SOUTHERN BRAZILIAN
JOURNAL OF CHEMISTRY

INFLUENCE OF FAST PYROLYSIS WITH TEMPERATURE ON GAS, CHAR AND BIO-OIL PRODUCTION

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Received 12 May 2017; received in revised form 30 June 2017; accepted 14 August 2017

ABSTRACT

Rice husk is among the products that stand out in use, and it is used as an alternative source of energy. The use of rice husk as biomass in the feeding of pyrolytic reactors for power generation and chemical products can reduce the environmental problem destination of this waste. The advantages of this process are in the proper disposal of this waste and energy generation. Fast pyrolysis of the rice husk was carried out in temperatures of 400-600°C. This work aims to evaluate the influence of temperature on yield and product composition of the gas, bio-oil, and char. The yield of bio-oil proved to be efficient (62 wt.% at 450°C) due to the high heat transfer and mass, as well as the residence time in the reactor. In addition, bio-oil production decreases slightly due to increased gas yield (1 to 15 wt.%) as the temperature increases in the range of 400-600°C, with the composition being severely affected, i.e., The concentration of CO increases and that of CO_2 decreases. In addition, a slight increase in the concentration of CH_4 and C_2 -C_4 hydrocarbons occurs with increasing temperature. The yield of char at 400°C and 600°C was 41.14-34.77 wt.%, respectively, corresponding to a decrease of 16 wt.%. The char obtained is of low heating value but has good features for the production of active carbons and amorphous silica. These results demonstrate the efficiency and optimization of the fast pyrolysis of rice husk, in order to obtain bio-oil and char.

Keywords: *Biomass, Pyrolysis Conditions, Renewable Energy Potential, Thermal Treatments, Biofuel.*

1. INTRODUCTION

The shortage of fossil fuels has awakened the scientific community for the use of biomass as a source of renewable energy (Carpenter *et al.,* 2014; Demirbas, 2011). A fundamental characteristic of biomass is the possibility of being used as bases in the generation of energy (Mohan *et al.,* 2006).

Rice husk (RH) as biomass energy generation may reduce the environmental problem of the destination of this waste, besides contributing to reducing the use of fuels derived from petroleum. RH discarding is a serious environmental problem due to its properties (difficult decomposition), its constitution (highly phenolic) and the enormous quantity of this material generated annually (Diniz, 2005; Gómez, 2002). The chemical composition of the RH varies according to the type of soil and the main components are cellulose, hemicellulose, lignin, and minerals (Mullen *et al.,* 2009; Moens *et al.,* 2009; Khan *et al.,* 2009; Boateng *et al.,* 2008; Petrus and Noordermeer, 2006).

The inorganic residue contains on average 94-97 wt.% of silica in the hydrated form, totaling from 10 to 30 wt.% of the total husk (Mullen and Boateng, 2009; Boateng *et al.,* 2008). Cellulose is the main component of the cell wall of vegetables and the most abundant organic compound in nature. It consists of a polymer formed of glucose units, through chemical bonds involving oxygen atoms (Huber *et al.,* 2006). The denomination of hemicellulose comprises the non-cellulosic polysaccharides present in the biomass. Generally, they are polymers constituted by monosaccharides of 5 carbon atoms (pentoses) and are therefore known with pentosans. The most frequent component in the pentosan composition is xylan formed by anhydroxylose units (Mullen and Boateng, 2009; Huber *et al.,* 2006). Lignin is a macromolecule chemical that is totally different

DOI:10.48141/SBJCHEM.v25.n25.2017.6_2017.pdf

from cellulose and hemicellulose. The lignin can be represented as a heterogeneous and amorphous polymer whose repeating structural unit is a phenyl propane unit, substituted at various positions on the benzene ring. (Mullen and Boateng, 2009; Huber *et al.,* 2006).

