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Article:

Onwudili, JA and Williams, PT (2013) Enhanced methane and hydrogen yields from catalytic supercritical water gasification of pine wood sawdust via pre-processing in subcritical water. RSC Advances, 3 (30). 12432 - 12442. ISSN 2046-2069

https://doi.org/10.1039/c3ra41362d

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Enhanced methane and hydrogen yields from catalytic supercritical water gasification of pine wood sawdust via pre-processing in subcritical water

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Abstract

A two-stage batch hydrothermal process has been investigated with the aim of enhancing the yields of hydrogen and methane from sawdust. Samples of the sawdust were rapidly treated in subcritical water and with added Na_2CO_3 (alkaline compound) and Nb_2O_3 (solid acid) at 280 °C, 8 MPa. Each pre-processing route resulted in a solid recovered product (SRP), an aqueous residual and a small amount of gas composed mainly of CO_2. In the second stage, the SRP and the liquid residuals were gasified in supercritical water in the presence of Ru/Al_2O_3 catalyst for reaction times of up to 60 min for the SRP at 500 °C, 30 MPa. With the catalyst, carbon gasification efficiencies and methane selectivity increased with increasing reaction time. Overall, SRP from the Na_2CO_3 pre-processing route produced 51% more hydrogen and 61% more methane than the original sawdust under identical reaction conditions. The cumulative yields of methane and hydrogen were 57.1 mol/kg, 42.5 mol/kg and 47.7 mol/kg, from Na_2CO_3, Nb_2O_5 and neutral pre-processing routes, respectively. The combined yield of the two gases from direct SCWG of the original sawdust was 24.6 mol/kg. The entire process may re-present a step-change in future energy production from biomass as the products from the first stage can be used as feedstocks for various other biomass conversion technologies.

Key words: hydrothermal biomass pre-processing catalytic hydrothermal gasification, methane, hydrogen

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1.0. Introduction

The proposed wet biomass bio-refinery agenda appears to be skewed towards biochemical production of biofuels based on anaerobic digestion. However, thermochemical processing of biomass will play a significant role either as a separate industry or in tandem with the biochemical programme, towards achieving the goals of biomass-based chemical feedstocks and energy production. Advantages of thermochemical processing include fast reaction rates, complete conversion of biomass and the development and use of selective catalysts. Among the thermochemical processes, supercritical water gasification (SCWG) of biomass feedstocks has the advantage of high gasification efficiencies at moderately low temperatures [1]. Different types of biomass and biowastes, both wet and dry, can be used as feed for the production of fuel gases and through the process. However, research has shown that carbohydrate-rich biomass types are much more readily converted than biomass with rich fractions of proteins and lipids [2-3]. Catalytic hydrothermal gasification is a growing research area for synthetic natural gas (SNG) production from biomass. Methane and hydrogen are clean energy carriers for the future; while methane produced from biomass can readily be utilized in existing facilities, hydrogen is the energy carrier of choice in fuel cells.

Torrefaction of biomass has been developed to produce bio-coal with higher calorific value and more uniform thermal behaviour than the original biomass [4-7]. The process removes volatile components of biomass including moisture, carbon monoxide, carbon dioxide, simple carboxylic acids (formic, acetic and lactic acids), hydroxyacetone, furfural, methanol, hydrogen sulfide [6, 8]. Biomass upgrading via a torrefaction-type process in hydrothermal media appears to have potential benefits, particularly for wet wastes. Recently, Wood [9] investigated the influence of different pre-processing methods to produce supernatant liquor from activated sewage sludge prior to hydrothermal gasification. The author concluded that the supernatant obtained from alkaline pre-treatment produced the best yields of hydrogen gas compared to neutral and acid pretreatment. Onwudili and Williams [10-11], in a one-stage direct process, also suggested that sodium hydroxide was able to degrade different types of biomass, producing biomass-alkali liquor that was suitable for hydrothermal gasification, yielding mainly hydrogen and some methane. Jin et al. [12] also demonstrated the potential of producing chemicals such as acetic and formic acids via alkaline hydrothermal biomass processing. In addition, many researchers have investigated the supercritical water gasification of waste biomass liquor from various biomass-based industries [13-17]. For instance, black liquor containing lignin derivatives and high content of alkali wastes is a byproduct in pulping process and contains about 90% COD of the pulping wastes. Gou et al. [13] gasified alkaline black liquor containing 7.8wt% solid material in supercritical water in a continuous tube flow reactor at the pressure of 22.5 MPa and temperatures of 650 °C and 750 °C. They obtained gasification efficiency and carbon gasification efficiency of 123% and 88%, respectively, along with complete removal of COD.

Ruthenium- and nickel-based catalysts have been well researched for the production of combustible gases from biomass via hydrothermal processing [18-21]. Extensive work has been carried out by Osada et al. [22-25] using ruthenium catalyst for methane and hydrogen production from biomass SCWG, including the influence of sulphur on gasification efficiencies. For instance, Osada et al. [25] found that catalyst poisoning ability by sulfur could depend on the feed material e.g. the presence of sulfur affected the SCWG of 4-propyl phenol by inhibiting C-C bond breaking but not that of formaldehyde. Chakinala et al [20] found that aqueous fractions of bio-oil derived from biomass pyrolysis, could be selectively converted to hydrogen gas using a selection of catalysts and catalyst supports in supercritical water. Ruthenium-based catalysts gave the best conversion and the selectivity for hydrogen gas depended on concentration of organic components in the aqueous fractions. In addition, there has been an indication that ruthenium-alumina catalyst has the potential to catalyze both methanation and methane-reforming reactions [26]. In this present study, a two-stage hydrothermal process is investigated for the supercritical water gasification of wood sawdust as a real biomass. The main aim of the research is to investigate the influence of pre-processing a sample of sawdust in different subcritical water media on the products of its SCWG. The original sawdust will be pre-processed in subcritical water and with the addition of niobium pentoxide (as solid-acid catalyst) and sodium carbonate (as alkaline catalyst). The original sawdust and the solid recovered products from the pre-processing stage will be characterized and individually reacted in supercritical water in the presence of ruthenium-alumina catalyst. In addition, the aqueous liquid residuals obtained after the different pre-processing routes will also be gasified under similar experimental conditions. The results of this research may contribute to the development of the thermochemical bio-refinery for the future.

