promoting access to White Rose research papers



Universities of Leeds, Sheffield and York http://eprints.whiterose.ac.uk/

This is an author produced version of a paper published in **Journal of the Energy Institute**

White Rose Research Online URL for this paper:

http://eprints.whiterose.ac.uk/id/eprint/77988

Paper:

Waheed, QMK, Nahil, MA and Williams, PT (2013) *Pyrolysis of waste biomass: investigation of fast pyrolysis and slow pyrolysis process conditions on product yield and gas composition.* Journal of the Energy Institute, 86 (4). 233 - 241. ISSN 1743-9671

http://dx.doi.org/10.1179/1743967113Z.0000000067

White Rose Research Online eprints@whiterose.ac.uk

Pyrolysis of waste biomass: Investigation of fast pyrolysis and slow pyrolysis process conditions on product yield and gas composition

Qari M.K. Waheed, Mohamad A. Nahil and Paul T. Williams*

Energy Research Institute, University of Leeds, Leeds, LS2 9JT, UK

(Tel: #44 1133432504; Email: p.t.williams@leeds.ac.uk)

Abstract

High temperature fast pyrolysis of wood, rice husk and forestry wood residue was carried out in a laboratory scale fixed bed reactor. The results were compared with pyrolysis of the biomass samples in a different reactor under slow pyrolysis conditions. There was a marked difference in product yield depending on heating rate, for example, the gas yield from slow pyrolysis was, 24.7wt.% for wood, 24.06wt.% for rice husks and 24.01wt.% for forestry residue; however, for fast pyrolysis the gas yields were 78.63 wt.%, 66.61wt.% and 73.91wt.% respectively. There were correspondingly significantly lower yields of oil and char from fast pyrolysis whereas for slow pyrolysis oil and char yields were higher. The composition of the product gases was also influenced by the heating rate. In additional experiments the influence of pyrolysis temperature was investigated under fast pyrolysis conditions from 750 to 1050 °C. It was found that the increase in temperature increased overall gas yield and also increased hydrogen gas concentration with a decrease in CH₄, CO₂ and C₂-C₄ hydrocarbons. High gas yields of ~90 wt% conversion of the biomass to gas was obtained during the pyrolysis of biomass at 1050°C. Steam was also added to the fast pyrolysis system to enhance the hydrogen production. The amount of hydrogen produced was found to significantly increase in the presence of added steam.

Key words: Biomass; Pyrolysis; Heating Rate;

^{*}Corresponding author

Introduction

Biomass plays a very important role in the world energy system, especially for developing nations, accounting for approximately 38% of their primary energy supply¹. Annual global production of biomass is estimated at 220 billion tonnes². Because biomass is carbon neutral, there is increasing interest in the use of biomass to replace fossil fuels and thereby reduce the impacts of climate change. Combustion, pyrolysis and gasification are the three major thermochemical processes used to produce energy from biomass. Pyrolysis is the thermal degradation of biomass in the absence of oxygen to produce a carbonaceous char, oil and combustible gases. Biomass is mainly composed of cellulose, hemicellulose and lignin polymeric molecules and the process of pyrolysis results in these polymers breaking to produce shorter molecular weight compounds. These shorter molecules result in the formation of the oils and gases characteristic of pyrolysis of biomass. The proportion of the end products is highly dependent on the process conditions, particularly temperature and heating rate.³⁻⁹. Very slow heating rates coupled with a low final maximum temperature (e.g. 400 °C) maximises the yield of char. Moderate heating rates in the range of about 10 °C min⁻¹ and maximum temperatures of 600 °C gives an approximate equal distribution of oils, char and gases referred to as conventional pyrolysis or slow pyrolysis.⁸ Because of the slow heating rates and generally slow removal of the products of pyrolysis from the hot pyrolysis reactor, secondary reactions of the products can take place. Very high heating rates of about 100 °C/s at temperatures below 650°C and with rapid quenching lead to the formation of a mainly liquid product, referred to as fast or flash pyrolysis.⁹ At high heating rates and high temperatures the oil products quickly breakdown to yield a mainly gas product.

The influence of temperature and heating rate on the pyrolysis of biomass have been investigated in the literature, for example, Chen et al.⁴ investigated the effect of temperature on pyrolysis of cotton stalk, an increase in the gas content was reported with the rise in temperature. Williams et al.⁸ investigated the effect of temperature and heating rate on the composition of syngas from pyrolysis of pine wood. Increase in both temperature and heating rate showed an increase in overall gas yield. Using saw dust, Zhang et al.¹⁰ investigated the influence of pyrolysis temperature from 600°C to 1400°C on product yield and composition. They reported an increase in gas yield from 600°C to 800°C (30.9wt% to 65.3 wt%) and achieved a gas yield of 77.6 wt% at 1400°C. Zanzi et al.¹¹ performed rapid pyrolysis of birch wood, straw, straw pellets and olive waste in a free fall reactor from 800°C to 1000°C. Gas yield was reported to be 86 wt%, 85.5 wt%, 75.3wt% and 87wt% for straw, straw pellets, olive waste and birch wood respectively

In this paper, the influence of the process conditions of fast pyrolysis and slow pyrolysis of three different biomass samples was carried out in two different laboratoryscale fixed-bed reactors at 850 °C. The influence on product yield and gas composition was determined. In addition, for three biomass samples, fast pyrolysis was carried out at high temperatures of 750°C-1050°C, to determine the influence on gas yield and composition. Steam gasification of the wood biomass sample was also carried out to further enhance the gas yield, particularly hydrogen yield.