Several conversion technologies (mechanical, biological and thermochemical) have been developed for the exploitation of RH in industry. Thermochemical conversion processes (combustion, gasification, and pyrolysis), the latter has been distinguished by the capacity to produce biofuels in different stages of incorporation. Pyrolysis is a process in which the RH is subjected to a temperature range of 450°C to 750°C in an inert medium. Solid (char), liquid (bio-oil) and gaseous (pyrolytic gas) products are obtained (Meesuk *et al.,* 2011). Bio-oil, a product of fast pyrolysis, can be used as a substitute to fossil fuels and raw material to produce chemicals (Delivand *et al.,* 2011). Fast pyrolysis is a process of thermal decomposition in the absence of oxygen or when the oxygen content is at an incomplete combustion level (Vitali *et al.,* 2013; Zhang *et al.,* 2010). In this thermal conversion process, up to 70% of the biomass energy can be converted into a liquid product (Anex *et al.,* 2010). Great efforts were made to develop new processes for the conversion of biomass into bioenergy (Brown *et al.,* 2013; Bridgwater, 2012).

Fast pyrolysis is a well-studied technology that is reaching an early stage marketing (Jiang and Ellis, 2010; Effendi *et al.,* 2008). The aim of this work is to use rice husk as raw material for the production of bio-oil by fast pyrolysis process in a nitrogen atmosphere, considering a large amount of this material in the form of waste from the world food industry.

Experiments were performed in a tubular furnace and a fixed bed reactor. The chemical composition of the gases and bio-oil was determined using gas chromatography coupled to mass spectrometry. For gas sampling, solid phase microextraction (SPME) was used with polydimethylsiloxane (PDMS)/polyacrylate.

2. MATERIALS AND METHODS

2.1. Raw material

RH was used as raw material, coming from a farm without pre-treatment. The proximate and ultimate analyses of RH are listed in Table 1. The analysis has been carried out in LECO elemental analyzers (CHNS-O) (FlashSmart - Thermo Scientific^{TM}) and thermogravimetric analyzer (TGA-1000 - NAVAS INSTRUMENTS^{TM}), respectively. The calorific value was measured in an isoperibolic calorimeter (C 6000 ISOPERIBOL PACKAGE 1/10 - IKA^{TM}). The chemical composition of ash (Table 2), including silica and major metal compounds, was determined by X-ray fluorescence (S6 JAGUAR EasyLoad – Bruker^{TM}).

2.2. Pyrolysis experimental procedure

The system consists of a vessel equipped with a vertical shaft connected to a piston placed below the bed of the material and allows the continuous feeding of up to 100 g/hour of RH. Nitrogen has been used as an inert gas with a flow rate of 20 L/min. The total height of the reactor is 42 cm, the conical section is 25 cm, and the angle of the conical section is 35°. The diameter of the cylindrical section is 15 cm, the bottom diameter is 2.5 cm, and the gas inlet diameter is 1.25 cm.

The volatiles products leave the reactor together with the inert gas and pass through a forced convection oven maintained at 300°C, which prevents the condensation of heavy compounds. In addition, the residence time of the generated vapors is in the range of seconds, avoiding the cracking of the vapors before their condensation. Thus, the liquid collected in the condenser is primarily the aqueous phase of the bio-oil, while the heavier compounds forming the organic phase are retained in the filters. To study the effect of the pyrolysis temperature on the characteristics of the product, the pyrolysis tests were performed at 400, 450, 500, 550 and 600°C. The tests were carried out in continuous mode feeding 1 g/min of biomass.

2.3. Product analysis

Volatiles leaving the reactor were analyzed with a gas chromatograph (Perkin Elmer^{TM}). The reactor output is diluted with an inert gas to ensure that all volatile products formed during pyrolysis enter the chromatograph and are analyzed. The liquid product identifications were performed in a gas chromatograph, and char has been characterized by means of elemental and proximate analysis and higher heating value.