2.0. Materials and Methods

2.1. Materials

Sample of sawdust was obtained from a UK timber company and a portion was taken and pulverized to 3 mm mesh size for the tests. Niobium (V) oxide (Nb_2O_5) and sodium carbonate (Na_2CO_3) were obtained from Sigma-Aldrich, UK and used as additives for sawdust pre-processing. Hydrated niobium (V) oxide and niobium-based compounds have been used as solid-acid catalysts for organic chemical reactions [27]. Reduced ruthenium (5 wt% loading) on alpha-alumina in powdered form was obtained from Sigma-Aldrich, UK and employed for the catalytic supercritical water gasification tests. Some of the characteristics of the catalyst include, particle size of >150 μm; BET surface area of 74.6 m^2/g; metal dispersion of 6.3%, pore volume of 0.2 cm^3/g and average pore size of 8.2 nm. Two batch reactors from Parr Instrument Co. USA were used. One was a 500 ml stainless steel reactor [3], which was used for the pre-processing of the sawdust and the second was a 75 ml Inconel reactor [10-11], used for the SCWG tests.

2.2. Methods

2.2.1. Pre-processing of sawdust

For the pre-processing stage, 50 g of sawdust was placed into the 500 ml reactor and 300 ml of distilled water added. Thereafter, 10 g of either sodium carbonate or niobium (V) oxide was added. For neutral pre-processing of sawdust, no additive was added. The reactor was sealed and purged for 5 minutes with nitrogen gas and then heated to 280 °C, 8 MPa Once the reactor reached 280 °C, the heating was stopped and reactor withdrawn and cooled to room temperature. The gas product from the pre-processing stage was sampled and analyzed on gas chromatographs as briefly described in sub-section 2.2.3 below. After the gas effluent was released, the reactor content comprising solids and liquid phases was quantitatively transferred into a beaker using copious amounts of distilled water. The mixture of solid and liquid residuals was filtered under vacuum, with continuous washing with distilled water until the colour of the resulting liquid became clear. Each aqueous liquid residual was made up to 600 mL each in a 1 L glass bottle and stored in a refrigerator until use. The solid filter cake, known here as solid recovered product or SRP, was transferred into a large Petri dish and dried to a constant weight at 105 °C. For the purpose of this paper, the following identities are used for samples; original sawdust was designated as SD, while solid products from Na_2CO_3, Nb_2O_5 and neutral pre-processing routes were denoted as SA, SB and SN, respectively. In addition, the corresponding liquid residuals were similarly designated as LA, LB and LN.

2.2.2. Procedure for supercritical water gasification tests

For the solid samples, 1.0 g of sample and 15 ml of distilled were added in the 75 ml reactor. Where catalyst was used, 1.0 g of Ru/Al_2O_3 powder was added and the reactor content mixed with a glass rod before the reactor was purge with nitrogen and sealed. The reactor was then placed in a heater and heated at a rate of 30 °C /min to 500 °C and 30MPa. Once the designated temperature was reached, the tests were held for either 30 min or 60 min in each case. One test on the SCWG of sawdust was run and stopped on reaching 500 °C (zero reaction time at designated reaction conditions). At the end of the test, the reactor was then withdrawn from the heater and rapidly cooled within 15 min to less than 80 °C by means of compressed air. On cooling to room temperature, the temperature and gas pressure were noted before gas sampling. The solid products/residues were collected on a filter paper after filtration and dried to a constant weight in an oven at 105 °C. In addition, 15 ml of each of the liquid residuals was each reacted under identical catalytic SCWG conditions. Each test was carried out 2 to 3 times to check for reproducibility, with standard deviations of less than 5 %.

2.2.3. Gas analysis

The pressure gauge reading showed that the gas effluents from the gasification tests exerted pressures of between 5-23 bar depending on the reaction conditions. The gas effluents were analyzed off-line with a system of gas chromatographs [9]. Briefly, the gas samples were analysed using three packed column gas chromatographs using standard gas mixtures as external standards. 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. Quantitative gas analysis was carried out using external standard method. Three separate standard gas mixtures containing 1% each of hydrogen, oxygen, CO, CO_2 and the hydrocarbon gases in nitrogen were used for standard calibration. Sample injection volumes were adjusted accordingly for analysis within the linear working range of the gas chromatographs. 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.

2.2.3. Analysis of solid products/residues

Ash determination was carried out for the sawdust [SD], solid recovered products [SA], [SB], [SN] and the solid residues from the second-stage supercritical water gasification tests. In the procedure, between 0.25 g and 0.5 g of oven-dried sample was placed in a clean dried, pre-weighed porcelain crucible and ashed overnight (20 hours) at 575 °C in a muffle furnace [28].

The percent ash in the solid samples was calculated as;

% Ash =

$$\frac{(Weight\ of\ crucible + ash - Weight\ of\ crucible\ alone)\ x\ 100}{Dry\ weight\ of\ sample}$$

In addition, elemental analyses (CHNS) of the solid products were carried out using a Carlo Erba Flash EA 1112 compact analyser for automated determination [26]. The results of CHNS analyses are reported in this paper on dry-ash-free (daf) basis. The higher heating values (HHV) of the samples SD, SA, SB, and SN were estimated from their elemental compositions using the following equations [29-30].