Materials and Methods

Biomass

Three different biomass samples were investigated, wood produced from saw dust, rice husk and a mixture of forestry wood residue of Meranti (*Shorea acuminate*) and Karas(*Aquilaria malaccensis*) tropical trees obtained from Malaysia. The size distribution of the biomass samples was between 2.8 and 6mm for wood, while for rice husk and forest residue biomass, particle size was between 1.4 and 2.8mm. A Shimadzu TGA-50 thermogravimetric analyser was used to determine the proximate analysis of the biomass samples and elemental analysis was carried out using a Carlo Erba Flash EA 11112 elemental analyser; the results are shown in table 1.

Reactor Systems

The fast pyrolysis reactor was constructed of inconel and was 60 cm long with 2.5 cm inner diameter. The reactor was heated using electrical furnaces with controlled heating rate and final temperature. Two N type thermocouples were installed in the middle of each furnace to monitor the temperature inside the reactor. Nitrogen, used as a purge gas, was injected from the bottom of the main reactor while the output gases exited the chamber from the top. The biomass sample was held in a water cooled chamber before being dropped into the reactor where fast pyrolysis took place at the desired temperature. Two condensers were connected to the output of the reactor to capture liquid oils in the gas stream. The first condenser was water cooled while the second condenser was cooled with dry ice. Glass wool trap was employed in second condenser to capture any low molecular weight oil vapours. Gas sample bags were used to collect the gas samples. A schematic diagram of the experimental system is shown in figure 1.

The repeatability of the experimental procedure was confirmed by performing five experiments under identical conditions. Product yield and gas composition were compared and were shown to be acceptable confirming the reliability and reproducibility of the reactor systems. During all experiments, the deviation in wt.% of gas, solid and oil was less than 3%. In terms of individual gases, the maximum deviation was less than 2vol%.

During fast pyrolysis experiments, 5g of biomass sample was placed inside the water-cooled chamber which maintained ambient conditions until the reactor reached the desired temperature. Once the desired temperature was achieved, the sample was dropped into the reactor. The biomass sample was immediately pyrolysed under fast pyrolysis conditions at temperatures up to 1050 °C, with an estimated heating rate of 300-500 °C s⁻¹. Volatiles were swept out from the top of the reactor using nitrogen as a carrier gas. Liquid oils were collected in the condenser system and gas was collected using a Tedlar gas sample bag. Additional experiments were carried out using the fast pyrolysis reactor to determine the influence of pyrolysis temperature of different biomass samples on the product yield and gas composition. Temperatures investigated were 750-1050 °C. Also for the wood biomass sample, steam was introduced into the lower reactor to produce high temperature steam pyrolysis conditions to determine the influence on product gas yield and composition. For 5g of biomass sample, around 5g of steam was injected at a steam to biomass ratio of 1. Water injected from the syringe pump was immediately converted into steam at high temperature inside the reactor and swept through the reactor by the nitrogen carrier gas.

The slow pyrolysis reactor was constructed of steel and was 250 mm long with 30mm inner diameter and continually purged with nitrogen. The reactor was heated using a tube furnace and heating rate, final temperature and hold time was controlled by an electronic controller using a K type thermocouple placed inside the reactor. A sample crucible held the biomass sample in the reactor. The reactor was heated to the

final temperature of 850°C at a heating rate of 10°C min⁻¹. Final temperature was maintained for 30 min. Condensers were used to condense the oils and condensable liquids consisting of water-cooled and dry-ice condensers. Gases were collected in a gas sample bag and were analysed off-line using gas chromatography technique. A Schematic diagram of the slow pyrolysis reactor system was shown in figure 2.

During slow pyrolysis experiments, 5g of biomass was placed in a sample crucible inside the reactor. The reactor was heated from ambient temperature to 850°C at a heating rate of 10 °C min⁻¹. Nitrogen was used as a carrier gas. Oils produced during slow pyrolysis were collected using the condenser system and gas was collected in the gas sample bag. The weight of char and liquid pyrolysis oils was determined from the weight of sample crucible and condenser system before and after every experiment.