3. RESULTS AND DISCUSSION

3.1. Product yields

The pyrolysis products were grouped into three different fractions: gas fraction, liquid (bio-oil) and char. The evolution with the temperature of the yields of these fractions (on wet basis) is shown in Figure 1.

Bio-oil is the main fraction of the product in all temperature ranges studied, with the maximum yield at 450°C. In general, as the pyrolysis temperature increases, we also observe an increase in the gas yield, due to the efficiency of the secondary cracking in the pyrolysis vapors. The drop in char yield becomes more pronounced between 400 and 450°C. The high yield of bio-oil obtained (62.10 wt.% at 450°C) shows the good performance of the fast pyrolysis of RH due to the high rates of heat transfer and mass, which promote devolatilization reactions, and the short residence times the volatiles, which minimize the cracking of these components. (Kabir and Hameed, 2017; Damartzis and Zabaniotou, 2017; Naqvi *et al.,* 2014; Alavrez *et al.,* 2014; Abu Bakar and Titiloye, 2013). The high char yield (41 wt.% at 400°C) is due to the high ash content in RH. The main responsible for this behavior of RH is in the textural properties, thin layers composed of cellulose, hemicellulose and lignin (Hossain *et al.,* 2017; Naqvi *et al.,* 2015; Yu *et al.,* 2016; Tripathi *et al.,* 2016; Angin, 2013; Ertaş and Hakkı Alma 2010). Thus, the devolatilization rate of each particle will be extraordinarily high, favored by the nitrogen flow in the pyrolysis reaction environment. Such conditions promote the rapid devolatilization of this residue, which gives rise to high yields of bio-oil in the 400-600°C range. (Tripathi *et al.,* 2016; Tripathi, Sahu and Ganesan 2016; Stefanidis *et al.,* 2011).

3.2. Gas composition

The gas fraction is composed mainly of carbon dioxide and carbon monoxide (Figure 2). The yields increase with temperature due to the increase in decarboxylation and decarbonylation reactions (Zhang, 2016; Ding *et al.,* 2016; Zhang *et al.,* 2015; Naqvi 2012; Wang *et al.,* 2013; Artes, 2012).

In addition, this fraction is also composed of small amounts of hydrocarbons (C_2-C_4). As observed in Figure 2, the concentration of CO increases with temperature, while that of CO_2 decreases. This is because at temperatures below 450°C the decarboxylation reactions prevail, but at temperatures above 450°C the main secondary reactions are those of decarbonylation, and therefore the release of CO is greater (Tripathi *et al.,* 2016; Tripathi, Sahu and Ganesan 2016). The yield of light hydrocarbons (C_2-C_4) and H_2 also increases with temperature due to cracking reactions. These non-condensable gases are of the low energy value in a pyrolysis process due to dilution with the entrainment gas (N_2). In addition, the low CO_2 yield at 600°C is a favorable environmental feature involving the RH pyrolysis process (Stefanidis *et al.,* 2011).

3.3. Bio-oil composition

The bio-oil compounds were in Table 3 according to functional groups together with the major individual compounds. Oxygenated compounds (phenols, cyclopentenones, furans, ketones, aldehydes, carboxylic acids) make bio-oil unstable and reduce miscibility with hydrocarbons and calorific value (Bridgwater, 2012; Heo *et al.,* 2010). In addition, the heterocyclic compounds of the bio-oil make it viscous and easy to polymerize (Heo *et al.,* 2010-1). The water content in the bio-oil is slightly affected by the pyrolysis temperature since its yield remains in the range of 25 to 27 wt.%. As noted in Table 3, the major organic compounds in the bio-oil are phenols, which are formed on the decomposition of lignin macromolecules above 350°C, and their yields increase considerably at 600°C (33 wt.%). (Chiaramonti *et al.,* 2007; Lu et al., 2009; Lu *et al.,* 2008; Park *et al.,* 2008). The high yield of phenolic compounds in the bio-oil is consistent with other literature results for the rapid pyrolysis of RH. (Li *et al.,* 2012; Lu *et al.,* 2011). Ketones are the second largest organic group in the bio-oil. As observed in Table 5, both groups decrease with temperature, especially at 600°C. Ketones are formed by condensation reactions of the fraction derived from carbohydrates and decomposition of the various oxygenates and furans (Jacobson *et al.,* 2013; He and Wang, 2012; Bulusheva and Rossa, 2011; Peterson *et al.,* 2008; Mohan *et al.,* 2006).

