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Onwudili, JA, Nahil, MA, Wu, C et al. (1 more author) (2014) High temperature pyrolysis of solid products obtained from rapid hydrothermal pre-processing of pinewood sawdust. RSC Advances, 4 (66). 34784 - 34792. ISSN 2046-2069

https://doi.org/10.1039/c4ra04761c

High temperature pyrolysis of solid products obtained from rapid hydrothermal pre-processing of pinewood sawdust

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Abstract

A sample of pinewood sawdust was rapidly pre-processed in a torrefaction-type procedure, separately in subcritical water (neutral) and with added Na_2CO_3 (alkaline compound) and Nb_2O_5 (solid acid) in a batch reactor. The original sawdust and the three friable solid recovered products from the hydrothermal procedure were characterized in detail. The solid recovered products gave higher C/O and C/H ratios, higher calorific values and reduced moisture contents compared to the original sawdust. The four solid samples were then subjected to rapid high temperature pyrolysis in a fixed-bed reactor to investigate the effect of the pre-processing routes on the yields and compositions of pyrolysis products. With increasing pyrolysis temperature, the pre-processed samples produced more CO and H_2, far more char and less tar than the original sawdust. The trends in the composition of gases and the yields of char suggested a combination of Boudouard reaction and CO_2 dry reforming as the predominant reactions during pyrolysis. For all samples, increased temperature led to reduced tar production with an increase in the aromatic oxygenates and aromatic hydrocarbons contents of the tar. At 800 °C, the ratio of aromatic hydrocarbons increased dramatically particularly from the sample pre-processed with Nb_2O_5 indicating possible deoxygenation catalysis.

Key words: pinewood sawdust, hydrothermal torrefaction, high-temperature pyrolysis, syngas, tar

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1.0. Introduction

Lignocellulosic biomass is now an attractive energy resource due to the combined impending effects of climate change and energy security issues associated with the world's depleting non-renewable fossil energy resources. Biomass offers benefits to the environment in terms of its renewability and carbon-neutrality. Beyond these, biomass energy has fuelled human survival from pre-historic times and raw wood fuel continues to provide a huge proportion of energy needs in developing countries. The insertion of biomass energy into the global modern energy mix requires that the energy content of biomass be provided in readily useable forms and in line with technological development. The majority of the world's mobile energy is in liquid and gaseous forms for ease of storage, load reduction and for quick ignition requirements. Hence, for biomass to play a significant role in energy provision, it must be converted to some form of fluid energy. Transportation biofuels including bioethanol and biodiesel are now popular and have readily been accepted worldwide for this reason.

However, compared to solid fossil fuels such as coal, biomass suffers from low bulk density, high moisture content, low calorific value and high hydrophilic nature. These properties influence the economics of biomass as fuel. Low bulk density means large volumes per unit mass of biomass be transported which affects transportation and storage. Due to high moisture content and its ability to absorb moisture, biomass often needs to be dried prior to application for conventional energy purpose, which is expensive. Raw biomass tends to have low net calorific values, for example, Miscanthus, a popular energy crop, has a calorific value of about 13 MJ/kg for 25 % moisture content [1]. Oven dried wood pellets have top-range high heating values (HHV) of about 19 MJ/kg [2], this means that roughly 1.5 times as much mass of biomass would be required to replace coal, for example in a coal-firing power plant. In addition, the physical properties of the components of biomass including cellulose, hemi-cellulose and lignin affect biomass densification. For instance, cellulose which is about 40-60 wt% of biomass is tough, fibrous and crystalline, whereas both lignin and hemi-cellulose tend to be amorphous. Hence the composition of biomass and the binding characteristics within and between biomass components have significant effect on biomass processing and application [3].

It has been variously proposed that efficient utilization of biomass for energy would involve some forms of transformation processes to improve the thermal behaviour of biomass by improving its compression and compaction characteristics [2]. Various methods of disrupting the lignocellulosic matrix of biomass materials have been postulated, including chemical, physico-chemical (steam explosion, microwave, and radio frequency heating), and biological pre-treatment [4, 5]. Pre-treatment can alter the crystalline and amorphous regions of biomass, leading to significant changes in its structural and chemical nature that can favour large-scale energy applications [6]. Torrefaction is one method of pre-processing biomass for energy application. The process removes volatile components of biomass including moisture, carbon monoxide, carbon dioxide, simple carboxylic acids (formic, acetic and lactic acids), hydroxyacetone, furfural, methanol and hydrogen sulfide [7, 8]. Torrefaction of biomass has been developed to produce solid biofuels or “bio-coal” with higher density, higher calorific value and more uniform thermal behaviour than the original biomass or as a biomass pre-treatment process for other biofuels production [9 - 12].

Biomass upgrading via a torrefaction-type process in hydrothermal media appears to have potential benefits, particularly for wet biomass such as agricultural wastes - a non-food renewable material. The proposed process is similar to hydrothermal carbonization (HTC) which is currently been developed for bio-char as a product for agricultural land application and for energy applications [12]. However, HTC may appear too severe a process if the objective is to further process the solid product into liquid and gaseous fuels. The benefits of hydrothermal torrefaction include all the benefits of ‘dry’ torrefaction and HTC, such as increased energy density, increased grindability, high hydrophobic nature, increased C/O ratio and improved combustibility [6, 13]. In addition, hydrothermal torrefaction offers the possibility of using the water medium as a collective solvent for the volatile components and can also extract metals present in biomass. Bach et al. [14] compared wet (hydrothermal) and dry torrefaction of Spruce and found that wet torrefaction at 225 °C, yielded a solid product with more than 50% less K and Ca than the original biomass. However, the solid product from dry torrefaction at 275 °C, contained more than twice the amounts of K and Ca. Onwudili and Williams [15], showed that the liquid residuals obtained after hydrothermal pre-processing of pinewood sawdust could produce up to 15.3 molkg^{-1} hydrogen and 10.1 molkg^{-1} of methane via supercritical water oxidation. The liquid residuals were gasified in the presence of Ru/Al_2O_3 catalyst. It was also proposed that the liquid residual could be used for further biofuels production via biochemical conversion routes e.g. fermentation.

