vapours have a more efficient cracking producing lighter chemical compounds causing a lower viscosity level. For that reason, the best results were achieved at 700 °C (12.1 and 17.8 mm^2/s for SB and OH bio-oil, respectively). A low viscosity level would be beneficial to the flow characteristics and consequently results in complete pumping and combustion creating a better engine power with reduced blockages [25]. A bio-oil with a reasonable viscosity content is beneficial for the prevention of internal leakages located in the fuel pump and line, increasing the brake power and the lubricity. On the other hand, a bio-oil containing high viscosity limits the fuel flow and favours engine blockages causing incomplete combustion and engine power loss [36].

Density is a significant characteristic for the determination of the consumption rate of the pyrolysis oil and it is associated with the engine performance in terms of fuel injection time and fuel spray penetration in the cylinder [37]. The density of the SB and OH bio-oil did not change significantly with increasing the post reformer temperatures. It is reported that fuels with lower density led to better combustion and more stable engine operation [36].

In comparison to biodiesel, the heating value of bio-oil from SB and OH on average at 700 °C was very close to the measured heating value of this fuel (37.0 MJ/kg). The TCR oil was found to be satisfactory, however this is lower than fossil based diesel (42 MJ/kg). The difference between pyrolysis liquid and diesel is related to the higher oxygen content of biomass-derived fuels, due to the presence of certain compounds such as carboxyl hydroxyl, aldehyde, ether and carbolic groups [38]. The oxygen content of OH was slightly higher with 8.4 wt% for biodiesel, but almost 10 times higher than the diesel (1.0 wt%). Regardless of a modest oxygen level in a liquid fuel requires less air for combustion and benefits the emissions in engines, the SB/OH bio-oil and biodiesel present lower combustion power due to the higher oxygen amount in their chemical composition [39]. SB and OH trials contain more water content than biodiesel (0.37 wt%) and diesel (0.05 wt%) attributed to the higher amount of oxygen in the bio-oil.

Consequently, the HHV of the pyrolysis liquid is less attractive as an energy vector. The acid number found in this work is relatively high compared to biodiesel (0.49 mg KOH/g) and diesel (0.03 mg KOH/g). This may be caused by the water content of the SB/OH oils and a chemical composition rich in phenolics. In general, a high acid number is not suitable for engine applications as it causes corrosion and damage to fuel system components [27]. Results from the viscosity show a SB oil at 700 °C (12.1 mm²/s) with more than the double of the value of the biodiesel (6.0 mm²/s) and diesel (5.5 mm²/s). A reasonable viscosity is positive to lubricate the engine system reducing mechanical wear, however is harmful to the flow characteristics provoking engine power loss and inefficient combustion [21]. In terms of density, SB/OH bio-oil has higher values when compared to biodiesel (880 kg/m³) and diesel (850 kg/m³). The existence of more oxygenated compounds in the pyrolysis oil causes a liquid denser due to the presence of higher weight molecules. When a bigger mass of dense liquids are injected in the system, the heating process of the oils is not so efficient affecting the performance of the engine [37].

In conclusion, TCR oil from SB and OH indicated some positive aspects to be applied as fuel for engines when compared to other pyrolysis technologies as fast pyrolysis. It demonstrated sufficient quality to be burned in CHP engines, boilers, combustors or similar applications. However, some of the physical and chemical properties may affect the performance and the lifetime of the engine contrasting with the utilisation of the biodiesel and diesel. Therefore, to be used as a transportation fuel or blended with fossil fuels, it is necessary to submit this bio-oil to a hydro-deoxygenation (HDO) upgrading treatment. Moreover, the pyrolysis liquid is highly miscible with diesel and biodiesel which can improve the characteristics of the fuel alleviating some negative aspects during the operation of the engine [35].

Table 2. SB and OH bio-oil characterisation at different reforming temperatures (pyrolysis Temperature = 450 °C).