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A$$

Where; C = wt% carbon; H = wt% hydrogen; S = wt% sulfur; O = wt% oxygen; N = wt% nitrogen, and A = wt% ash

2.2.4. Analysis of liquid residuals

A portion of the liquid products from the pre-processing stage as well as the liquid residuals from the gasification tests were analyzed for total organic carbon (TOC) and inorganic carbon (IC) contents. These were used to compute the carbon balance closures for these experiments. The instrument used was a Hach-Lange IL550 TOC-TN analyzer fitted with two NDIR held at 800 °C and was operated in the differential TOC determination mode [26]. The procedure was standardized using 1 M glucose solution. The measured TOC of the glucose solution was within 98% of the calculated value. The pH of the aqueous residuals was measured with a Hanna 211 Instrument.

3.0. Results and Discussions

3.1. Products from sawdust pre-processing

Table 1 presents the yields of products on mass-basis and the carbon balances from the pre-processing of the sawdust sample at 280 °C and 8 MPa. This approach has been used since it would be difficult to estimate the contribution of water as a reactant in the formation of products. In this present study, the mass of aqueous products was calculated by difference; hence the total yields of 100%. However, since the sawdust was the main source of carbon during these processes, a much better accounting of products distribution would be achieved by monitoring the distribution of the carbons in the feed. Both the total organic carbon (TOC) and inorganic carbon (IC) contents of the aqueous phases have been used, thereby taking account of the contribution of sodium carbonate in the sample of LA. Detailed analysis showed that LA contained 7.24 g of carbon as TOC and 1.08 g as IC. Considering that 10 g of sodium carbonate, containing 1.13 g of carbon was used, the 95.6% recovery of inorganic carbon was reasonable.

The inorganic carbon contents in both LB and LN was less than 0.02 g confirming that sodium carbonate was the source of IC in LA. The pH of the liquid residuals were 7.88 for LA, 2.18 for LB and 2.15 for LN; these pH values indicate that both neutral and Nb_2O_5 pre-processing routes produced acidic liquid residuals, which could result from the presence of simple organic acids such as acetic and lactic acids [12, 31-33]. The liquid residual LA, from the alkaline pre-processing appeared darker and contained more carbon than those from either the Nb_2O_5 or neutral pre-processing, according to TOC results. This agrees with the work of previous research which showed that alkali metals have a great tendency to solubilize biomass materials under subcritical water conditions [9-10].

With respect to carbon distribution, Table 1 shows that only a small fraction (< 2%) of the carbon in the feed was obtained in the gas products during sawdust pre-processing, with an average of more than 60% in the solid phase. The highest yield of carbon in the solid recovered product was obtained when niobium pentoxide was used, which could be related to the dehydrating effect of the solid-acid [27]. A similar dehydrating effect could be responsible for the yields obtained from and carbon content of SN. On the other hand, the presence of sodium carbonate led to increased leaching of carbon in the sawdust into the aqueous phase; hence SA has the lowest yield and content of carbon compared to SB and SN. Table 1 also shows that the material balance of the sodium carbonate pre-processed sawdust retained much of the sawdust as liquid and solid products. In contrast, the use of Nb_2O_5 and neutral pre-processing routes led to slight formation of ethyl acetate oily products. Qualitative analysis of these oily liquids on a GC/MS found that they contained mainly furfural and substituted furfurals. The amount of the ethyl acetate -soluble product was determined by liquid extraction with ethyl acetate followed by gentle nitrogen blow-down to obtain a jelly-like material. The carbon content of these materials was determined using the elemental analyzer described earlier. Hence, the liquid phase reported on Table 1 is the sum of both the aqueous-phase and ethyl acetate-soluble phase. However, the material balances for Nb_2O_5 and neutral pre-processing methods were still lower compared to Na_2CO_3 pre-processing route, possibly due to loss of volatile components during sample handling.

The proximate and ultimate compositions as well as the calorific values of the original sawdust and recovered solid products from sawdust pre-processing are presented in Table 2. Although biomass is variable feedstock, the use of standard methods of proximate and elemental analyses will enable comparison of the results from this pine wood sawdust sample with those of other biomass feedstocks. Sawdust pre-processing under the different hydrothermal conditions led to an increase in the carbon/oxygen ratio in the solid recovered product. Consequently, there was an increase in the calculated higher heating values (HHV) of the solid recovered products compared to the original sawdust as shown in Table 2. Both neutral and Nb_2O_5 pre-processing routes led to approximately 35% increase in HHV in relation to original sawdust. This is almost twice the value (ca 20%) reported by Prins et al. [7] from the torrefaction of wood, which may suggest an improvement of hydrothermal pre-processing over torrefaction with respect to energy densification of biomass. These authors however, found that conventional gasification of the torrefied wood sample proved to be slightly more efficient than untreated wood using an entrained-flow gasifier. More importantly, they found that there was an increased conservation of the chemical exergy in the gasification product gas from torrefied wood due to the loss of some volatile components during the torrefaction process

Fig. 1 shows the pictures of the solid recovered products and the liquid residuals from the pre-processing of sawdust. The solid recovered product from Na_2CO_3 pre-processing appears lighter than the products from the Nb_2O_5 or neutral pre-processing routes. The striking similarities between SB and SN are conspicuously depicted in the TGA and DTG diagrams displayed in Fig. 2 for each of the solid samples. These may indicate the similarity in the degree of depolymerization of the two solid samples. SB and SN have the wider DTG dips which showed a much longer degradation window, which may indicate the presence of different biomass fractions and degradation products compared to SA and SD. In contrast, SA showed the sharpest dip, indicating a uniform degradation pattern, which in turn indicated that the solid recovered product consisted of similar thermally degrading fractions or products. SD showed a small early shoulder often due to the distinct degradation of hemi-cellulose and the large dip representing the overlapping degradation of cellulose and lignin. From the figure, it can be seen that the T_{max} for the decomposition of SA was at about 375 °C, while that of SD was approximately at 390 °C; hence these two samples have T_{max} values of less than 400 °C. In contrast both SN and SB have T_{max} points at slightly above 400 °C. This suggested that SA and SD were easier to thermally degrade than SN and SB. As shown on the table, neutral and Nb_2O_5 processing led to an increase in the proportion of fixed carbon in the solid recovered products. Literature shows that there is usually an increase in fixed carbon in the solid residue after torrefaction of different biomass samples [4].