When the pyrolysis temperature is increased, cracking reactions are more severe and lighter compounds are formed (Graça *et al.,* 2013). Ketones are present in nature and are synthesized for many applications. They are mainly used as solvents and intermediates in the chemical industry (Mansur *et al.,* 2013; Shiramizu and Toste, 2012; Honnery *et al.,* 2008; Stamatov *et al.,* 2006).

Acid functional groups have their highest yield at the temperature of 450°C (9.89 wt.%), and the main compound of this group is acetic acid. These compounds are formed by the thermal decomposition of constituent components in RH, and the presence of acetic acid is specifically attributed to the deacetylation of hemicelluloses (Zheng, 2007; Mohan *et al.,* 2006; Uzun *et al.,* 2006; Özbay *et al.,* 2006). The presence of these carboxylic acids is responsible for the strong acidity of this bio-oil (pH in the 2.5–3.5 range) (Graça *et al.,* 2013; He and Wang, 2012; Mortensen *et al.,* 2011; Wildschut, 2009). They can cause corrosion in subsequent processing when the equipment is made of poor quality material. In addition, organic acids are valuable by-products after separation. Therefore, the removal of acids is important for the use of bio-oil as an intermediary in the production of fuels and chemicals (Elliot *et al.,* 2009; Huang *et al.,* 2009; Onay, 2007).

3.4. Char characterization

Evolution of physical, chemical, structural and morphological properties has been analyzed at different pyrolysis temperatures. The results are summarized in Table 4. The proximate analysis shows that the volatiles and the fixed carbon content in the char decrease as the temperature is increased, which is explained by the higher ash content in the residue (Pecha and Garcia-Perez, 2015; Paulsen Patwardhan *et al.,* 2010, Lehmann and Joseph, 2009). This conclusion is also reflected in the elemental analysis because the total carbon content is also lower when the temperature is elevated. The main consequence of the high ash content is that the calorific value of char decreases as the pyrolysis temperature is increased (Zhou, 2013; Mayes and Broadbelt, 2012; Mamleev *et al.,* 2009). Ash yields obtained in the pyrolysis of other lignocellulosic residual materials are lower, generally below 5 wt.%. In view of these results, it can be concluded that the combustion of this char is an undesirable option due to the large amount of ash that must be handled, which causes serious environmental and health problems (Hawash *et al.,* 2017; Sadaka *et al.,* 2014; Yanik *et al.,* 2007; Bogale, 2009). In addition, the calorific value (18.7 MJ/kg for char obtained at 400°C) is low when compared to other solid fuels, such as lignite (28 MJ/kg) or coke (29 MJ/kg) (Fairous, 2009; Oasmaa and Kuoppala, 2003). As noted in Table 4, BET surface areas are low (12-41 m^2/g), and macro and mesopores are formed primarily at 400°C, and microporosity is created in the material as the pyrolysis temperature is raised. In fact, the surface area depends on the mass of carbon removed during pyrolysis, creating pores in the material whose size increases as the temperature is increased (Zhaoying *et al.,* 2018; Hasan Khan Tushar *et al.,* 2012; Shen *et al.,* 2009).

Therefore, upgrading this by-product of activated carbon waste will improve the BET surface areas, and therefore a valuable material will be obtained with good adsorption properties for water and sewage treatment (Chen *et al.,* 2011). Furthermore, due to its high silica content, rice husk ash can be an economically viable feedstock for the production of silicates (An *et al.,* 2011). Amorphous silica can be extracted with alkaline compounds such as sodium hydroxide or sodium carbonate (Adam *et al.,* 2012).