Reforming Temperature (°C)	SB			OH		
	500	600	700	500	600	700

<u>Ultimate analysis</u>						
C (wt%)	71.3	74.6	77.2	72.2	77.4	78.8
H (wt%)	7.1	7.4	8.0	8.1	7.5	7.2
N (wt%)	0.69	0.56	0.54	1.9	2.7	2.5
S (wt%)	0.10	0.10	0.18	0.68	0.76	0.77
O (wt%)	20.8	17.4	14.1	17.1	11.7	10.7
<u>Fuel Properties</u>						
HHV (MJ/kg)	31.1	33.0	34.9	33.0	34.6	35.0
Ash (wt%)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Water (wt%)	4.7	2.2	1.9	4.8	3.9	2.3
TAN (mg KOH/g)	27.7	17.3	15.6	40.5	21.4	17.7
Kinematic Viscosity (mm ² /s)	24.9	13.7	12.1	36.5	35.4	17.8
Density (kg/m ³)	1062	1060	1059	1074	1082	1072

3.3 GC-MS Analysis of Bio-oil

Figure 2 and **3** show the chromatograms of the bio-oils at different reforming temperatures, where the 16 most important and abundant peaks were identified. The organic fraction of SB and OH bio-oils were analysed through GC-MS and the results are demonstrated in **Table 3**.

Generally, the pyrolysis oils are a mix of complex chemical compounds containing carbons chains between C5 and C15 [40]. It can be analysed that the SB and OH bio-oils are mostly composed of aromatics and oxygenated organic compounds such as phenols and furans. Aromatics and phenols are collectively the biggest fractions of the pyrolysis liquids and furans are the less abundant compound.

Benzene, toluene and naphthalene abundance increased significantly with increasing the reforming temperature. Naphthalene was the most abundant aromatic compounds within the SB and OH oils at 700 °C with a relative abundance of 14.3% and 7.1%, respectively. The increase of aromatics (such as benzene, toluene and naphthalene) could improve the fuel properties.

Phenols are derived from lignin while furans from hemicellulose and its presence in TCR liquids proves that both compounds were efficiently thermally degraded during the pyrolysis conversion [41]. Phenols and furans are all flammable organics, however, phenols are also one of the reasons for high acidity of the oils [18]. This can explain the high acid number found in SB and OH bio-oils (**Table 2**). Inversely, aromatic hydrocarbons may guarantee good combustibility of the oil for application as energy fuels which can improve blending capabilities with fossil fuels [42].

Higher temperatures in the post reformer generate less furans, however, an increment of phenols and aromatics was observed. After the lignin degradation in the auger pyrolysis reactor secondary reactions favoured the formation of phenols when higher reforming temperatures were applied. Additionally, the presence of biochar in the reformer might help to stimulate the production of phenols breaking more complex compounds.

When the reforming temperature was set at 700 °C, a significant reduction of furans in the bio-oil was observed. Interestingly, the same trend occurred in the phenols yields when compared to the pyrolysis oils produced at lower reforming temperatures.

One of the explanations can be the occurrence of secondary reactions such as deoxygenation which converted phenols to aromatics [43]. Moreover, the increase of aromatics in the bio-oil at 700 °C is evident in **Table 3**. It is visible that the variation of reforming temperature has a substantial effect on the properties of the pyrolysis liquid changing its chemical composition and quality.