Table 3 shows the yields (in mol/kg of sawdust) and compositions (in mol %) of gas products from the pre-processing of the sawdust sample. Carbon dioxide was the main gaseous product from these reactions, with over 80% of the total gas yield from each pre-processing method. Interestingly, the gas products from sodium carbonate pre-processing route contained only carbon dioxide, carbon monoxide and small amount of hydrogen.

In contrast, the gas products from the neutral and Nb_2O_5 pre-processing routes contained some hydrocarbon gases, although at very low yields. This observation suggests that the addition of Na_2CO_3 appeared to suppress the formation of hydrocarbon gases during the pre-processing stage. It would appear that different mechanisms were involved during alkaline, neutral and acidic pre-treatment processes. For instance, neutral and acid treatment of biomass mostly involved dehydration [27], while the use of alkaline additives led to biomass degradation to simple water-soluble molecules [10, 31-33]. Research has shown that hydrothermal degradation of biomass could proceed via two distinct routes depending on the reaction medium [10, 34]. Under acidic or neutral hydrothermal conditions, biomass readily degrades by dehydration leading to the formation of furfural and hydroxy furfurals with the release of simple molecules such as CO_2, CO, hydrocarbon gases and simple carboxylic acids, especially acetic acid [35]. Furfurals are the precursors for tar and char formation [10, 34, 36]. However, the presence of alkaline additives appears to suppress the dehydration route and provides a direct route for the formation of simple carboxylic acids in the form of carboxylates such as acetate and formate [10, 37].

3.2. SCWG of sawdust and solid recovered products

3.2.1. Non-catalytic SCWG

Table 4 presents the results of the supercritical water gasification of samples in the absence of a catalyst for 60 min reaction time at 500 °C. The maximum yield (25.1 mol/kg) of gas was obtained from the original sawdust sample, SD of which 46.6% was carbon dioxide. SA also gave gas yield of about 22 mol/kg, which was the closest to the yield from SD. This may suggest that the presence of sodium carbonate during the pre-processing stage to obtain SA did not profoundly alter the structure of the sawdust; indicating that the additive mainly acted to solubilize the sawdust in water.

Onwudili and Williams [9] suggested that sodium hydroxide could completely solubilize different biomass samples under hydrothermal conditions. The observation in this present study indicates that the ability of Na_2CO_3 to solubilize biomass was weaker than that of NaOH, and thus may require longer reaction time. The solid recovered product from the pre-processing with niobium pentoxide gave the lowest yield of gas. Part of the reasons for the low gas yield from SB, may be the low actual feed content in the sample, since the use of niobium pentoxide resulted in 28.5% ash content. However, it may also be the case that the presence of ash also prevented extensive gasification. Compared to the other sample, the gas yield from SB was far too low to have resulted from the high ash content alone.

3.2.2. Catalytic SCWG with Ru/Al_2O_3

Table 5 shows the yields of gas components obtained from the catalytic supercritical water gasification of the sawdust and the three solid recovered products in the presence of ruthenium-alumina catalyst. The results are presented in relation to reaction times of 30 min and 60 min, respectively, at 500 °C. For comparison, the gas yield from the SCWG of sawdust at 0 min is included in the table.

Compared with Table 5, it can be seen that there was a considerable increase in the yields of gas from the catalytic work compared to tests without the catalyst. Considering results obtained after 60 min reaction time, SA gave the highest gas yield of about 55 mol/kg, which is more than twice the gas yield without catalysts. In addition, carbon dioxide and methane gave very similar yields, with methane being slightly higher at 42.3% of the total gas yield. The methane yield from SA with Ru/Al_2O_3 increased nearly 3-fold compared to its yield without the catalyst, indicating the selectivity of the catalyst towards methanation. In addition, hydrogen yields also increased nearly twice with the catalyst from the same sample.

The tests conducted at 60 min reaction time gave higher gas yields than those at 30 min but the differences between total gas yields at both reaction times depended on sample-types. For instance, the yield of gas increased by 42.6% after a reaction time of 60 min for sample SA compared to 30 min. Meanwhile, the difference in reaction time only increased gas yields from SD by only about 14%. This suggests that the SCWG of the SD reached thermodynamic equilibrium quicker than the reaction of SA. Reactions of samples SB and SN gave gas yields generally closer to SD than SA at both reaction times. Interestingly, SB produced more hydrogen in the presence of the catalyst than did other samples.

Results suggest that methane yield increased at a faster rate than the rate at which hydrogen yield decreased (as a result of methanation). For example, hydrogen yield from SA decreased by nearly 9% whereas methane yield increased by 48.5% when reaction time was extended from 30 min to 60 min. In addition, the methane/hydrogen molar ratio was 1.6 after 30 min but increased to 2.6 after 60 min. Moreover, the cumulative yields of the two combustible gases increased by about 26% from 30 min to 60 min. Recently, Onwudili and Williams [26] showed that the same sawdust sample gave a hydrogen yield of 7.3 mol/kg, methane yield of 11.1 mol/kg and carbon dioxide yield of 10.5 mol/kg after 10 min at 500 °C using Ru/Al_2O_3 catalyst in the same reactor. The reported gas yields from glucose were lower that the gas yields in this present study. In addition, the single SCWG test carried out of SD at 500 °C for 0 min gave a total gas yield of only 29.7 mol/kg. These observations show that in general, reaction time can influence the yields of gasification products; these could involve both single gas-phase reforming and combined solid/liquid phase-gas phase reactions. The increase in total gas yields with extended reaction time suggests that the latter was occurring faster than the former; that is, increased overall solid/liquid phase gasification with time, and possibly followed by gas-phase reforming.