Pre-treated biomass samples have been reported to give enhanced biofuels yields via enzymatic hydrolysis [16, 17], pyrolysis [18] and gasification [19, 20]. Pyrolysis is a popular thermochemical conversion technology applied to biomass. High temperature pyrolysis occurs at temperatures above 600 °C. The aim of such high temperature pyrolysis is often to produce a high yield of gaseous products due to a combination of a series of thermal degradation processes including primary, secondary and tertiary decompositions [21]. Gas formation and gas compositions during these processes are favoured by high residence time and high temperatures [22-23]. Often the major gas components include CO, H_2, CO_2 and CH_4 using biomass as feedstock.

In this present study, the original pinewood sawdust and the solid recovered products (SRP) obtained from hydrothermal pre-processing of the sawdust have been subjected to high temperature pyrolysis to investigate the effects of the hydrothermal pre-processing routes on the yields and compositions of pyrolysis products. The aim of this study is to use the detailed analysis of pyrolysis products to assess the benefits of hydrothermal torrefaction as a pre-treatment step for thermochemical conversion. To do this, products from high temperature pyrolysis of raw pinewood sawdust and the solid residues obtained from the hydrothermal pre-processing routes will be compared. In addition, products from the solid residues from the different pre-processing routes will also be compared to determine the influence of the different additives used on products.

2.0. Materials and Methods

2.1. Materials

The sample of pine wood sawdust used in this work and the pre-processing methods has been described in detail previously [15]. Briefly, 50 g of sawdust was placed into a 500 ml hydrothermal reactor [3] and 300 ml of distilled water added. Thereafter, 10 g of either sodium carbonate or niobium (V) oxide was added. These chemicals have been respectively selected as alkaline and acidic additives in an attempt to promote hydrothermal biomass hydrolysis and dehydration - two important reactions for biomass densification. For neutral pre-processing of sawdust, no additive was added. The reactor was sealed and purged for 10 min with nitrogen gas and then heated to a temperature of 280° C and pressure of 8.0 MPa. Once the reactor reached 280 °C, the heating was stopped and the reactor withdrawn and rapidly cooled to room temperature. The original sawdust and recovered solid residues from the pre-processing routes were dried in the oven at 105 °C for 2 h, weighed and stored in cleaned bottled prior to use. In this present study, these solid recovered products are designated as SA for the Na_2CO_3 route, SB for the Nb_2O_5 route and SN for the neutral pre-processing routes, while the original sawdust will be referred to as SD.

2.2. Methods

2.2.1. Characterization of the solid recovered products and original pinewood sawdust

The products yields (in the form of carbon balance) from the pre-processing of the pinewood sawdust are presented in Table 1, which also shows the elemental compositions of the solid samples used in this present work and to compare, the elemental compositions of the three main components of lignocellulosic biomass have been included in the table. In these cases, beech wood xylan has been used as hemi-cellulose, microcrystalline cellulose for cellulose and alkali lignin for lignin; these were all purchased from Sigma-Aldrich and used as received.

Table 1: Carbon balances of products from the pre-processing routes and elemental compositions of the sawdust, the solid recovered products and biomass model compounds

	Products' carbon balance (wt%)			**[a] Ultimate composition of solid samples (wt%)**			
Samples	**Solid**	**Liquid**	**Gas**	**C**	**H**	**N**	**O [b]**
SD	-	-	-	46.9	5.49	0.31	47.3
SA	60.1	36.2	1.54	54.9	5.65	0.35	39.1
SB	66.5	25.1	1.36	68.8	4.87	0.43	25.9
SN	64.8	25.7	1.54	70.1	4.83	0.47	24.6
Xylan	-	-	-	40.3	5.45	2.65	51.6
Cellulose	-	-	-	41.7	5.69	0.41	52.2
Lignin	-	-	-	61.3	5.18	1.12	32.4

[a] dry-ash-free basis; [b] oxygen obtained by difference;

In addition, the solid samples were analyzed by Infra-Red Spectroscopy (FT-IR) and x-ray diffraction (XRD) to study changes in their structural properties resulting from the pre-processing methods. FT-IR (Fourier transform infrared) spectrometry was used to characterise SD, SA, SB and SN in terms of their functional group composition. A Nicolet Magna IR-560 FT-IR spectrometer was used in conjunction with OMNIC data-handling software. X-Ray Diffraction (XRD) patterns of the original pinewood sawdust and solid recovered products were obtained on X'pert PRO MPD, PANalytical, Almelo, (The Netherlands), in the range of 5 – 80 degree 2 Theta with a scanning step of 0.033° using Cu Kα radiation (1.54060 nm wavelength). The scans would indicate the presence and levels of ash in the samples.

2.2.2. High-temperature pyrolysis of solid samples

High-temperature pyrolysis experiments were carried out in a horizontal tube fixed-bed reactor at 600 °C, 700 °C and 800 °C, respectively under nitrogen flow. The schematic diagram of the stainless steel reactor is shown in Figure 1. It consists of a stainless steel 650 mm cylindrical tube with internal diameter of 11 mm. The 450 mm long heated zone was embedded in an electrical tube furnace which provided fast external heating.