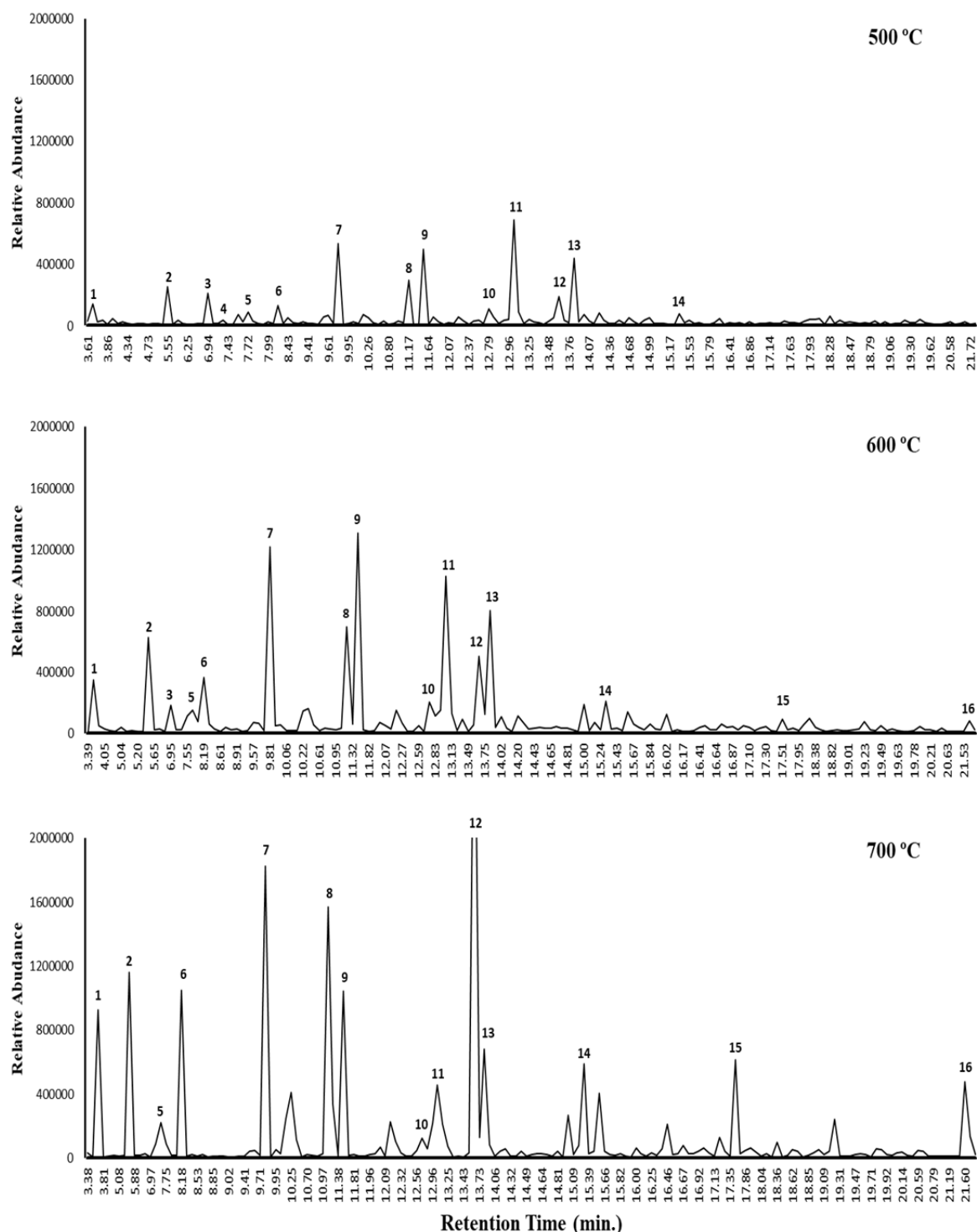


Figure 2. GC-MS chromatograms of SB bio-oil and compounds detected at 450 °C (reactor temperature) and different reforming temperatures (500, 600 and 700 °C).