Of particular interest is the variation in the yields of methane and hydrogen from SA and SD, the original sawdust. In general, SA produced more gas than SD at both 30 min and 60 min reaction times. Using gas yields from SD as the background yields, it can be seen that methane from SA over SD increased by about 11% after 30 min and by 61% after 60 min. In contrast, the yield of hydrogen from SA over SD increased by nearly 52% after 30 min but by only 8.28% after 60 min. These results show that methanation was favoured at longer reaction times. However the amount of carbon dioxide present was probably the most important determinant of the extent of methanation. SD produced less hydrogen and methane but more carbon dioxide than SA. It could be argued that over-saturation of the reaction system and catalyst surface with carbon dioxide affected the reaction equilibrium and that prior removal of some carbon dioxide during pre-processing produced the right reaction environment for methanation. SA produced more methane than SB, SN and SD, indicating that the formation of this gas was not only influenced by activity of the ruthenium catalyst but also possibly by the hydrothermal reforming reactions of the components of the solid recovered products. Essentially, the general composition of SA was probably better for methane formation than those of SB, SN and SD.

3.2.3. Carbon balance from the SCWG of solid samples

The carbon balances for all the SCWG tests are presented in Table 6. The carbon balances have been computed based the carbon contents of the gas products, aqueous residuals and solid residues from the SCWG experiments. The mass of carbon in the gas was obtained from the mass of each carbon-containing gas component; the mass of carbon in the liquid residuals was obtained from the TOC and IC analyses; while the mass of carbon in the solid residues was obtained from the mass of solid residues produced and results of their elemental analyses on ash-free-basis. Cleaning the reactor with dichloromethane (DCM) after each experiment showed the presence of oil/tar, in test without catalyst or after 30 min reaction time in the presence of the catalyst, due to the observed brown – light yellowish colouration of the DCM aliquots. The analyses of the DCM extracts have not been included accounted for in this paper, since the proportion of oil formed could be estimated from the carbon balances computed with other three products (gas, aqueous residuals and solid residue).

The tests in the absence of catalyst gave the lowest set of carbon balances ranging from 83% to 87% because of the formation of oil. As expected, most of the carbon atoms from the sawdust were transformed to the char as solid residue, with up to 60 % carbon for SB and SN, The tests with the catalyst gave higher carbon balances and almost complete balance closures after 60 min catalytic reaction. Noticeably, the carbon balances after 30 min were lower for SA, SB and SN compared to the balances obtained after 60 min, but these differences can be attributed to the presence of oil at the shorter reaction time. This suggests that the catalysts either prevented oil formation or was able to convert any oil formed into gas. Hence, the catalyst did not prevent oil formation but was able to convert the formed oil into gas. The carbon balance for SD was over 98% both at 30 min and 60 min, which suggested that the reaction of the sawdust was faster than those of the solid recovered products.

Carbon gasification efficiency (CGE) values were obtained as follows;

$$\mathrm{CGE} = \frac{(C_{(gas)} + C_{IC\ (aqueous)}) \times 100\%}{\text{Carbon amount in the feed}}$$

Carbon gasification efficiency (CGE) values shown in Table 6 also reflect the trend in the conversion of the sawdust and solid recovered products during these SCWG tests. The results show that the catalyst enhanced the CGE values but even more so after 60 min. For instance, the SCWG of SA gave the highest CGE of 98.7%, followed by SD with a CGE of 94.5% after 60 min. CGE values of between 97 and 100 % have been achieved during hydrothermal gasification of biomass using ruthenium supported on different supports including carbon and rutile [21, 38-39]. Hence, the possible dehydrating effect on sawdust of neutral and Nb_2O_5 processing routes may have produced solid recovered products that were seemingly difficult to gasify. High turnover numbers (TON) indicate high catalytic performance in the feed conversion process and in this study the TON values were calculated on the basis of feed carbon conversion to gas [22]. Considering that the amount of ruthenium metal catalyst used in this work was approximately 1 mol% in relation to the feed carbon content for each of the SRP, the maximum theoretical TON would be ~100. The values of the TON in Table 6 show that the catalyst performance for the conversion of SA for the 60 min reaction approached the maximum with a value of 91.1, and was more than 70 for the other samples for the same reaction time. In addition, the TON values were higher with the reactions at 60 min compared to those at 30 min, suggesting increased productivity of the catalyst for solid phase – gas phase reactions with time. Osada et al. [22] reported a TON value of 89 for 5 wt% Ru/Al_2O_3 catalyst during supercritical water gasification of 0.1 g lignin at 400 °C for 15 min, which is comparable with the result of this work except that more catalyst per feed was used in their work.