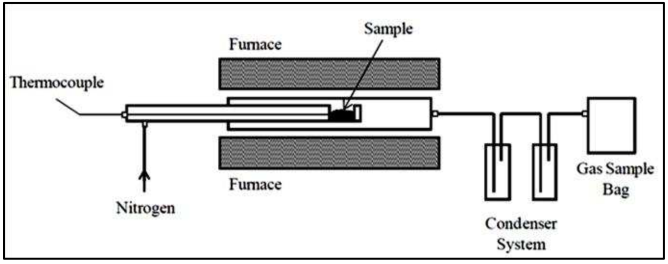

Figure 1: Schematic of horizontal tube reactor for high temperature pyrolysis

The sample was introduced into the reactor using a stainless steel sample boat consisting of a cup attached to the end of a cylindrical tube. The 85 mm sample-bearing cup at the end of the sampling boat lay at the centre of the heated length of the horizontal reactor. A J-type thermocouple was placed concentric to the walls of the sample boat which directly measured the temperature at the centre of the sample cup. The inlet of the reactor was gas-tight, while the outlet was piped into a series of condensers and finally into a 25 L Tedlar^{TM} bag for gas sampling. Nitrogen flow was introduced at the inlet at a constant rate of 100 ml min^{-1}. The residence time of the volatiles during pyrolysis was estimated to be 9 sec. Prior to the start of each fast pyrolysis experiment, the reactor tube, sample boat and condensers were weighed and recorded. In each experiment, 0.5 g of the solid samples was each weighed accurately into the sample boat. The reactor was quickly heated at ~325 °C min^{-1} to the desired temperatures of between 600 - 800 °C before the samples were introduced into the hot zone for fast pyrolysis to occur. The pyrolysis vapours were carried by the nitrogen flow gas through two glass condensers; the first was water-cooled and the other cooled by dry-ice. The condensable volatiles (including water) were retained in the two condensers, while the non-condensable gases were collected in the gas sample bag for analysis. For quality assurance, the reactor was held at the stipulated temperature for 20 min and swept by nitrogen gas to ensure complete sweep of volatiles into the condensers and gases into gas bag for all experiments.

At the end of each pyrolysis experiment, the sample boat and reactor were reweighed in order to obtain the weight of solid product. Similarly, the amount of liquid product was determined by the difference in the weight of the condensers before and after experiments. The liquid products were collected from the condensers with dichloromethane. The weight of oil was obtained after correction for water content determined by Karl Fischer titration of the liquid products collected from the condensers.

2.2.3. Gas analysis

The gas effluents from the pre-treatment process and from both high-temperature pyrolysis tests were collected in 25 L Tedlar^{TM} gas bags and analyzed off-line with a system of three gas chromatographs [24]. Briefly, the gas samples were analysed using three packed column gas chromatographs. The permanent gases, hydrogen, oxygen, nitrogen and carbon monoxide, were analysed using a Varian CP-3380 gas chromatograph with a Thermal Conductivity Detector (GC/TCD). Hydrocarbon gases, C_1 to C_4, were analysed using a second Varian CP-3380 gas chromatograph with a Flame Ionisation Detector (GC/FID). Carbon dioxide was analysed using a third gas chromatograph fitted with a TCD. The results obtained from the GCs were given as a volume percent and were converted into masses of each gas using the ideal gas equation. The higher heating values (HHV) of the gas products were estimated based on the volume percent of gas components

$$HHV = \sum_{i=1}^{n} X.CV$$

Where i …n = each combustible component in the gas product
X = volume fraction of gas component
CV = calorific value of gas component in MJ kg^{-1}

2.2.4. Analysis of oils/tars from high-temperature pyrolysis

As mentioned earlier, the liquid products were sampled from the condensers using 20 ml dichloromethane (DCM). Each collected fraction was homogenized by adding a little amount of ethanol prior to water content determination by Karl Fischer Titration with a Swiss made Metrohm 890 Titrando equipment. After water determination, 2-hydroxyacetophenone, used as internal standard, was added to the samples before the next set of analytical steps. For this study, products obtained at 600 ℃ are referred to as oils, while those obtained above 700 ℃ are called tars. Each liquid sample containing the internal standard was passed through a column of anhydrous sodium sulphate to remove the water from the oil prior to gas chromatographic analysis. The sodium sulphate was initially dried at 140 °C for 2 h in an oven before use. Each sample was made up to 30 ml for ease of comparing the yields of the major components. The samples were analysed using a Varian CP-3800 gas chromatograph coupled with a Varian Saturn 2200 mass spectrometer (GC/MS/MS). For the GC/MS/MS analysis, 2 µl of the oil solutions were injected into the GC injector port at a temperature of 290 ºC; the oven programme temperature was 40 ºC for 2 min, then ramped to 280 ºC at 5 ºC min^{-1} heating rate, and finally held at 280 ºC for 10 min. The transfer temperature line was 280 ºC, manifold at 120 ºC and the ion trap temperature was held at 200 ºC. The ion trap was initially switched off for 4 min to allow the elution of the solvent prior to data acquisition to safeguard the life of the trap. The major compounds identified in the tar samples were quantified using internal standard method.

3.0. Results and Discussions

3.1. Yields and characterization of products from hydrothermal torrefaction

Table 2 shows the proximate and energy characteristics of the original sawdust (SD), and solid residues. Sawdust pre-processing under the different hydrothermal conditions led to an increase in the C/O and C/H ratios in the solid residues. Compared with the three major components of biomass; cellulose, hemicellulose and lignin, results show that the pre-processed samples and sawdust can be divided into two categories – SD and SA have C/O and C/H ratios higher than xylan and cellulose but lower than lignin, while SN and SB have C/O and C/H ratios higher than even lignin. These ratios indicate the similarities between SD and SA on one hand and SN and SB on the other.