Gas Analysis

The gases collected in the gas sample bag were analysed for hydrocarbons (C_1 - C_4) using a Varian CP-3380 gas chromatograph with a column packed with an 80-100 mesh Hysep with a flame ionization detector (GC/FID) and using nitrogen as carrier gas. Permanent gases (H₂, CO, N₂, O₂, CO₂) were analysed using a second Varian CP-3380 chromatograph comprised of two columns with two thermal conductivity detectors (GC/TCD). One column packed with a 60-80 mesh molecular sieve, was used to separate hydrogen, carbon monoxide, nitrogen, and oxygen; and the other column packed with 80-100 mesh Hysep was used to analyse carbon dioxide; the carrier gas used was argon.

In order to calculate the amount of gas in grams, the area obtained for each gas from gas chromatography was compared with the area of calibration gas and the percentage of each gas in the mixture was calculated. As a known quantity of nitrogen was introduced into the reactor during the experiment, the total gas volume could be calculated. Using the volume percentage of each gas and the total gas volume, the number of moles for each gas were calculated. The number of moles of each gas were converted into grams using their molecular weights and the total mass of the gas mixture was obtained from the sum of all individual gases.

Results and Discussion

Product yield from fast pyrolysis and slow pyrolysis of biomass at 850 °C

Figures 3, 4 and 5 show the comparison of product yield and gas composition from the fast and slow pyrolysis of biomass in relation to the wood, rice husks and forestry residue respectively. The product yield from slow pyrolysis of the biomass samples at 850°C was drastically different from that of fast pyrolysis. As shown in figure 3, for the wood, only 24.7wt.% gas yield was obtained from slow pyrolysis as compared to 78.63 wt.% from fast pyrolysis. For rice husk only 24.06wt.% gas yield from slow pyrolysis was obtained in contrast of 66.61wt.% from fast pyrolysis as shown in figure 4. For forestry residue (figure 5), only 24.01wt.% of biomass was recovered as gas from slow pyrolysis while 73.91wt.% of biomass was converted into gas from fast pyrolysis. The product yield from pyrolysis of biomass mainly depends on the process conditions of temperature and heating rate, but also the residence time for which the volatiles stay at that final temperature. Zanzi et al.¹² investigated the fast pyrolysis of wood and agricultural residues using a free-fall reactor to determine the effects of heating rate, temperature, particle size and residence time on the product distribution and gas composition. They reported that higher heating rates favoured the cracking of tar and hydrocarbons into gaseous products. Also, higher heating rates lead to lower char and higher gas yield during fast pyrolysis. In contrast, during slow pyrolysis, longer residence time favours increased secondary reactions of recondensation and repolymerization of volatiles and hydrocarbons present in the reactor which increases the formation of char.¹²

The majority of the products obtained from slow pyrolysis of the three biomass samples were volatiles and tars which were collected in the form of liquid oils and an aqueous phase. The yield of liquids from slow pyrolysis was 59.4, 40, and 50.4wt.% as compared to 12.31, 10.22 and 16.98wt% from fast pyrolysis for wood , rice husk and forestry residue respectively.

Low char yields were obtained during fast pyrolysis when compared with the results of slow pyrolysis. For fast pyrolysis char yield from wood was 9.63wt.% compared with 15.4wt.% for slow pyrolysis. Rice husks have a high ash content which contributes, together with the char, to a high solids yield, which was 16.21wt.% for fast pyrolysis and 37.2wt.% for slow pyrolysis. Forestry residue char yield was similarly higher for slow pyrolysis (23.6 wt.%) compared to fast pyrolysis (7.69wt.%). Onay et al.¹³ performed a comparative study of slow and fast pyrolysis of rapeseed biomass and also reported that for slow pyrolysis experiments 18.3wt.% of char was produced.

When the solid yield shown in figures 3, 4 and 5 were compared with the proximate analysis results in table 1, the difference was primarily due to the method of calculation as the results presented in table1 are on ash-free basis while the results in figures 3, 4 and 5 are presented including ash. Furthermore, the proximate analysis was carried out at 25 °C min⁻¹ up to a final temperature of 935°C as compared to 850°C at 10°C min⁻¹. The difference in other factors including the design of reactor and other process conditions such as residence time may also have affected the solid yield.

Gas composition from fast pyrolysis and slow pyrolysis of biomass at 850 °C

In terms of gas composition, figures 3, 4 and 5 show that the main gases produced during both fast and slow pyrolysis were CO, CO₂, H₂, CH₄ and C₁-C₄ hydrocarbons. The figures also show that during fast pyrolysis, higher ratios of CO:CO₂ were found with fast pyrolysis compared to slow pyrolysis. During the fast pyrolysis of various agriculture residues, gas composition reported by Zanzi et al.¹¹ also showed a high CO:CO₂ ratio for fast pyrolysis of the biomass. In all thermochemical processes, thermal decomposition of biomass is the primary step while cracking, gas to gas and gas to solid interaction takes place during secondary reactions. Secondary reactions occur due to the interaction among the volatiles and between the volatiles and solid residue.