3.3. SCWG of liquid residuals

Apart from CO and CO_2, most of the volatile organic compounds released during torrefaction of biomass are appreciably soluble in water [6, 8]. Similar water-soluble compounds could be evolved during hydrothermal pre-processing of sawdust but in this case, they would be trapped in the aqueous media. 20 mL portions of the liquid residuals, LA, LB and LN, obtained from the sawdust pre-processing stage, were each reacted at 500 °C. TOC analyses showed that more than 99% TOC removal was achieved from these liquid samples after zero min at 500 °C using Ru/Al_2O_3 catalyst; hence there was no need to use extended reaction times. Given that the liquid residuals were homogeneous aqueous solutions, the result obtained from the experiments were extrapolated for the total volume of liquid residuals obtained. Hence, the mass of each gas component was obtained from the equation;

$$\frac{mass\ of\ each\ gas\ component\ obtained\ x\ total\ volume\ of\ liquid\ residual}{volume\ of\ liquid\ residual\ reacted}$$

Similarly, the yield of each gas was obtained in mol/kg as follows;

$$\frac{mol\ of\ each\ gas\ component\ from\ the\ total\ liquid\ residual}{mass\ of\ solubilized\ sawdust\ in\ total\ liquid\ residual\ (Table\ 2)}$$

The yields of gas components both in the presence and absence of the ruthenium catalyst are shown in Table 7. Without the catalyst, the liquid residual from Na_2CO_3 pre-processing produced nearly twice as much hydrogen as the other two liquid residuals from Nb_2O_5 and neutral pre-processing routes. However, the three samples gave very similar low yields of methane of just about 0.5 mol/kg each. In each case though, carbon dioxide was the predominant gas in the absence of the catalyst. The results show that the Ru/Al_2O_3 catalyst has a prominent effect in the yields of the gases, particularly hydrogen and methane. For each of the liquid residuals, total gas yields nearly doubled in the presence of the catalyst, with more than 98% carbon gasification ratio in each case. Specifically, hydrogen yields increase about two-fold from both liquid residuals from Na_2CO_3 and Nb_2O_5 pre-processed sawdust. However, with liquid residual obtained after neutral pre-processing, hydrogen yield was about five times more in the presence of the catalyst compared to its absence. More interestingly, the yields of methane increased dramatically in the presence of the catalyst. For instance, both LB and LN produced in excess of 13 times more methane, while LA was even higher at 18.4 times more methane, in the presence of Ru/Al_2O_3 compared to its absence. These results again show that Ru/Al_2O_3 was capable of producing both methane and hydrogen from biomass [26].

3.4. Cumulative yields of methane and hydrogen

The cumulative yields of the overall SCW gasification of the products (solid recovered product and liquid residual) of each of three pre-processing routes were obtained by combining the yields (in mol/kg) of methane and hydrogen (target combustible gases). Fig. 3 shows that in the absence of the Ru/Al_2O_3 catalyst, similar total yields of methane were obtained from all three pre-processing routes, with the Na_2CO_3 pre-processing route giving slightly higher methane yield than the rest of the samples.

Also the Na_2CO_3 route gave much higher hydrogen yields compared to the other samples without the catalyst. With the ruthenium catalyst, there was a significant increase in the total yields of both methane and hydrogen from all the samples. Similar results were obtained from the Nb_2O_5 and neutral pre-processing routes but the Na_2CO_3-processed sample gave the highest total yields of hydrogen, and particularly of methane. The combined yields of both gases were 57.1 mol/kg, 42.5 mol/kg and 47.7 mol/kg, from Na_2CO_3, Nb_2O_5 and neutral pre-processing routes, respectively.

4.0 Conclusions

In this study, portions of a sawdust sample were separately pre-processed in subcritical water or with the addition of sodium carbonate or niobium pentoxide, resulting mainly in liquid and solid products. These products were gasified in supercritical water in the presence of a ruthenium-alumina catalyst using a batch Inconel reactor. It was found that the use of sodium carbonate as a pre-processing reagent for sawdust resulted in both solid and liquid residuals that produced the most methane and hydrogen during SCWG, compared to other pre-processing routes. In fact, the solid recovered product from the Na_2CO_3 pre-processing route produced 51% more hydrogen after 30 min reaction time and 61% more methane after 60 min, compared to the original sawdust sample. Experimental results showed that depending on the pH of the pre-processing medium, pre-processing of biomass in subcritical water media may be a viable process for obtaining high yields of fuel gases via thermochemical processes, in this case supercritical water gasification. In addition, the SCWG results indicate that the selectivity of the ruthenium catalyst (Ru/Al_2O_3) towards methane formation increased dramatically in relation to reaction time. Overall, the development of a torrefaction-type process under hydrothermal conditions may be highly advantageous in the following respects; (a) capturing the released volatile organic components of the biomass into a water-soluble fraction fit for SCWG in a continuously fed reactor; (b) producing mainly carbon oxides in the gas phase for easy separation and purification for industrial uses; (c) increasing the carbon/oxygen ratio in the solid product, thereby producing a richer energy-dense solid fuel as feedstock for direct use or for further thermochemical processing.

5.0. References

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Table 1: Product yields and carbon balance after pre-processing sawdust sample in different subcritical water media

Products yields				
Sample	**Solid (g)**	**Gas (g)**	**#Liquid Phase (g)**	**Total %**
Na_2CO_3 pre-processing	21.7	1.22	27.1	100
Nb_2O_5 pre-processing	26.8	1.23	22.0	100
Neutral pre-processing	25.1	1.04	23.9	100

Carbon balance				
	Solid Phase	**Gas Phase**	**Liquid Phase**	**% Carbon Balance**
Na_2CO_3 pre-processing	60.1	1.54	36.2	97.7
Nb_2O_5 pre-processing	66.5	1.36	25.1	93.3
Neutral pre-processing	64.8	1.54	25.7	92.7

= Liquid phase obtained by difference

Table 2: Proximate and ultimate compositions of sawdust and the solid recovered products after pre-processing