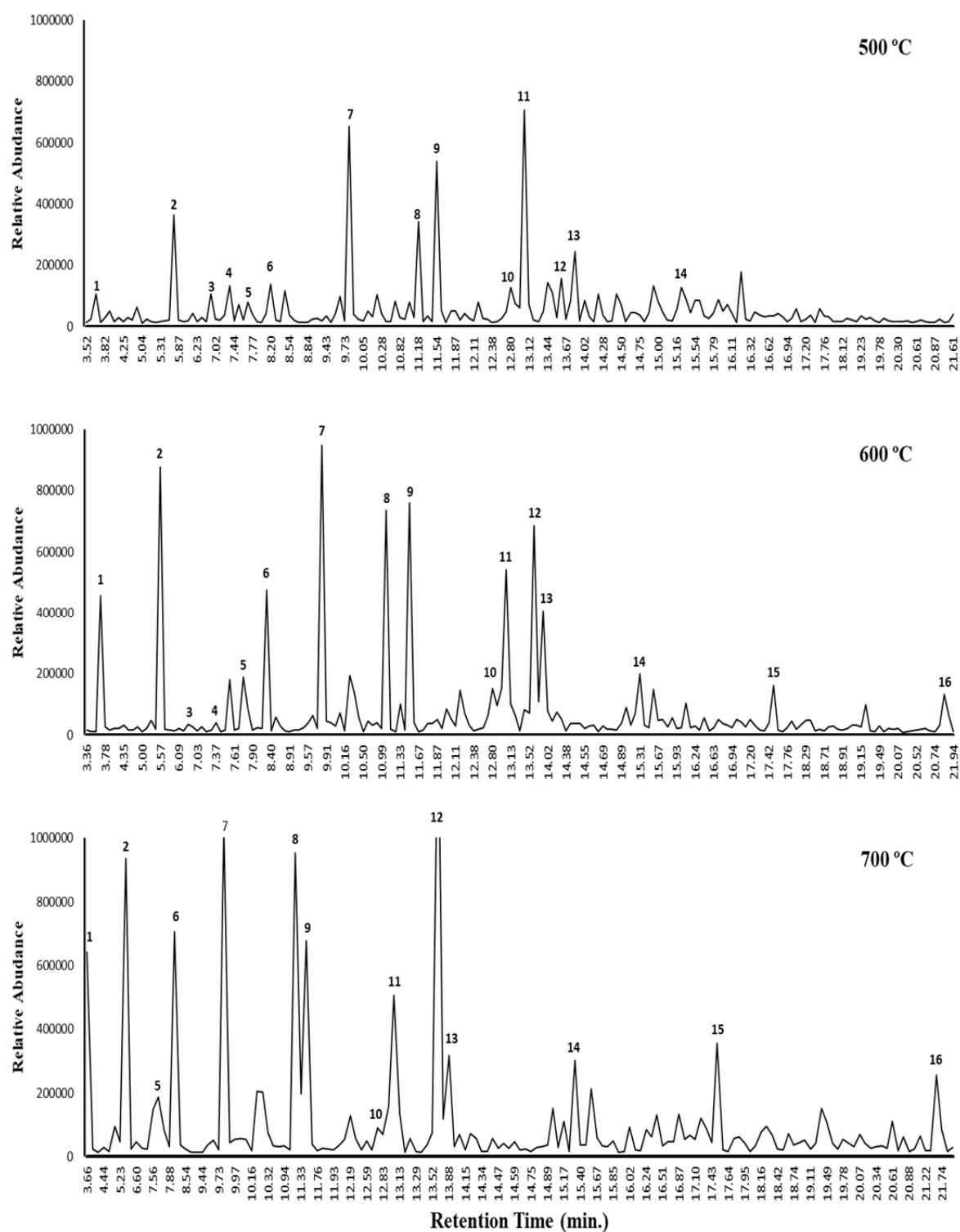


Figure 3. GC-MS chromatograms of OH bio-oil and compounds detected at 450 °C (reactor temperature) and different reforming temperatures (500, 600 and 700 °C).

Table 3. Compounds detected and identified by GC-MS of the SB and OH bio-oil at different reforming temperatures (pyrolysis temperature = 450 °C).

				SB			OH		
Reforming Temperature (°C)				500	600	700	500	600	700
#	Group	Chemical Compound	Conc. (%)				Conc. (%)		
1	Aromatic	Benzene	1.6	2.2	3.9		0.93	3.2	3.2
2	Aromatic	Toluene	2.9	3.99	4.9		3.2	6.1	4.6
3	Furan	Furfural	2.4	1.2	-		0.93	0.19	-
4	Furan	2-Furanmethanol	0.39	0.16	-		1.2	0.29	0.13
5	Aromatic	Benzene, 1,3-dimethyl-	1.0	0.9	0.9		0.71	1.3	0.93
6	Aromatic	1,3,5,7-Cyclooctatetraene	1.5	2.3	4.4		1.2	3.3	3.5
7	Phenol	Phenol	6.1	7.6	7.7		5.7	6.6	5.1
8	Phenol	Phenol, 2-methyl-	3.3	4.4	6.6		3.0	5.2	4.7
9	Phenol	Phenol, 3-methyl-	5.6	6.9	4.4		4.7	5.3	3.4
10	Phenol	Phenol, 2,4-dimethyl-	1.3	1.3	0.52		1.1	1.1	0.44
11	Phenol	Phenol, 4-ethyl-	7.8	6.4	1.9		6.2	3.8	2.5
12	Aromatic	Naphthalene	2.1	3.2	14.3		1.4	4.8	7.1
13	Furan	Benzofuran, 2,3-dihydro-	5.0	5.1	2.9		2.2	2.8	1.6
14	Aromatic	Naphthalene, 1-methyl-	0.88	1.3	2.5		1.1	1.4	1.5
15	Aromatic	Acenaphthylene	0.34	0.60	2.6		0.51	1.1	1.8
16	Aromatic	Phenanthrene	0.31	0.16	2.0		0.37	0.45	1.3

3.4 Gas Analysis

The gases detected from gas fraction (**Table 4**) were H₂, CH₄, CO, CO₂ and C_xH_y. There is no oxidation-reduction reaction during this process due to the total absence of oxygen.