Table 2: Proximate compositions and energy characteristics of sawdust, solid recovered products and model compounds of lignocellulosic biomass

Proximate compositions (wt%)					**Energy characteristics**		
Sample	**Moisture**	**VM**	**FC**	**Ash**	**HHV (MJkg^{-1})**	**C/O ratio**	**C/H ratio**
SD	5.62	81.4	12.6	0.38	22.1	0.99	8.54
SA	4.05	74.8	20.2	0.95	25.3	1.4	9.72
SB	0.16	40.8	30.8	28.2	29.4	2.66	14.1
SN	1.34	53.8	43.7	0.17	28.5	2.85	14.5
Xylan	-	-	-	-	15.2	0.78	7.33
Cellulose	-	-	-	-	15.9	0.8	7.3
Lignin	-	-	-	-	24.2	1.93	11.9

VM = volatile matter; FC = fixed carbon; HHV= higher heating value

Consequently, there was an increase in the calorific values of the solid recovered products compared to the original sawdust and components of lignocellulosic biomass as shown in Table 2. Both neutral and Nb_2O_5 pre-processing routes led to approximately 35% increase in calorific values compared to the original sawdust. This is nearly twice the value (ca 20%) reported in literature from the dry torrefaction of wood [18], suggesting an improvement of hydrothermal pre-processing over torrefaction with respect to energy densification of biomass. As shown in the table, the ash content of the neutral-processed sawdust sample (SN) decreased by 55% compared to the original sawdust. This agrees with the work of Bach et al., [14] who found a similar decrease in ash content during wet torrefaction of biomass. Presence of ash, usually in the form of alkali metals, is often responsible for boiler and heat-exchanger fouling during biomass combustion; hence the decrease in ash content during the production of SN showed that hydrothermal torrefaction of wet biomass may address this problem. However, SA showed increase in ash content, while the ash content of SB was the highest due to the presence of the water-insoluble niobium pentoxide. The ash content of SB corresponded to 98.8 wt% of the added Nb_2O_5, showing that almost all of it remained in the solid residue after the pre-treatment procedure. On the contrary, comparing the ash content of SA with that of the original biomass indicates that only about 5.7 % of the Na_2CO_3 used in the pre-treatment remained in the solid product, since Na_2CO_3 has high solubility in water. Thus, effective washing of SA with tap water may remove all the ash.

Since all four solid samples were subjected to the same oven drying conditions, the differences in their moisture contents as shown in Table 2 could be attributed to the change in the structural properties of the original biomass, resulting in increased hydrophocity or decreased water retention capacity. Both SN and SB showed considerably lower moisture contents than SD and SA. The thermograms from the thermogravimetric analysis (TGA) of all four samples are given in the Electronic Supplementary Information (ESI). Briefly, it shows that both SD and SA gave similar thermogravimetric profiles, except for the loss of the shoulder in SA compared to SD. This disappearance of the shoulder in the thermogram could most probably be as a result of hydrolysis and dissolution of the hemi-cellulose fraction [2, 5, 25]. In addition, the profiles of SN and SB are so identical that they are almost indistinguishable.

Further evidence of the composition of the solid recovered products can be seen from the FT-IR spectra and XRD patterns in Figure 2. The Infra-red spectra in Fig. 2A show the structural similarities between SB and SN on one hand and SA and SD on the other. For comparison, the FT-IR of xylan, cellulose and lignin have been presented in the ESI. Clearly, SD and SA contain bonds similar to those in cellulose and xylan, with absorptions 1000 – 1050 cm^{-1} corresponding to C-O bonds in aliphatic alcohols and at 3300 cm^{-1} for the presence of aliphatic O-H alcohols. On the other hand the FT-IR spectra of SN and SB show absorptions at around 1200 – 1300 cm^{-1} for C-O of aromatic ethers as well as at 3340 cm^{-1} for O-H of phenols. Essentially, the FT-IR spectra of SN and SB closely resembled that of lignin, while those of SA and SD have close matches with the spectra of cellulose and xylan. Interestingly, while SD, SN and SB showed absorptions around 1500 – 1600 cm^{-1} due to C=C bonds in para-substituted aromatic compounds, SA did not. This suggested that while SD, SN and SB may have evidence of the presence of lignin, this was virtually absent in SA. Thus from these analysis, SN and SB were lignin-type products, while SA appear to be composed of cellulose and hemi-cellulose. Hence, the results show that there was compelling evidence to suggest that the neutral and Nb_2O_5 pre-processing routes leached out cellulose and hemicellulose from the original sawdust into the aqueous phase, leaving behind a lignin-rich solid. Conversely, the use of Na_2CO_3 leached out of lignin from the sawdust into the aqueous phase leaving a solid fraction rich in cellulose.

The XRD patterns show that all four samples have high contents of amorphous materials. However, the important features are the crystalline signal from the ash materials. On the one hand, SN and SD showed poor crystalline contents. The obvious peak in the XRD pattern of SD corresponded to potassium calcium carbonate, while that of SN showed almost a complete absence of ash thus indicating the removal of ash through the hydrothermal pre-processing route. This evidence is also supported by the low ash content in SN reported in Table 2 above. On the other hand, SB showed a large presence of three Nb_2O_5 crystalline phases, indicating the apparent stability of the solid acid in the hydrothermal medium, while SA showed the presence of sodium carbonate and potassium calcium carbonate. The intensity of the signal from Nb_2O_5 was so strong that it masked any other possible signal. The large presence of Nb_2O_5 in SB may influence its thermochemical conversion during pyrolysis. The presence of sodium carbonate in SA indicated that further washing of the solid recovered product may be required to remove the soluble additive.

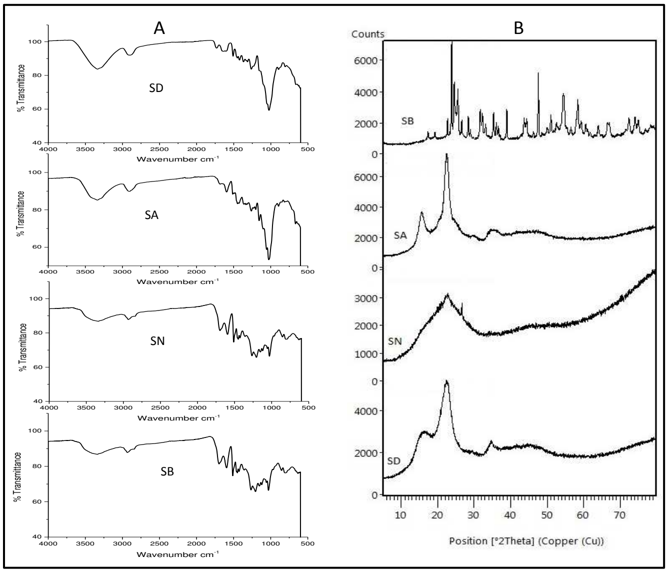

Figure 2: [A] FT-IR spectra and [B] XRD patterns of original pinewood sawdust and the SRPs indicating the presence of ash