4. CONCLUSIONS

Fast pyrolysis of RH, used in this study, achieved favorable yields of bio-oil, as well as the reduction of char. These results are due to the high rates of heat and mass transfer and to the reduced permanence time of the volatiles in the reaction system. The maximum yield of bio-oil (62.10 wt.%) was obtained at 450°C, with low gas yield (2.21 wt.%). It should be noted that a temperature increase between 400 and 600°C range leads to a small reduction in the production of bio-oil, whose composition is slightly modified by increasing the concentration of phenolics, furans, and the reduction of acids and ketones. The gas yields increase from 1 to 15 wt.% as the temperature increases in the 400-600°C range, with the composition being severely affected, i.e., the concentration of CO increases and that of CO_2 decreases. In addition, a slight increase in the concentration of CH_4 and C_2 -C_4 hydrocarbons occurs with increasing temperature. The char yield at 400°C and 600°C range was 41.14 - 34.77 wt.% respectively, corresponding to a decrease of 16 wt.%. The char obtained is of low heating value but has good features for the production of active carbons and amorphous silica. In addition, the production of amorphous silica by rapid pyrolysis of RH is an attractive alternative to conventional methods, such as combustion and solvent treatments.

5. ACKNOWLEDGMENTS

The authors acknowledge the Brazilian agencies CNPq (National Council of Technological and Scientific Development – Brasília, DF, Brazil), CAPES (Coordination for the Improvement of Higher Education Personnel) for the research funding, and the generous assistance of all the people from the company who granted us access to their database and perception information. We can acknowledge the Tyumen Industrial University in Department of Geology of Oil and Gas Fields (Russian Federation).

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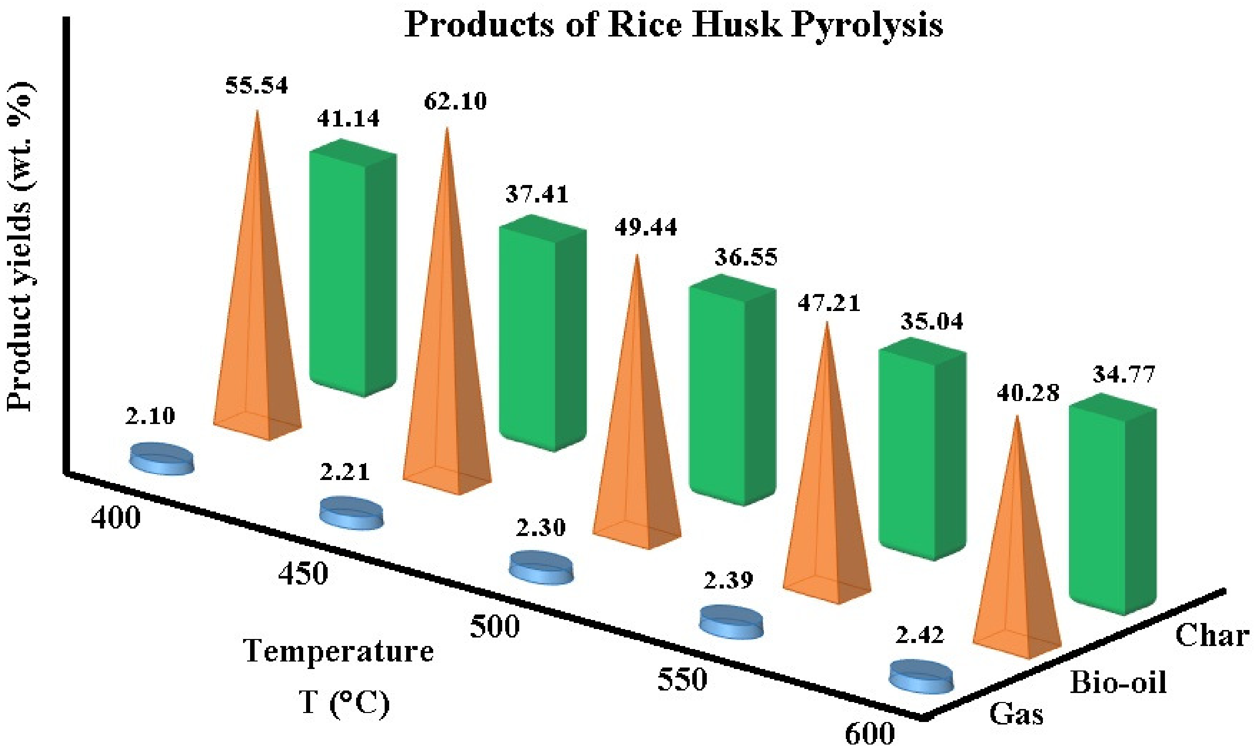