Effect of temperature on product yield from fast pyrolysis

The influence of temperature over the range of 750 – 1050 °C on product yield was investigated using the fast pyrolysis reactor and the results are shown in Table 2. The gas yield increased with the rise in temperature for all of the biomass samples under fast pyrolysis conditions with a corresponding decreasing trend in char and oil yield. For example, gas yield was increased from 79.36wt% to 91.71wt% for wood, from 76.77wt% to 98.36wt% for rice husk and for forestry residue, the overall gas yield increased from 63.56wt% to 90.80wt% when the fast pyrolysis temperature was increased from 750°C to 1050°C. In terms of highest gas yield on an ash-free basis (Table 2), 98.36wt.% gas was obtained from rice husk, followed by 91.71wt.% from wood. The gas yield from forestry residue was 90.80wt.%, slightly less than the gas yield obtained from wood at 1050°C.

The results obtained clearly indicate that the gas yield increased with the rise in temperature. In addition, the very high pyrolysis temperature not only leads to the instantaneous decomposition of oils into gaseous products but also the secondary char forming reactions are reduced at high temperature. As suggested by Shuangning et al.¹⁴, yield of gaseous products from fast pyrolysis of biomass depends on the heating rate, final temperature as well as the time interval for which biomass sample is exposed to that higher temperature. Dupont et al.¹⁵ used an entrained flow drop reactor to investigate the effect of temperature on fast pyrolysis of commercial beech wood. They investigated the fast pyrolysis at high temperature reported that more than 75wt% of biomass was converted into gas at 1000 °C. Sun et al.¹⁶ investigated the effect of temperature on fast pyrolysis of rice husk and saw dust in an entrained flow reactor. Their investigated temperature range was from 700 °C to 1000 °C. They reported that 89.2 wt% of sawdust was converted into gaseous products at 1000°C. Zanzi et al.¹¹ investigated the fast pyrolysis of various biomass samples in a free fall reactor at 800°C and 1000°C. They reported that the 86 wt%, 85.5 wt%, 75.3 wt% and 87 wt% of straw, straw pellets, olive waste and birch wood were converted into gas at 1000°C respectively

During fast pyrolysis experiments, samples were instantaneously exposed to the higher temperature (750°C -1050°C). This leads to very high heating rates and short residence time as the products of pyrolysis are quickly swept from the reactor by the nitrogen purge gas. Due to the rapid heat transfer, instantaneous devolatilization of biomass particles takes place inside the reactor. Tar and volatiles evolved from the biomass particles released into the surrounding gas phase while the surrounding gases diffuse into the biomass particles.¹⁵ Although the exact mechanism of biomass pyrolysis is not clear, several kinetic models of varying complexity have been developed.¹⁵⁻¹⁹

However the overall process can be explained using empirical models, such as presented by Kilzer and Briodo et al.²⁰ According to their model, lignocellulosic materials follow one of two available pathways. At higher temperature, tar formation is favoured by the low activation energy of the reaction while at low temperatures, cellulose in the biomass sample converts into dehydro-cellulose which is converted into char and syngas. However in another kinetic model,²¹ Briodo explain the conversion of cellulose into "active-cellulose" which subsequently decomposes to either tar or char and gases. After initial devolatilization, secondary gas phase reactions between the permanent gases and tar add towards the overall gas yield. Furthermore, thermal cracking of these hydrocarbons and tar contribute significantly towards the increase in gas yield.

Effect of fast pyrolysis temperature on gas composition

The gas composition for the fast pyrolysis of the biomass samples in relation to temperature of pyrolysis from 750-1050 °C are shown in Table 3. The results show that there was small increase in CO and a decrease in CO₂ with increased pyrolysis temperature. The hydrogen yield was significantly increased with temperature and there was a consequent decrease in methane and C₁-C₄ hydrocarbons. Dupont et al.²² investigated the fast pyrolysis of pine and spruce wood in an entrained flow reactor. They reported around 55 vol % CO along with 23 vol % H₂ at 950°C. Also around 5 vol % CO₂ and 15 vol % CH₄ along with less than 10 vol % lighter hydrocarbons were observed in the gas mixture. Chen et al.⁴ performed the fast pyrolysis of cotton stalks in a fixed bed reactor. They reported the increase in hydrogen concentration with the rise in temperature, from 27.74 vol% H₂ at 750°C and 36.66 vol% of H₂ at 950°C. Zanzi et al.¹⁰ performed the rapid pyrolysis of straw, straw pellets, olive waste and birch wood at

 800° C and 1000° C. Higher hydrogen and CO concentrations were reported with the rise in temperature. However a decrease in concentrations of CO₂, CH₄ and other hydrocarbons was reported.

Increase in CO concentration with the simultaneous decrease in CO_2 concentration and char at higher temperature indicate the increase in forward Boudouard reaction (Eq. (1)). As reported by Yang et al.²³ this reaction is favoured at higher temperatures.