3.2. Products from high-temperature pyrolysis of solid recovered products

Figure 3 presents the yields of products from the high temperature pyrolysis of the four solid samples, the original sawdust (SD), the solid residue from the sodium carbonate pre-processing route (SA), the niobium pentoxide pre-processing route (SB) and the neutral pre-processing route (SN). As expected the samples were converted into gas, tar and solid. The results have been presented on an ash-free basis to take account of the contribution of additives to the ash products. The yields of tar and solid products consistently decreased as pyrolysis temperature was increased from 600 °C to 800 °C, while gas products increased. When dissolved in dichloromethane the tar products obtained at 600 °C formed much darker colours than the tars obtained as temperature increased; the colour was light yellow at 800 °C. This physical change may have resulted from the thermochemical refining of the oil products due to more active cracking reactions with increasing temperature.

The liquid products contained a mixture of water and tar and Figure 3 shows that the tar products from the pre-processed samples contained less water than the original sawdust. This may be one of the key advantages of torrefaction-type pretreatment of biomass, resulting in lower water content in biomass due to primary dehydration reactions as well as loss of moisture. The lower aqueous fraction contents in the liquid products of SA, SB and SN compared to the original biomass can be linked to changes in the structures of the sawdust samples from the pre-processing procedure. The solid residues were highly powdery and appeared porous, thereby decreasing their water absorption/retention capacity. Interestingly, there appears to be a positive correlation between the aqueous fractions of the oil/tar products and the moisture contents of the dried solid samples prior to pyrolysis, such that samples with lower moisture contents produced lower aqueous fractions in the tar. Oil/tar products from both SB and SN have much lower water content that SD and even SA, again suggesting increasing hydrophobicity of the pre-processed samples, particularly for SN and SB.

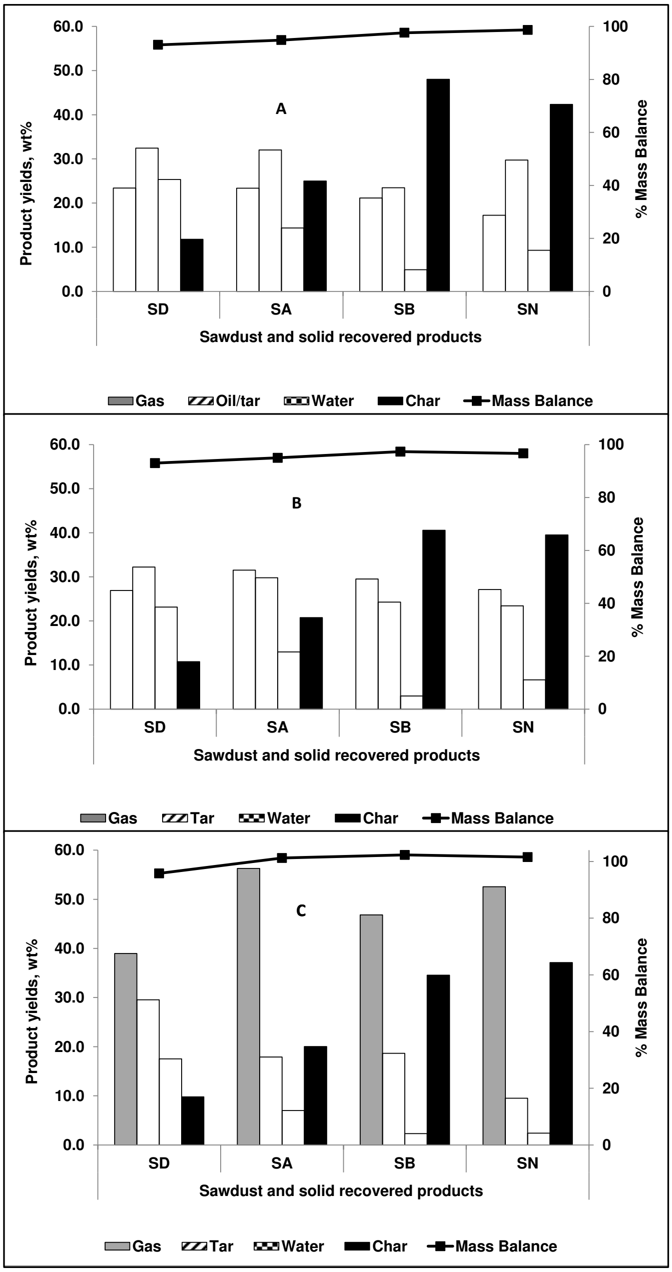

Figure 3: Product yields (ash-free basis) from rapid high temperature pyrolysis of the samples; [A] 600 °C; [B] 700 °C, [C] 800 °C (Sawdust (SD), the solid residue from the sodium carbonate pre-processing route (SA), the niobium pentoxide pre-processing route (SB) and the neutral pre-processing route (SN).

The three SRPs produced more char than the original biomass due to their increased carbon contents resulting from possible increase in lignin contents and/or carbonization during the pre-processing procedures. Lignin is known to produce a large amount of char during pyrolysis [26], mainly due to cross-linking condensation reactions. In all tests, SB produced the largest amount of solid product after fast pyrolysis due to its high ash content as shown in Table 2. Niobium pentoxide used in preparing SB is hardly soluble in water, and so expectedly remained with the solid residue after the pre-processing procedure. However, the results presented on ash-free basis, show nearly identical char production from both SN and SB. At 600 °C, SB produced the highest amount of char but this decreased with increasing temperature, such that at 800 °C, the char product from SN was the highest. Gas production during pyrolysis is highly favoured by high temperature resulting from the conversion of liquid products to gas due to cracking reactions [21-23]. Figure 3 shows the effect of temperature on the gas/oil ratios from the different samples from 600 to 800 °C. For all samples there were more oil products than gas products at 600 °C, whereas at 700 °C all samples gave roughly similar yields of oil and gas. However, at 800 °C the gas products became dominant for all samples, with SN giving the highest gas/oil ratio of 5.68. Results therefore show that there was a progressive increase in gas/oil ratio from the original sawdust to the neutral-processed sawdust in the order SN>SA>SB>>SD. Hence, the pre-processing procedure led to an increase in the production of gas products compared to original sawdust. During high temperature pyrolysis, primary decomposition of biomass produces simple gases and heavier hydrocarbons, which undergo further cracking to produce more gases [21], involving a combination of chemical reactions