At the lowest reforming temperature (500 °C) CO₂ is the main component for both feedstocks (28.8 vol% and 25.6 vol% for SB and OH, respectively). CO₂ production is associated to the decomposition of hemicellulose and cellulose due to the thermal cracking of carbonyl and carboxyl groups [44]. It was noticed a reduction of CO₂ volume when the reformer reached higher temperatures attributed to water gas and boudouard reactions converting CO₂ to CO and H₂. The higher presence of CO₂ rather than H₂ in the syngas is the main reason for a lower HHV at 500 °C.

The pyrolysis gas was composed mostly of H₂ and CO at higher reforming temperatures. When there is a rise of temperature, the degradation, devolatilisation and thermal cracking of feedstock are promoted. Simultaneously, secondary reactions such as decarboxylation, dehydrogenation, decarbonylation and deoxygenation stimulate the production of H₂ and CO [45]. It can be noted that the increase of H₂ in the syngas causes a superior HHV. Accordingly, the OH pyrolysis gas at 700 °C is the one containing higher H₂ yield (31.6 vol%) and consequently the better caloric value (18.8 MJ/kg).

The non-detectable gas fraction can be the presence of hydrocarbons such as propane and ethylene which could not be read by the gas analyser. Light hydrocarbons

and short-chain compounds result in the fragmentation and disintegration of the linkage between the polymer and monomers [46]. This may be a cause of the reduction in C_XH_Y components and density when the reforming temperature is increased.

Ouadi et al. [32] and Neumann et al. [17] used the intermediate pyrolysis reactor to process de-inking sludge and digestate at 450 °C. The existence of the reforming unit in the present study affected drastically the H_2 yield and consequently the HHV. Comparing the lowest HHV of this section of runs shows the significant difference between 15.3 MJ/kg (OH at 500 °C) and 6.2 and 9.7 MJ/kg for de-inking sludge and digestate, respectively [17, 32]. In the reforming stage, the biochar works as a catalyst and favours the deoxygenation reactions resulting in the formation of H_2 and improving the calorific value [47]. Moreover, when the organic vapours are in contact with the biochar at high temperatures different types of chemical reactions occur (water gas shift reaction, steam reforming reaction and hydrogasification reaction) increasing the yields of fuel gases such as H_2 and CH_4 [17, 35].

In the present work, the increment of the reforming temperature increased the H_2 volume but reduced the amount of CO_2 and the density of the syngas. The same trend was observed in the work of Neumann et al. [17] using digestate as a feedstock.

The pyrolytic gas produced in this section at high reforming temperatures contains a reasonable amount of combustible gases (H_2 , CO , CH_4 and other hydrocarbon gases) and HHV to be used as an energy vector. One of the applications could be the generation of heat and power through CHP units or burnt as a fuel onsite to meet the thermal energy demands of the pyrolysis process.

Table 4. SB and OH permanent gas composition at different reforming temperatures (pyrolysis temperature = 450 °C).

Reforming Temperature (°C)	SB			OH		
	500	600	700	500	600	700
Component						
H_2 (vol%)	25.7	30.4	30.9	15.8	30.1	31.6
CH_4 (vol%)	13.5	9.6	10.2	7.0	5.8	6.9
CO (vol%)	20.2	18.5	23.6	25.5	21.2	25.2
CO_2 (vol%)	28.8	25.6	21.8	25.6	20.9	18.5
C_XH_Y (vol%)	2.3	2.0	1.4	2.7	2.4	1.5
Non-detectable (vol%)	9.5	13.9	12.1	23.4	19.7	16.5
HHV (MJ/kg)	15.9	17.0	18.4	15.3	18.0	18.8
Density (kg/m^3)	0.89	0.78	0.73	1.2	1.0	0.96

3.5 Char Analysis

The elemental composition of the biochar, ash and its energy content are represented in **Table 5**. Biochar is composed of fixed carbon and ash. Fixed carbon is the solid left after the extraction of volatiles, ash and moisture and is the combustible substance of biochar contributing for the increment of the calorific value. The SB and OH biochar contain more ash than the initial feedstock (4.0 and 2.4 wt%, respectively) since non-volatile inorganics always remain inside of the solid particle [48].