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = 172 KJ/mol$$
 (1)

In their study of pyrolysis of palm oil waste, they had pointed out that not only the Boudouard reaction accounts for the increase in CO concentration but thermal breakdown of tar also leads to the formation of methane, hydrogen, water and lighter hydrocarbons. Furthermore, reaction between CO_2 and CH_4 (Eq. (2)) is also favoured at low pressure and high temperature. This might be one of the possible explanations for the decrease in CO_2 and CH_4 concentration with the increase in temperature during the pyrolysis.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H = 247 \text{KJ/mol}$$
 (2)

During pyrolysis, water comes from both initial biomass moisture and gas phase reactions.²⁴ This water can react with the char, resulting in the water gas reaction (Equation (3)). This water can also react with other gases such as methane to perform the steam reforming reaction (Equation (4)) and also water gas shift reaction (Equation (5)). However the concentration of water molecules was not high enough to bring about large changes in gas composition.

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = 131.3 \text{kJ/mol}$$
 (3)

$$CH_4 + H_2O \rightarrow CO + 3H_2 \Delta H = 206.4 \text{kJ/mol}$$
 (4)

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \Delta H = -41.2 kJ/mol$$
 (5)

Effect of steam on the fast pyrolysis of biomass

The pyrolysis/gasification of wood biomass sample was carried out in the presence of steam at temperatures of 750 °C, 850 °C, 950 °C and 1050 °C to determine the influence of steam on product gas yield, but in particular on hydrogen gas yield. Less than 5 wt.% of solid was obtained from all steam pyrolysis experiments The results are shown in Table 4. The presence of steam would increase the gasification type reactions of the biomass sample (e.g. equations (1)-(5)). It is evident that the increase in temperature showed an increase in hydrogen production. Comparison of the H₂ gas composition for wood pyrolysis in Table 3 and in the presence of steam (Table 4) shows that the hydrogen in the gas increased from, for example, 26.91 vol.% in the absence of steam to 44.13 vol.% in the presence of steam at the reaction temperature of 750 °C. As the temperature was increased in the presence of steam, there was a small but significant decrease in H₂. It can be suggested that the addition of steam into the reaction system had a positive effect in terms of hydrogen production. In terms of CO gas yield, there was a decrease in the presence of steam compared to the fast pyrolysis results shown in Table 3.

It can be assumed that the addition of steam has geared the water gas shift reaction (Equation (5)). This is evident from the increase in hydrogen concentration and corresponding decrease in CO concentration. It is evident from the decreased methane concentration that the endothermic methane reforming reaction (Equation (4)) was also

favoured by the presence of steam. This also contributed towards the enhanced CO and H_2 concentration at higher temperatures.

$$C_m H_n + n H_2 O \rightarrow nCO + [n + (m/2)] H_2$$
(8)

As illustrated in Equation (8), steam reforming of hydrocarbons also takes place at higher temperature; this statement can be supported by the decrease in C₂-C₄ hydrocarbons concentrations when the fast pyrolysis results were compared with steam gasification results at any given temperature. Yan et al.²⁵ performed the steam gasification of char produced from pyrolysis of saw dust produced at 500°C. They investigated the effect of temperature on gas composition of char from 600°C to 850°C. With steam flow rate of 0.165g/min/g of biomass char, they received 52.41vol% H₂, 14.03vol% CO, 27.60vol% of CO₂, 1.74vol% CH₄ and less than 5vol% C₂-C₄ hydrocarbons at 850°C. They also suggested that at higher temperature, water gas reaction, Boudouard reaction and steam methane reforming reaction has a significant influence on gas composition.

The hydrogen gas yield can be expressed in terms of millimoles of hydrogen per gram of biomass sample. For wood pyrolysis in the absence of steam, hydrogen yield increased from 4.66 mmoles/g of biomass at 750°C to 8.77 mmoles/g at 850°C. the highest hydrogen yield of 11.44 mmoles/g was obtained at 950°C, however further increase in temperature from 950°C to 1050°C led to a slight decrease in hydrogen yield with a determined value of 10.01 mmoles/g of biomass. In the presence of steam, hydrogen yield increased from 14.58mmoles H₂ g⁻¹ biomass at 750°C to 21.35mmoles H₂ g⁻¹ at 850°C however, with the further increased in temperature to 950°C and 1050°C, hydrogen yield slightly decreased. The slight decrease in hydrogen yield at

higher temperature suggests that the forward water gas shift reaction (Equation (5)) is favourable at lower temperatures. Higher temperature may lead to the reverse water gas shift reaction which leads to an increase in CO concentration and decrease in hydrogen concentration.