3.2.1 Gas compositions from high temperature pyrolysis

The components of the gas products are given in weight percent of the feeds in Figure 4, which shows the general trend in the increase in yields of hydrogen and CO with temperature increase. It also shows that the yields of carbon dioxide and methane decreased under the same conditions. The trend in gas composition with increasing temperature in Figure 4 shows clearly defined trends in the yields of carbon dioxide and carbon monoxide with increasing temperature. Apart from SB, all the other three samples produced similar yields of CO and CO_2 at 600 °C, but as the temperature increased CO yields became consistently higher than CO_2 yields. This may suggest the occurrence of three possible reactions that favour CO production; (1) Boudouard reaction; (2) CO_2 dry reforming of hydrocarbon gases and (3) steam gasification of char;

$$CO_2 + C \rightarrow 2CO$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

$$C + H_2O \rightarrow CO + H_2$$

The pre-processed samples produced more solid products than SD, indicating that the larger presence of char from the three pre-processed samples may have favoured solid-gas reactions involving char conversion. Results shown in Figure 3 demonstrate a consistent but gradual decrease in the yields of solid product with increasing temperature for all four samples. Also the decrease in the yields of methane and C_2-C_4 hydrocarbons as well as oil yields with increasing temperatures suggest the possibility of dry reforming of these hydrocarbon gases by CO_2. Although, char steam-reforming was also possible, results suggest that this process was not very significant due to the low yields of hydrogen. For instance, since SD contained more moisture and produced more water that the pre-processed samples, it would have been expected that steam gasification would produce more hydrogen from SA than with the other samples. However, the pre-processed samples, (SA, SB and SN) still produced more hydrogen gas than original sawdust, indicating that gas formation including the increase in CO and H_2 yields could have resulted instead from both Boudouard reaction and CO_2 dry-reforming as temperature increased. Boudouard reaction is known to occur spontaneously for most types of carbons at temperatures of 700 ºC and above [27].

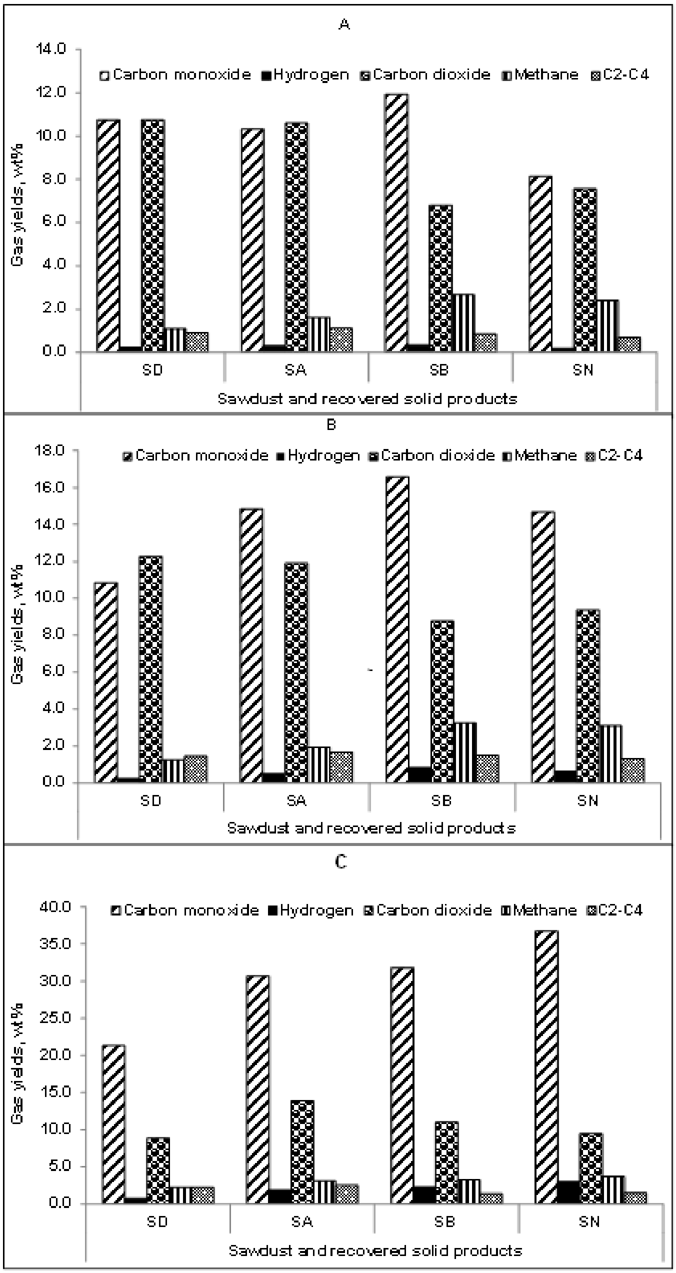

Figure 4: Mass % yields of components of the gas products; [A] 600 °C; [B] 700 °C; [C] 800 °C (Sawdust (SD), the solid residue from the sodium carbonate pre-processing route (SA), the niobium pentoxide pre-processing route (SB) and the neutral pre-processing route (SN).