Results show an increment of the carbon content and HHV of SB when the reforming temperature is increased but carbon content and HHV of OH did not change significantly. At higher temperatures, the aromatisation reactions are favoured increasing the aromatic rings and subsequently the C-C bonds in the char [49]. This means more fixed carbon is in the biochar [50].

The fixed carbon and ash contents calculated for SB (17.2 and 4.0 wt%, respectively) and OH (26.4 and 2.4 wt%, respectively) feedstocks are also a reflection of the results presented in **Table 5**. OH biochar has a better HHV for all reforming temperatures due to the higher fixed carbon and lower ash content found in the original biomass.

SB biochars from this study presented a better energy density when compared to Mesa-Perez et al. [51] (14.2 MJ/kg) and Doumer et al. [52] (24.3 MJ/kg) works, which applied fast and slow pyrolysis in the conversion of the same biomass (SB). The extended residence time of the biochar in the reforming unit might cause a secondary cracking reaction producing coke and consequently a TCR char with more carbon and less water.

Neumann et al. [17] and Ahmad et al. [43] processed digestate and SB using the same technology (TCR) and heating the biomass with different reforming temperatures. Surprisingly, the HHV of the biochar decreased when they submit the feedstocks at higher reforming temperatures which is the opposite effect occurred in the present tests. However, above 600 °C there are more aromatisation reactions increasing the aromatic rings and consequently the carbon content of the biochar [49]. Therefore, the HHV of biochar should be higher and not lower when the reforming temperature is increased.

Comparatively to classic sub-bituminous coal with a carbon content of 73.9% and a HHV of 29.05 MJ/kg [53], this set of experiments got a very similar HHV excluding the SB char produced at 500 °C.

The char energy content is influenced by the reforming temperature used in the TCR and its valuable HHV can be useful for combustion in furnaces, gasifiers and boilers to generate heat and power [25]. The same char has other promising applications, such as soil amendment, carbon sequestration and fertiliser [54]. Another application of the char is the catalytic conversion, which is related to its surface properties and inorganic composition [55].

Table 5. SB and OH biochar characterisation at different reforming temperatures (pyrolysis temperature = 450 °C).

Reforming Temperature (°C)	SB			OH		
	500	600	700	500	600	700
Ultimate analysis						
C (wt%)	70.3	77.0	78.2	79.3	81.0	78.6
H (wt%)	1.6	1.5	1.3	2.0	1.9	1.8
N (wt%)	0.39	0.34	0.43	1.1	1.0	1.0
S (wt%)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
O (wt%)	11.6	2.1	1.1	5.7	5.1	5.3
Ash (wt%)	16.1	19.0	18.8	11.8	10.8	13.2
HHV (MJ/kg)	24.9	28.0	28.4	29.2	29.7	28.7

3.6 Mass Balance and Energy Yield

Figures 4 and **5** indicate the mass balance and the energy yield for the SB and OH products obtained during the TCR experiments. Lower reforming temperatures enhance the formation of bio-oil and char minimizing the percentage of gas. The decomposition of hemicellulose and cellulose occurs at lower temperatures (220-350 °C and 315-400 °C, respectively) promoting depolymerisation and devolatilisation of volatiles resulting in better yields for bio-oil production [49]. Low temperatures also help for the non-oxidation of the carbonaceous substance and causes the condensation

of benzene rings through charring reactions stimulating the formation of biochar [56]. Moreover, it was found that low pyrolysis temperatures are beneficial for cross-linking reactions causing higher levels of biochar production [57]. The highest value for pyrolysis oil and char were obtained at 500 °C for both feedstocks. SB trial was the most productive one in terms of char formation (26.6 wt%), while OH run presented the highest value for bio-oil production with 7.6 wt%. Due to the low yields of organic oil, the application of this pyrolysis product is more suitable for onsite energy production (power and heating needs of the plant) using small devices such as boilers, combustors and CHP engines.