Potential hydrogen production

Potential hydrogen production is an indicator of the percentage of the elemental hydrogen from the biomass is converted into the gaseous hydrogen in the syngas. Potential hydrogen production for all three biomass samples was calculated on an ashfree basis for fast pyrolysis of biomass in the absence of steam (Figure 6). As shown in figure 6, it is clear that the temperature has a positive effect on potential hydrogen production, for example, in the case of wood, increasing from 16.68 wt% at 750°C to 34.87 wt% at 1050°C for wood. For rice husk, potential hydrogen production increased from 17.72wt.%, to 30.63wt.%, 40.41wt.% and to 36.18wt.% with the rise in temperature. For forestry residue, potential hydrogen production increased from 13.47wt.% at 750°C, to 28.56wt.% at 850°C, to 35.76wt.% at 950°C, however it decreased slightly to 33.02 wt.% at 1050°C. The increasing tendency in potential hydrogen production for wood pellets as the temperature was raised from 950°C to 1050°C is most likely due to the thermal cracking of various tar components in the gas phase at the higher temperature of 1050°C. The nature of these tar components might be different from the tar produced from rice husk and forestry residue owing to the different chemical nature and physical structure of wood biomass. Higher potential hydrogen production at high temperature can be explained on the basis of enhanced overall yield of syngas. This enhanced yield of syngas is mainly due to the secondary reaction taking place inside the reaction chamber and the thermal cracking of tar and

other hydrocarbon leads to the higher syngas yield and in turn higher conversion of the hydrogen in the biomass to higher hydrogen yield. Rice husk showed the highest potential hydrogen production of 40.41wt% at 950°C while pyrolysis of forestry residue resulted in 35.76wt% of potential hydrogen production at 950°C.

Conclusions

The influence of process parameters on the yield and composition of products and gases from the fast and slow pyrolysis of waste biomass has been investigated. In addition, the influence of temperature and the presence of steam on the yield of products and gas composition from fast pyrolysis was investigated. The following conclusions can be drawn from the study.

- Slow pyrolysis of the wood, rice husks and forestry residue was markedly different from that of fast pyrolysis. For wood, only 24.7 wt.% gas yield was obtained from slow pyrolysis as compared to 78.63 wt.% from fast pyrolysis. For rice husk 24.06 wt.% gas was obtained, for forestry residue 24.01 wt% gas was obtained compared to 66.61 wt.% and 73.91 wt% from fast pyrolysis respectively. There were correspondingly lower yields of oil and char from fast pyrolysis whereas for slow pyrolysis oil and char yields were higher.
- The composition of the product gases was also influenced by the heating rate. The main gases produced during both fast and slow pyrolysis were CO, CO₂, H₂, CH₄ and C₁-C₄ hydrocarbons. However, for fast pyrolysis, higher ratios of CO:CO₂ were found compared to slow pyrolysis.
- The influence of increasing fast pyrolysis temperature between 750 1050 °C showed that gas yield increased with a corresponding decreasing trend in char

and oil yield. Maximum gas yields, on an ash-free basis were 91.71wt% for wood, 98.36wt% for rice husk and 90.80 wt% for forestry residue.

 Addition of steam to the fast pyrolysis of wood produced increased yields of hydrogen. For example, hydrogen yield was 26.91 vol.% in the absence of steam increasing to 44.13 vol.% in the presence of steam at the reaction temperature of 750 °C.

Acknowledgements.

The financial support provided by the Government of Pakistan for one of us (Q.M.K.W.) is gratefully acknowledged.

3 REFERENCES

- [1] Y. Kalinci, A. Hepbasli, I.Dincer., 'Biomass-based hydrogen production: A review and analysis.' *Int. J. Hydrogen Energ.*, 2009, **34**, 8799-8817.
- [2] U. K. Mirza, *Ahmad N., Majeed T.,* 'An overview of biomass energy utilization in Pakistan.' *Renew. Sustain. Energ. Revs.*, 2008, **12**, 1988-1996.
- [3] D. Neves, H. Thunman, A. Matos, L. Tarelho, A. Gómez-Barea.,
 'Characterization and prediction of biomass pyrolysis products.' *Prog. Energ. Combust. Sci.*, 2011, **37**, 611-630.
- [4] Y. Chen, H.Yang, X. Wang, S.Zhang, H.Chen, 'Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: Influence of temperature.' *Biores. Technol.*, 2012, **107**, 411-418.
- [5] R. Isha, P. T. Williams, 'Pyrolysis-gasification of agriculture biomass wastes for hydrogen production.' *J. Energ. Inst.*, 2011, **84**, 80-87.
- [6] P. T. Williams, S. Besler, 'The Pyrolysis of municipal solid waste.' *J. Energ. Inst.*, 1992, **65**, 192-200.
- [7] N. Miskolczi, N. Borsodi, F. Buyong, A. Angyal, P.T.Williams,,
 'Thermogravimetric analysis and pyrolysis kinetic study of Malaysian refuse derived fuels.' *J. Energ. Inst.*, 2010, 83, 125-132.
- [8] P. T. Williams, S. Besler, "The influence of temperature and heating rate on the slow pyrolysis of biomass," *Renew. Energ.*, 1996, **7**, 233-250.
- [9] P.A. Horne, P.T. Williams P.T., 'Influence of temperature on the products from the flash pyrolysis of biomass'. *Fuel*, 1996, **75**, 1051-1059.
- [10] Y. Zhang, S. Kajitani, M. Ashizawa, K. Miur, 'Peculiarities of rapid pyrolysis of biomass covering medium- and high-temperature ranges.' *Energ. Fuel*, 2006, 20, 2705-2712.
- [11] R. Zanzi, K. Sjostrom, E. Bjornbom., 'Rapid pyrolysis of agricultural residues at high temperature.' *Biomass Bioenerg.*, 2002, **23**, 357-366.
- [12] R. Zanzi, K. Sjostrom, E. Bjornbom., 'Rapid high-temperature pyrolysis of biomass in a free-fall reactor.' *Fuel*, 1996, **75**, 545-550.
- [13] O. Onay, O. M. Kockar, 'Slow, fast and flash pyrolysis of rapeseed.' *Renew. Energ.*, 2003, 28, 2417-2433.