Figure 5 presents the gross calorific values (HHV) of the gas products from the samples with respect to temperature. The values represent the sum of the calculated HHV for each combustible component in each gas product i.e. hydrogen, methane, carbon monoxide and C_2-C_4 hydrocarbon gases. SB produced the gas products with the highest calorific values at 600 ºC and 700 ºC but was overtaken by SN at 800 ºC. In all cases, the results clearly show that the HHV of the gas products increased steadily for all samples as the pyrolysis temperature was increased from 600 to 800 ºC. The calorific values of gas products from SD were consistently lower than those of the pre-processed samples at each temperature due to the high carbon dioxide content compared to the other gases. This suggests that the pre-processing procedures were able to reduce the CO_2- forming potential of the sawdust possibly by the removal of simple water-soluble organic molecules such as carboxylic acids, methanol, formaldehyde, sugars and hydroxyacetone [7, 8].

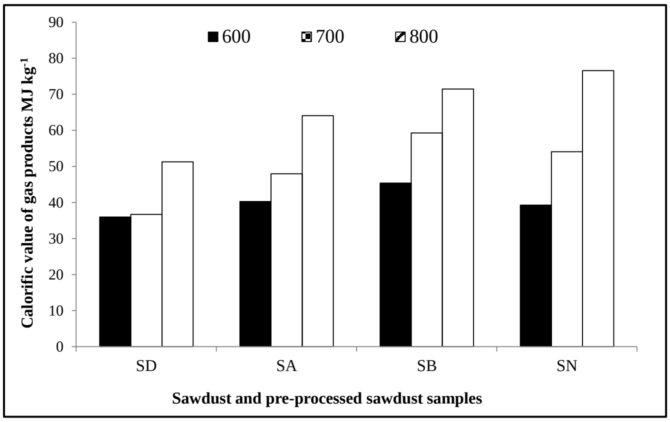

Figure 5: Gross calorific values of the gas products (Sawdust (SD), the solid residue from the sodium carbonate pre-processing route (SA), the niobium pentoxide pre-processing route (SB) and the neutral pre-processing route (SN).

The enrichment in the carbon contents of the SRPs as demonstrated in Table 1 would have occurred with the simultaneous removal of these oxygen-rich volatile compounds. Also, the gas products obtained from the initial pre-processing stages contained mostly carbon dioxide [15]. Thus structural changes caused by the pre-processing procedures appeared to have favoured the formation of combustible gases during the high temperature pyrolysis process. The gas products were rich in hydrogen and CO and so could be used for methanol/ethanol synthesis or liquid hydrocarbon fuel production via Fischer Tropsch synthesis.

3.2.3. Pyrolysis oil/tar compositions

As mentioned earlier, the appearance of the oil/tar products improved from dark to much lighter colours with increasing temperature. The total yields of oil/tar products was generally in the order SD>SA>SN>SB at all temperatures except at 800 ºC, when SB produced more tar than SN. There was also a consistent decrease in oil yields as temperature increased. In this study, the change in the composition of the oil/tar fractions was monitored using their solubility in the collecting solvent – dichloromethane (DCM). In general, the ability of DCM to dissolve the oil/tar products increased with increasing temperature, indicating the formation of mostly less polar compounds including hydrocarbons.

The components of the liquid solutions detectable by the GC/MS/MS were categorized into four main groups, namely aliphatic oxygenates, aromatic oxygenates, aromatic hydrocarbons and compounds containing nitrogen atoms (hetero-compounds). These are presented in Figure 6 for all four samples in relation to pyrolysis temperature. In addition, Figure 7 shows the ratio of the yields of aromatic hydrocarbons to the yields of aromatic oxygenates as a function of temperature. The number of peaks detected by the GC/MS/MS decreased as temperature increased for all four samples. For instance, there were >140 chromatographic peaks for the oil from SD at 600 ºC; the number of peaks decreased to 94 at 700 ºC and decreased further to 31 peaks at 800 ºC.

At 600 ºC, the main components of the aliphatic oxygenates included cyclopenten-1-one and its methyl and dimethyl derivatives, and alkylated furans such as 2-ethyl-5-methylfuran; these account for more than 60% of this category. The aromatic oxygenates were dominated by phenols, especially phenol, 2-methylphenol, 4-methylphenol, 3, 4-dimethylphenol, 4-ethyphenol and 2-ethylphenol. These are similar to the phenols obtained by Boateng and Mullen [18] from fast pyrolysis of torrefied biomass at 500 ºC. Other prominent oxygenated aromatics included dihydrobenzofurans, 1H-Indenol and methylnaphthols. Among the aromatic hydrocarbons, p-xylene, m-xylene, naphthalene, methyl- and dimethyl naphthalenes, biphenyl, phenanthrene, fluorene and 1H-phenalene were the most prominent compounds. The last category of nitrogen-containing compounds included pyrazole, pyrazines, indoles and indazoles, often in the methyl or dimethyl forms.

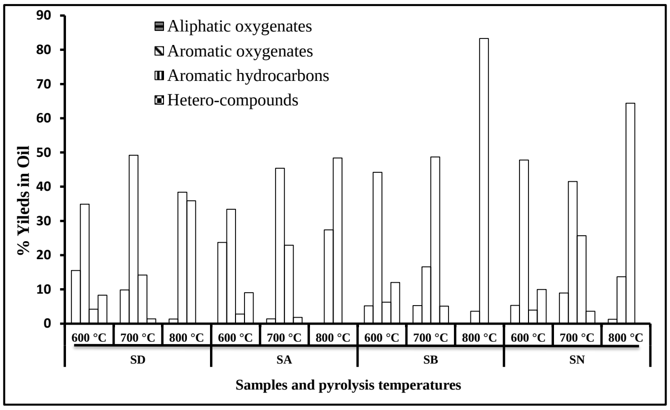

Figure 6: Yields of different classes of compounds in the oil/tar products from GC/MS/MS analysis (Sawdust (SD), the solid residue from the sodium carbonate pre-processing route (SA), the niobium pentoxide pre-processing route (SB) and the neutral pre-processing route (SN).