The rise in the reforming temperature reduced the amount of condensate (bio-oil and aqueous phase) and biochar, however it increased the formation of gas resulting in the decomposition of the biochar at higher temperatures in the post reformer. When the temperature is higher than 500 °C, the main reactions taking place are dehydrogenation, cracking, aromatisation and volatilisation [58]. Gas production is mostly dependent on cracking and volatilisation reactions, specifically above 575 °C where complex volatile compounds are reduced to lighter molecules such as CH₄, CO₂ and CO [47]. In addition, char acts as a catalyst at higher temperatures and enhances the deoxygenation reaction resulting in the formation of CO, CO₂ and H₂O [47]. Secondary degradation reactions also occur at higher temperatures decreasing the liquid amount in order to maximise the gas yield. The highest gas yields were found in the conversion of SB and OH at 700 °C where the results obtained were 50.4 and 53.2 wt%, respectively.

A good mass balance was obtained for all TCR experiments performed in this section. The biomass conversion into products was higher than 93 wt% and only 3.2 wt% was not converted in the best scenario case (OH at 500 °C). These results show the potential of the TCR process as an efficient technology for conversion of biomass into valuable products. The losses can be justified by errors during the weight measurements, the bio-oil left in the condensing unit after each run which is hard to determine during cleaning and escaping gases not detected by the gas totaliser. For both biomasses, it was noticed an increment of mass losses when the reforming temperature was raised. Higher reforming temperatures produce more syngas increasing the amount of escaping gases not measured through the gas totaliser.

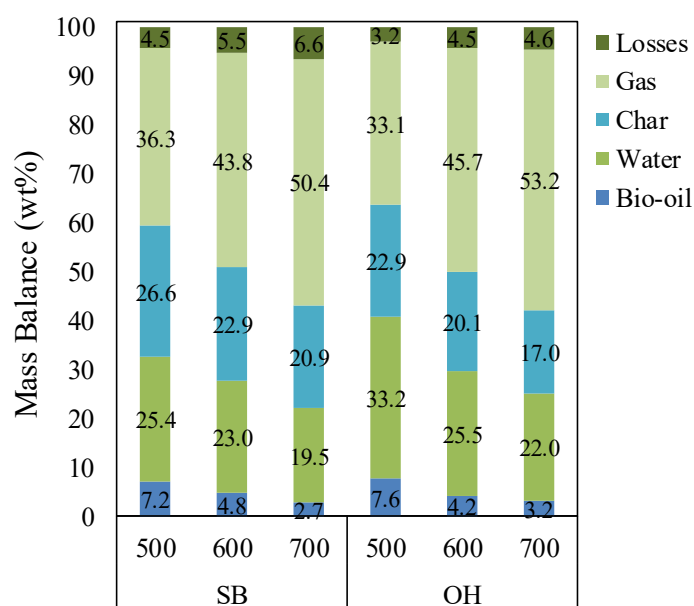


Figure 4. Mass balance of SB and OH trials at different reforming temperatures (pyrolysis temperature = 450 °C).

The energy yields are calculated as the chemical energy transferred from the feedstocks to the TCR products. The biggest energy fraction for the lowest reforming temperature (500 °C) was the biochar with 40.4% for SB and 41.7% for OH. At 500 °C, the energy yield of bio-oil and biochar from OH run were higher compared to SB trial. This may be explained due to the higher calorific value of the OH bio-oil and biochar observed in **Table 2** and **5**.

With reforming temperatures at 600 °C and 700 °C, the main energy vector was the pyrolysis gas for both feedstocks. The energy yields of the permanent gases at 600 and 700 °C were indicated as 45.4 and 56.5% for SB and 51.1 and 62.3% for OH, respectively. OH runs at 600 and 700 °C presented better results which can be attributed to the higher amount of syngas produced and better HHV of the gas fraction (**Table 4**).

In the energy yield, the experiments at 500 °C in the post reformer were less efficient with 10.9 and 11.1% of losses for SB and OH, respectively. Applying higher reforming temperatures (600 °C and 700 °C) the energy losses were 5.8 and 1.7% for SB and 2.7 and 0.3% for OH, respectively. It is evident a raise in energy losses when the reforming temperature is decreased. The higher amount of bio-oil produced at lower reforming temperatures can be the key to this trend. As we have more bio-oil in the system, more bio-oil is not extracted and remains in the condensing unit due to the difficulty of collecting all the liquid produced. Additionally, during the separation of the organic and aqueous phase of the pyrolysis liquid some organic oil is left in the aqueous phase to avoid the contamination of the bio-oil submitted to characterisation. Adding these technical issues, it is unavoidable to waste some energy content from the organic phase of the bio-oil affecting the energy yield of the process.