Figure 1. *Effect of temperature on the product yields in RH pyrolysis*

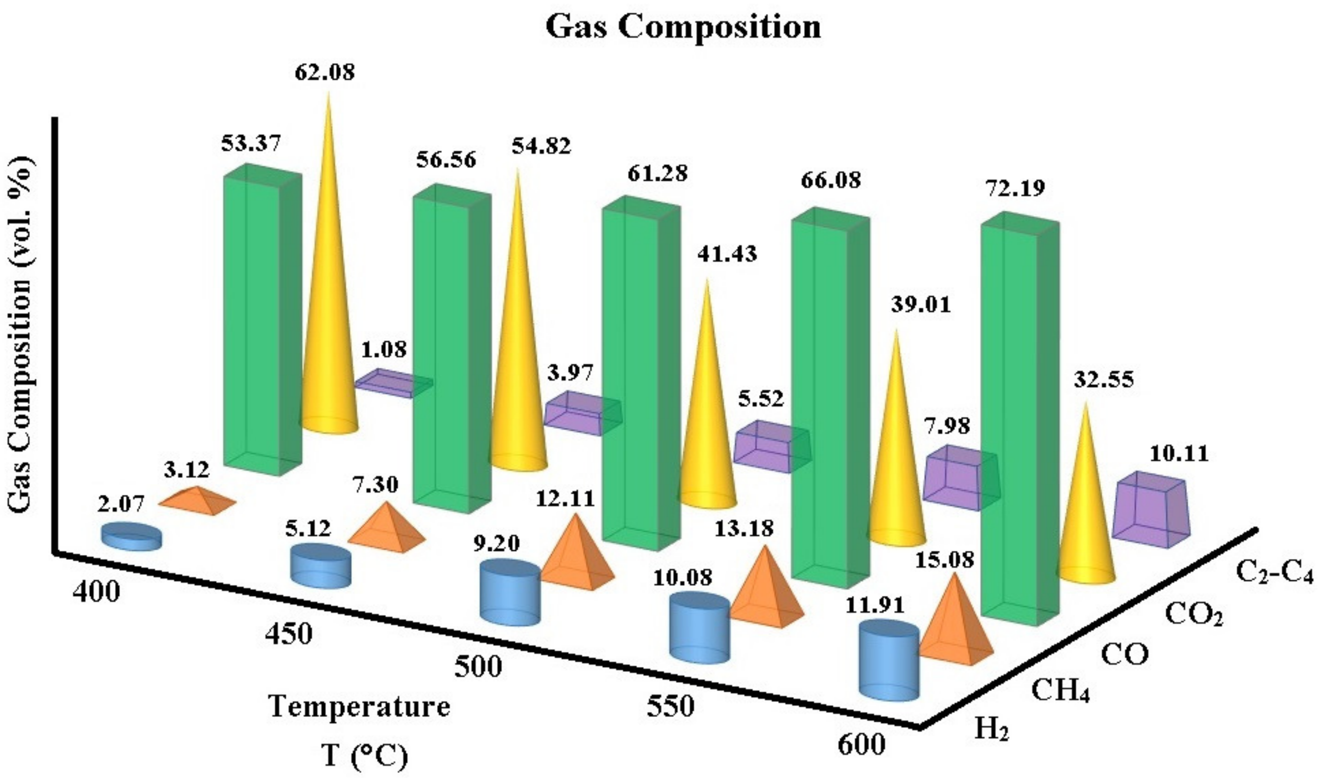

Figure 2. *Influence of temperature on gas composition*

Table 1. *Properties of the RH*

Proximate analysis		Ultimate analysis	
Parameters	**Weight (%) on dry basis**	**Elements**	**Weight (%) on wet basis**
Volatile matter	74.8	Carbon	48.5
Fixed carbon	18.91	Hydrogen	6.92
Ash	13.42	Nitrogen	0.75
Moisture	1.94	Oxygen	40.11
HHV* (MJ/kg)	19.51		

*HHV: Higher Heating Value

Table 2. *Chemical composition of the RH ash*

Compound	Weight (%)
SiO_2	97.92
Al_2O_3	0.41
Fe_2O_3	0.19
MnO	0.01
MgO	0.13
CaO	0.33
Na_2O	0.15
K_2O	0.29
TiO_2	0.03
P_2O_5	0.10
Others	0.22

Table 3. *Yields of the main chemical compounds in the bio-oil*

Compounds	400°C	450°C	500°C	550°C	600°C
Acids	8.26	9.89	8.22	7.67	6.65
Acetic acid	2.45	3.51	2.39	2.49	2.61
Propanoic acid	1.49	0.95	0.30	0.30	0.31
Aldehydes	1.96	2.49	2.26	2.34	2.38
Formaldehyde	0.31	0.48	0.50	0.52	0.59
Ketones	9.88	9.06	8.62	5.99	4.73
1-Hydroxy-2-propanone	1.63	1.36	0.92	0.74	0.44
1,3-Cyclopentanedione	3.24	2.75	2.67	1.96	0.84