The general trend in Figure 6 shows that when the temperature increased to 700 ºC, the presence of aliphatic oxygenates and hetero-compounds decreased dramatically. The main aliphatic oxygenates were methyl furan, pentyl furan and 2methyl-2-cyclopenten-1one. This trend indicated the conversions of these compounds to gas via cracking and also to more stable aromatic compounds via aromatization reactions [28]. It is therefore clear from the results that as temperature increased to 700 ºC, gas formation increased, but so also were the yields of aromatics (both oxygenates and hydrocarbons). However, the yields of aromatic oxygenates was consistently higher than those of aromatic hydrocarbons for all samples except for SB at 700 ºC. Solid acid catalysts such as alumina and Nb_2O_5 are well-known for catalyzing dehydration reactions of biomass [29-31]. Hence, the presence of Nb_2O_5 in SB, most probably catalyzed the rate of dehydration/deoxygenation of aromatic oxygenates to produce more aromatic hydrocarbons at 700 ºC.

At 800 ºC, virtually no nitrogen-containing compounds were detected in tars from all four samples. Also, only very small proportions of aliphatic oxygenates were found at this temperature for tars from SA and SD but none in tars from SB and SN. The tars were nearly completely composed of aromatic oxygenates and aromatic hydrocarbons. There were more aromatic hydrocarbons from SA, SB and SB but similar yields of aromatic oxygenates and aromatic hydrocarbons in the tar from the original sawdust sample. SD. Clearly, SN and SB gave the highest aromatic hydrocarbon/aromatic oxygenates ratio at this temperature as shown in Figure 7. Again, this can be attributed to the predominance of dehydration of the biomass during the sawdust pre-processing procedures. In addition, it appears that Nb_2O_5 acted as a deoxygenation catalyst at higher temperatures.

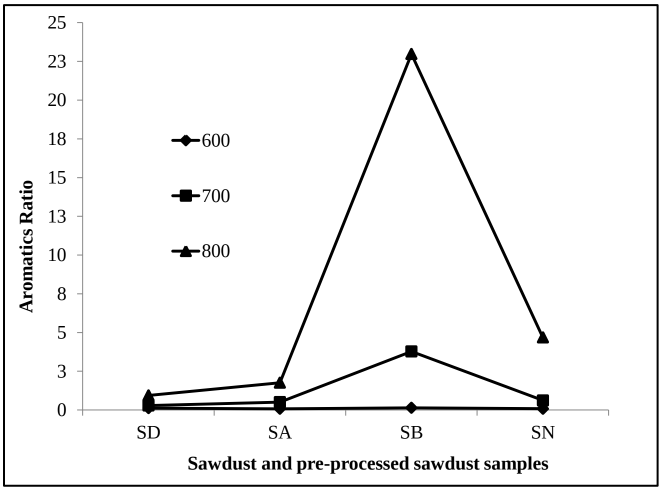

Figure 7: Aromatic hydrocarbons/aromatic oxygenates ratios in the oil/tar products (Sawdust (SD), the solid residue from the sodium carbonate pre-processing route (SA), the niobium pentoxide pre-processing route (SB) and the neutral pre-processing route (SN).

Biomass dehydration in subcritical water conditions is possible due to the increased ionic strength of the medium (for SN), and the presence of solid acids such as niobium pentoxide could only reinforce such reactions (for SB). Thus, both SB and SN would be much more dehydrated than SD and SA, and therefore would produce more aromatic hydrocarbons and char. However, SB produced 23 times more aromatic hydrocarbons than aromatic oxygenates, giving the highest aromatic hydrocarbon/aromatic oxygenates ratio. Compared to the composition of the oil/tar from SN, it would appear that the presence of Nb_2O_5 in SB may have contributed, possibly via catalysis, to the formation of aromatic hydrocarbons in the tar at high temperatures. In a typical pyrolysis process, high temperatures and/or long residence times often increase the yield of pyrolytic char as a result of severe aromatization and condensations of phenolic compounds [28] in the oil/tar. In this work however, both oil/tar and char formation decreased with increasing temperature in favour of gas production, indicating that the high temperature pyrolysis process led to significant gasification of both char and oil/tar. However, it is clear from results that the rate of decrease of oil/tar products was higher than that of solid products in relation to temperature, indicating the oil gasification was faster than char gasification. Hence, even though SB and SN gave higher aromatic hydrocarbon/aromatic oxygenates ratio, the actual oil/tar yields were smaller compared to sodium carbonate pre-processed residue and the original sawdust.

4.0 Conclusions

Hydrothermal pre-processing of biomass has been shown to increase the energy density of pinewood sawdust samples. Interestingly, the solid residue obtained from the neutral pre-processing procedure (SN) gave the highest C/O ratio, C/H ratio, gas production and up to 35% increase in calorific value in relation to the original biomass. In addition, all three pre-processed samples produced gas products with consistently higher calorific values than the original sawdust at all temperatures. Carbon dioxide was the dominant gas component at 600 ºC but was overtaken by CO at higher temperatures possible due to a combination of reactions including Boudouard reaction and CO_2 reforming of hydrocarbon gases and vapour-phase oil/tar products.

For all samples, gas yields increased while both oil/tar and char product yields decreased with increasing pyrolysis temperature. The oils/tars became increasingly aromatic hydrocarbon-rich such that virtually no aliphatic oxygenates and hetero-compounds were present in the tars at 800 ºC. There was also an increasing ratio of aromatic hydrocarbons to aromatic oxygenates as pyrolysis temperature increased. Overall, the pre-processing procedures improved the fuel properties of the sawdust sample and further thermochemical processing via high temperature pyrolysis showed that the pre-processed samples yielded more gaseous fuels and tars with fewer components. Results therefore showed that under the test conditions, SA gave the highest yield of gases during pyrolysis but SN produced the gas with the best calorific value. In addition, SB and SN yielded the highest char and their tar products had the least aqueous contents. In all, under the hydrothermal conditions used, the neutral-processing route can be judged as the best considering the improved characteristics of the solid recovered product, the yields of pyrolysis products and the cost-effectiveness of not using any additives. Further work will be carried out on the influence of pre-processing temperatures, pressure and reaction time on the characteristics of the recovered solid residue towards further thermochemical conversion.

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