- [14] X. Shuangning, L. Zhihe, L. Baoming, Y. Weiming, B. Xueyuan.,
 'Devolatilization characteristics of biomass at flash heating rate.' *Fuel*, 2006, 85, 664-670.
- [15] C. Dupont, L. Chen, J. Cances, J.M. Commandre, A. Cuoci, S. Pierucci, E. Ranzi, 'Biomass pyrolysis: Kinetic modelling and experimental validation under high temperature and flash heating rate conditions.' *J. Anal. Appl. Pyrol.*, 2009, 85, 260-267.
- [16] S. Sun, H. Tian, Y. Zhao, R. Sun, H. Zhou, 'Experimental and numerical study of biomass flash pyrolysis in an entrained flow reactor.' *Biores. Technol.*, 2010, 101, 3678-3684.
- [17] B. V. Babu, A. S. Chaurasia, 'Modeling for pyrolysis of solid particle: kinetics and heat transfer effects.' *Energ. Convers. Manag.*, 2003, **44**, 2251-2275.
- [18] C. Di Blasi, 'Modeling chemical and physical processes of wood and biomass pyrolysis.' *Prog. Energ. Combust. Sci.*, 2008, **34**, 47-90.
- [19] J. Lédé, 'Cellulose pyrolysis kinetics: An historical review on the existence and role of intermediate active cellulose.' *J. Anal. Appl. Pyrol.*, 2012, **94**, 17-32.
- [20] F. J. Kilzer, A. Broido, 'Speculations on the nature of cellulose pyrolysis.' *Pyrodynamics*, 1965, **2**, 151-163.
- [21] A. Broido, *Thermal Uses and Properties of Carbohydrates and Lignins*. New York: Academic Press, 1976.
- [22] C. Dupont, J.M. Commandre, P. Gauthier, G. Boissonnet, S. Salvador, D. Schweich, 'Biomass pyrolysis experiments in an analytical entrained flow reactor between 1073K and 1273K.' *Fuel*, 2008, 87, 1155-1164.
- [23] H. Yang, R. Yan, H. Chen, D. H. Lee, D. T. Liang, C. Zheng., 'Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases," *Fuel Proc. Technol.*, 2006, 87, 935-942.
- [24] S. Septien, S. Valin, C. Dupont, M. Peyrot, S. Salvador., 'Effect of particle size and temperature on woody biomass fast pyrolysis at high temperature (1000– 1400°C).' *Fuel*, 2012, **97**, 202-210.
- [25] F. Yan, S. Luo, Z. Hu, B. Xiao, G. Cheng, 'Hydrogen-rich gas production by steam gasification of char from biomass fast pyrolysis in a fixed-bed reactor: Influence of temperature and steam on hydrogen yield and syngas composition.' *Biores. Technol.*, 2010, **101**, pp. 5633-5637.

Proximate Analys	is(ash-free basis)			
Feed stock	Volatile matter	Fixed carbon	Moisture	
	(wt.%)	(wt.%)	(wt.%)	
Wood	80.57	13.41	6.02	
Rice husk	75.89	17.80	6.31	
Forestry residue	77.88	15.32	6.81	
Ultimate analysis	(ash-free basis)			
Feed stock	С	Н	Ν	O ^a
	(wt.%)	(wt.%)	(wt.%)	(wt.%)
Wood	48.49	6.18	0.82	44.52
Rice husk	49.01	5.87	1.07	44.05
Forestry residue	49.42	5.76	0.94	43.87