2-3-methyl-2-cyclopentenone	1.23	1.22	1.42	1.35	0.43
Phenols	10.11	10.63	10.28	11.57	13.42
Alkyl-phenols	3.16	3.84	3.89	4.08	6.82
Guaiacols	4.03	3.42	2.93	2.89	2.82
Catechols	2.99	3.44	3.53	3.61	3.88
Ethers	3.12	3.11	2.76	2.98	3.12
2,2,4-Trimethyl-1,3-dioxalane	2.48	2.37	1.70	1.57	1.00
Carboxylic Anhydrides	1.23	1.12	1.04	1.11	1.13
Furans	4.53	4.79	5.28	5.00	4.37
Nitrogenated compounds	1.11	1.40	1.66	1.38	1.14
Water	27.13	25.02	25.28	25.37	25.99

Table 4. *Influence of pyrolysis temperature on char properties.*

Char properties	400°C	450°C	500°C	550°C	600°C
Proximate analysis (wt.%)					
Volatiles	22.4	18.6	19.0	13.8	15.1
Fixed carbon	49.6	44.4	43.8	41.1	45.9
Ash	42.9	55.7	57.1	56.2	58.2
Ultimate analysis (wt.%)					
Carbon	55.4	54.3	54.0	53.8	52.3
Hydrogen	2.9	2.8	2.5	2.4	2.0
Nitrogen	0.8	0.7	0.5	0.5	0.5
Oxygen	12.5	3.8	5.9	3.0	2.7
C/H	2.4	2.5	3.1	3.4	3.8
Low Heating Value (MJ/kg)	18.7	16.8	16.0	15.4	14.7
Surface properties					
BET surface (m^2/g)	12.1	17.3	28.9	32.0	41.1
Average pore diameter (Å)	110.5	124.4	85.1	83.8	82.5
Pore volume (cm^3/g)	0.031	0.034	0.061	0.062	0.062