Heating SB and OH at 700 °C converted 98.3 and 99.7% of the total energy from the feedstocks into the chemical energy of the products, demonstrating the energy efficiency of the TCR technology. Nevertheless, the system energy losses can be reduced with better and efficient isolation and also by increasing the scale of the reactor.

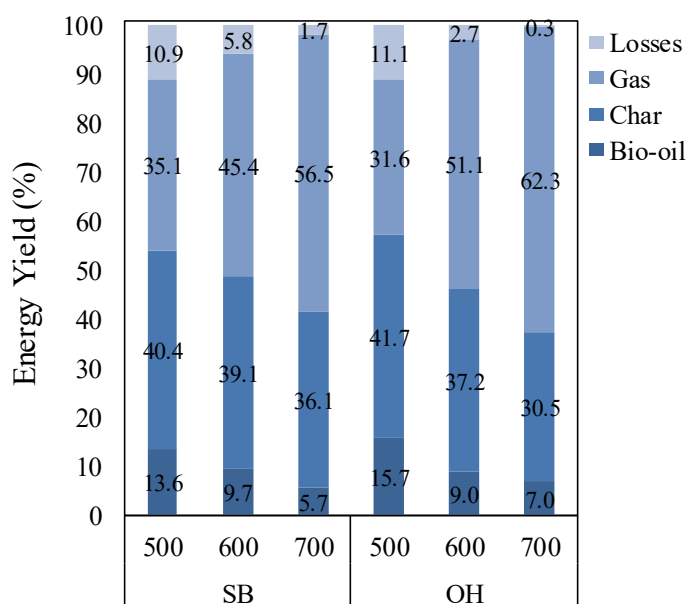


Figure 5. Energy yield of SB and OH trials at different reforming temperatures (pyrolysis temperature = 450 °C).

4. CONCLUSIONS

The increment of reforming temperature from 500 °C to 700 °C had a substantial effect on the properties of the TCR products changing its chemical composition, quality and quantity. The fuel properties of the pyrolysis liquid were improved with the reduction of the water, acid number, viscosity and density. For the bio-oil, the amount of carbon increased, while the oxygen content decreased thus improving the calorific value to 34.9 MJ/kg and 35.0 MJ/kg at 700 °C for SB and OH, respectively. Naphthalene was the most abundant aromatics within the SB and OH oils at 700 °C with a relative abundance of 14.3% and 7.1%, respectively.

Higher reforming temperatures resulted in higher hydrogen yields and better HHV. The hydrogen content of SB and OH reached 30.9 vol% and 31.6 vol% at 700 °C, respectively. The biochar also improved its quality in terms of carbon, oxygen and energy density when the reforming temperature was increased from 500 °C to 700 °C.

In terms of product distributions, lower reforming temperatures stimulated the formation of bio-oil and biochar while syngas production was more intense at higher reforming temperatures. TCR technology presented a high efficiency in terms of mass balance and energy yield. In all trials, the biomass conversion into valuable products was higher than 93 wt%. For the energy yield, it was possible to observe SB and OH runs at 700 °C converting 98.3% and 99.7% of the total energy from the feedstocks into the chemical energy of the products.

TCR oil from SB and OH indicated some positive aspects to be applied as fuel for engines when compared to other pyrolysis technologies. Moreover, TCR oil demonstrated sufficient quality to be burned in CHP engines, boilers, combustors or similar applications. The pyrolytic gas produced in the TCR contains a reasonable amount of combustible gases (H₂, CO, CH₄ and other hydrocarbon gases) and HHV to be used as an energy vector (generation of heat and power) through CHP units or burnt as a fuel onsite to meet the energy demands of the pyrolysis process. TCR biochar contains a reasonable HHV which can be used for combustion in furnaces, gasifiers and boilers to generate heat and power. The same char has other promising applications such as soil amendment, carbon sequestration, fertiliser and activated carbon.

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