	Proximate composition				Calorific Value
Sample	**Moisture %**	**Volatiles %**	**Fixed Carbon %**	**Ash %**	**HHV (MJ/kg)**
Original Sawdust (SD)	5.62	81.4	12.6	0.38	22.1
SA	4.05	74.8	20.2	0.95	25.3
SB	0.16	40.8	30.8	28.2	29.4
SN	1.34	53.8	43.7	1.16	28.5
	Ultimate composition				
	C wt%	**H wt%**	**N wt%**	**O^{a} wt%**	**Carbon/Oxygen Ratio**
Original sawdust (SD)	46.9	5.49	0.31	47.3	0.99
SA	54.9	5.65	0.35	39.1	1.40
SB	68.8	4.87	0.43	25.9	2.66
SN	70.1	4.83	0.47	24.6	2.85

	Ultimate composition of solid samples				Products carbon balance		
	C wt%	**H wt%**	**N wt%**	**O^{a} wt%**	**Solid (wt%)**	**Liquid (wt%)**	**Gas (wt%)**
SD (Sawdust)	46.9	5.49	0.31	47.3	-	-	-
SA	54.9	5.65	0.35	39.1	60.1	36.2	1.54
SB	68.8	4.87	0.43	25.9	66.5	25.1	1.36
SN	70.1	4.83	0.47	24.6	64.8	1.54	25.7

	Products carbon balance			Ultimate composition of solid samples			
	Solid wt%	**Liquid wt%**	**Gas wt%**	**C wt%**	**H (wt%)**	**N (wt%)**	**O (wt%)**
SD (Sawdust)	-	-	-	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	1.54	25.7	70.1	4.83	0.47	24.6

	Products' carbon balance			Ultimate composition of solid samples			
	Solid (wt%)	**Liquid (wt%)**	**Gas (wt%)**	**C (wt%)**	**H (wt%)**	**N (wt%)**	**O (wt%)**
SD (Sawdust)	-	-	-	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	1.54	25.7	70.1	4.83	0.47	24.6

Table 3: Gas compositions and yields from sawdust pre-processing in different subcritical water media

	SD + Na_2CO_3		SD + Nb_2O_5		SD + Neutral	
Gas components	**Mol %**	**mol/kg**	**Mol %**	**mol/kg**	**Mol %**	**mol/kg**
Hydrogen	1.42	0.43	1.56	0.39	1.88	0.57
Carbon monoxide	17.9	5.4	11.1	2.8	13.4	4.04
Carbon dioxide	80.7	24.2	87.1	21.8	84.0	25.2
Methane	-	-	0.19	0.05	0.24	0.07
Ethene	-	-	-	-	0.11	0.03
Ethane	-	-	-	0.01	0.07	0.01
Butene	-	-	-	-	0.26	0.08
Totals	**100**	**30.0**	**100**	**25.0**	**100**	**30.0**

Table 4: Gas yields from non-catalytic SCWG of solid recovered products

Sample	**Reaction Time (min)**	**H_2 (mol/kg)**	**CO (mol/kg)**	**CO_2 (mol/kg)**	**CH_4 (mol/kg)**	**C_2-C_4 (mol/kg)**	**Total (mol/kg)**
SA	60	6.01	0.07	8.92	5.79	1.79	22.6
SB	60	3.30	-	5.11	3.46	0.64	12.5
SN	60	5.24	0.02	6.3	4.97	0.97	17.5
SD	60	6.26	0.04	11.7	5.44	1.61	25.1

Table 5: Gas yields from ruthenium-catalyzed SCWG of solid recovered products

Sample	Reaction Time (min)	H_2 (mol/kg)	CO (mol/kg)	CO_2 (mol/kg)	CH_4 (mol/kg)	C_2-C_4 (mol/kg)	Total (mol/kg)
SA	60	9.10	0.07	22.1	23.6	0.31	55.0
SB	60	13.5	0.09	17.3	15.3	0.14	46.3
SN	60	8.12	0.07	15.4	16.5	0.02	40.0
SD	60	8.12	0.08	15.4	16.5	0.03	40.1
SA	30	9.84	0.23	14.1	16.0	1.12	41.3
SB	30	9.71	0.05	14.9	12.9	0.01	37.6
SN	30	6.53	-	13.0	15.5	0.01	35.0
SD	30	6.52	0.08	16.3	14.5	0.17	37.6
SD	0	7.31	0.4	13.5	8.11	0.36	29.7

Figure 1

Figure 2

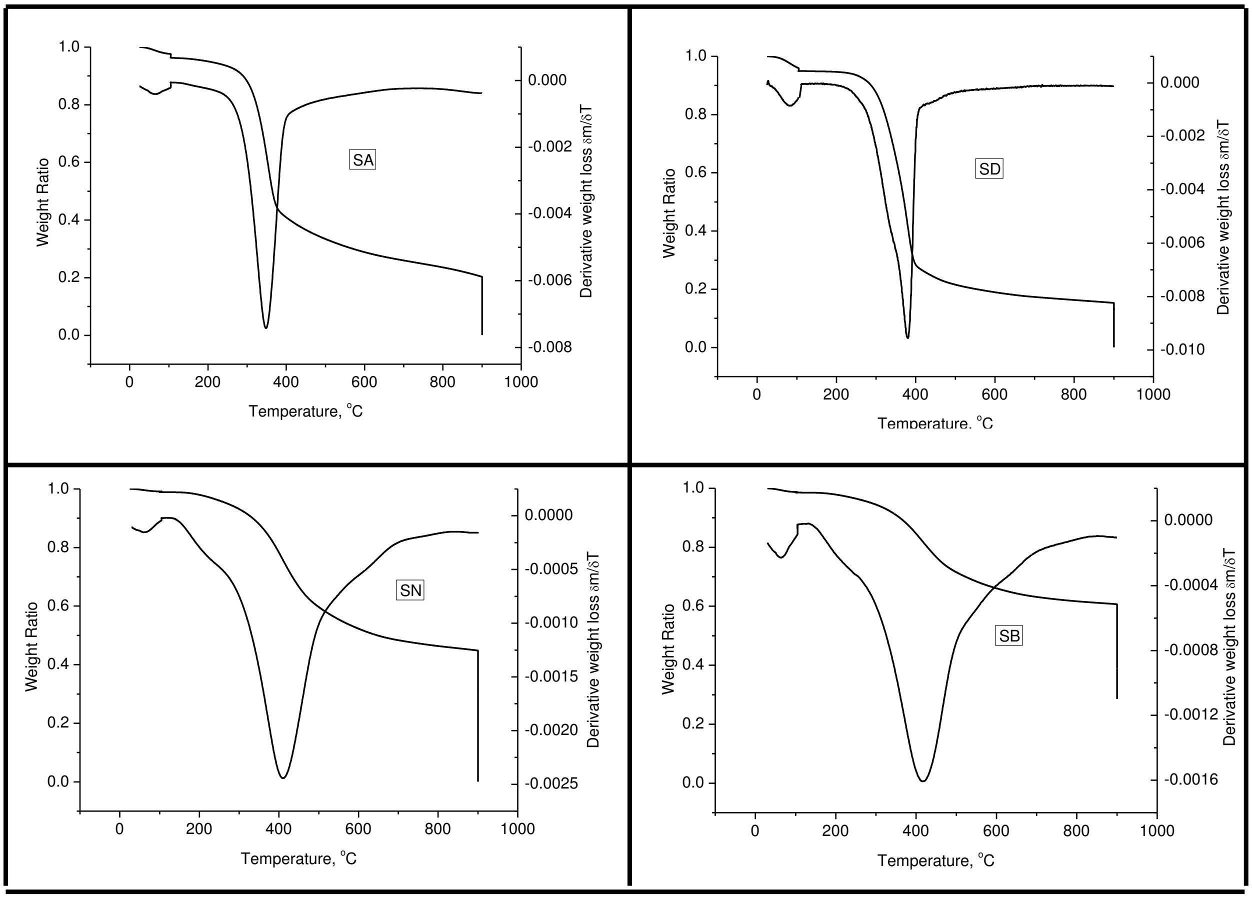
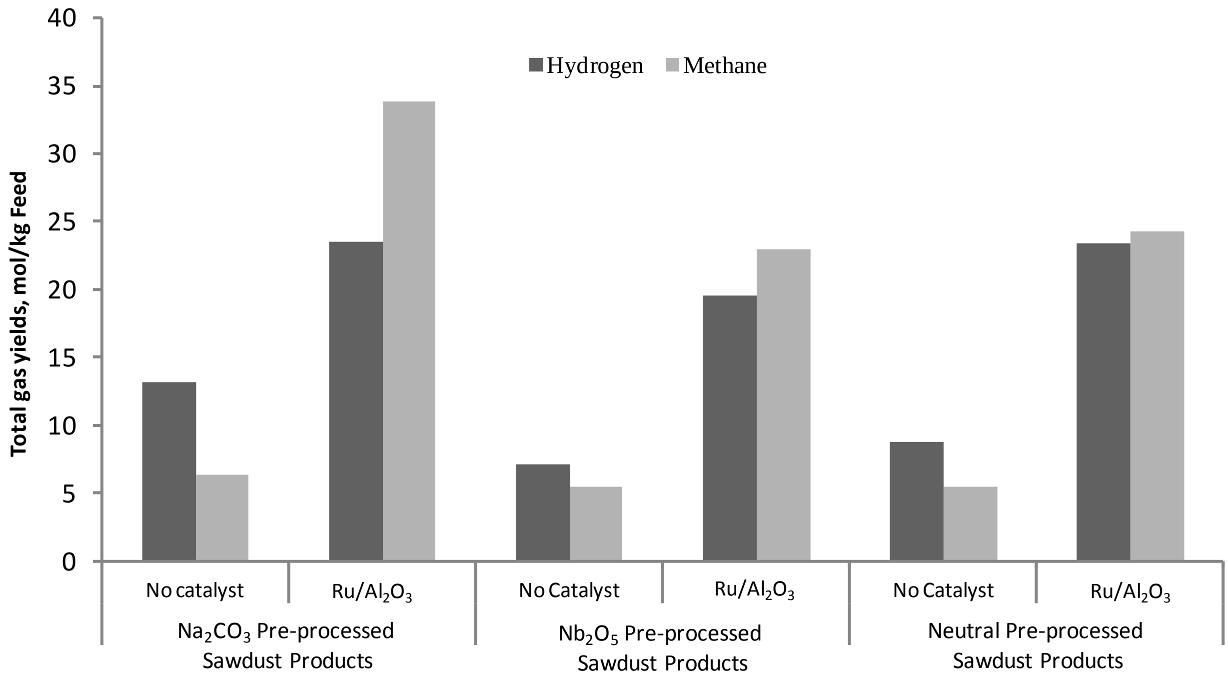

SA
SD
SN
SB
Weight Ratio
Derivative weight loss δm/δT
Temperature, °C
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
0.000
-0.002
-0.004
-0.006
-0.008
-0.010
0.0000
-0.0005
-0.0010
-0.0015
-0.0020
-0.0025
-0.0004
-0.0008
-0.0012
-0.0016

Figure 3



40
35
30
25
20
15
10
5
0
Total gas yields, mol/kg Feed
■ Hydrogen
■ Methane
No catalyst
Ru/Al$_2$O$_3$
No Catalyst
Ru/Al$_2$O$_3$
No Catalyst
Ru/Al$_2$O$_3$
Na$_2$CO$_3$ Pre-processed Sawdust Products
Nb$_2$O$_5$ Pre-processed Sawdust Products
Neutral Pre-processed Sawdust Products