Table 1 - Proximate and ultimate analysis of feedstock

^a Calculated by difference

	Temperature (°C)				
	750	850	950	1050	
Wood (wt%)					
Gas	75.81	78.63	81.87	87.61	
Gas (ash-free)	79.36	82.31	85.70	91.71	
Solid	10.39	9.63	6.26	4.32	
Oil	16.41	12.31	10.00	8.40	
Mass balance (wt.%)	102.61	100.57	98.13	100.33	
Rice Husks (wt%)					
Gas	60.43	66.61	74.55	77.43	
Gas yield (ash-free)	76.77	84.62	94.70	98.36	
Solid	20.60	16.21	15.86	13.21	
Oil	12.01	10.22	8.13	6.19	
Mass balance (wt.%)	93.04	93.04	98.54	96.83	
Forestry Residue (wt%)					
Gas	60.13	73.91	79.27	85.91	
Gas yield (ash-free)	63.56	78.12	83.79	90.80	
Solid	14.37	7.69	5.44	3.21	
Oil	20.11	16.98	12.21	10.31	
Mass balance (wt.%)	94.61	98.58	96.92	99.43	

 Table 2 – Product yield from the fast pyrolysis of wood, rice husks and forestry residue in relation to pyrolysis temperature

Feed stock	Gas	Temperature (°C)			
	(Vol%)	750	850	950	1050
Wood	СО	45.12	47.10	45.94	48.74
	H_2	26.91	27.46	29.21	31.01
	CO_2	11.35	9.69	9.34	7.81
	CH_4	11.29	10.89	11.24	9.33
	C_2 - C_4	5.33	4.86	4.28	3.11
Rice Husk	СО	45.01	46.17	48.31	49.40
	H_2	21.84	25.32	27.83	30.30
	CO_2	15.06	12.98	11.33	8.65
	CH_4	11.92	10.65	8.94	8.67
	C_2 - C_4	6.17	4.88	3.59	2.99
Forestry residue	СО	43.8	46.6	48.07	46.61
	H_2	23.7	26.5	29.05	30.53
	CO_2	15.6	12.6	10.45	9.48
	CH_4	11.62	9.7	9.14	9.62
	C ₂ -C ₄	6.1	4.5	3.29	3.76

 Table 3 - Gas composition from the fast pyrolysis of wood, rice husks and forestry residue in relation to pyrolysis temperature

Feed stock	Gas		Tempera		
	(Vol%)	750	850	950	1050
Wood	CO	33.27	36.61	39.42	43.11
	H_2	44.13	45.96	43.28	40.04
	CO_2	13.29	9.26	9.44	8.57
	CH_4	6.93	6.10	5.93	6.53
	C_2-C_4	2.38	2.07	1.94	1.76

Table 4.- Gas composition and hydrogen production from the steam gasification ofwood.

FIGURE CAPTIONS

Figure 1 Schematic diagram of ultra-high temperature fast pyrolysis/gasification reactor

Figure 2 Schematic diagram of slow pyrolysis reactor

Figure 3 Comparison of product yield and gas composition from slow and fast pyrolysis of wood at $850^\circ C$

Figure 4 Comparison of product yield and gas composition from slow and fast pyrolysis of rice husk at $850^\circ C$

Figure 5 Comparison of product yield and gas composition from slow and fast pyrolysis of forestry residue at $850^\circ \rm C$

Figure 6 Potential hydrogen production from the various biomass samples

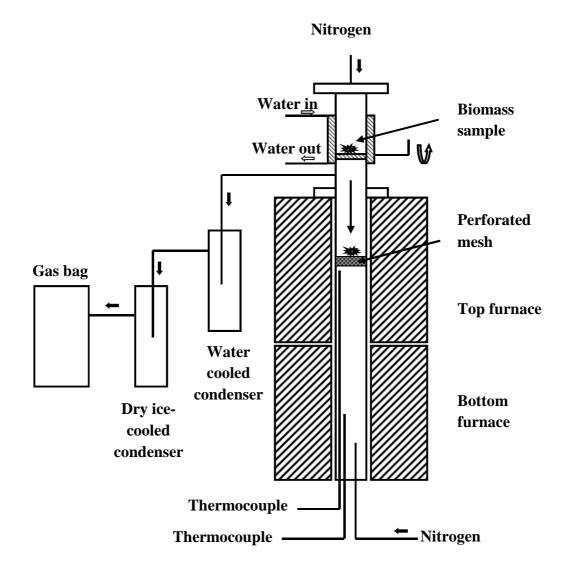


Figure 1 - Schematic diagram of ultra-high temperature fast pyrolysis/gasification reactor

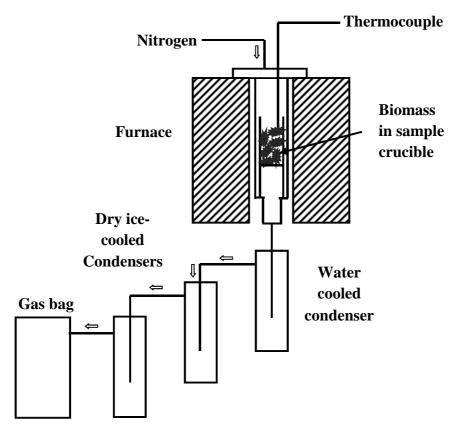


Figure 2 - Schematic diagram of slow pyrolysis reactor

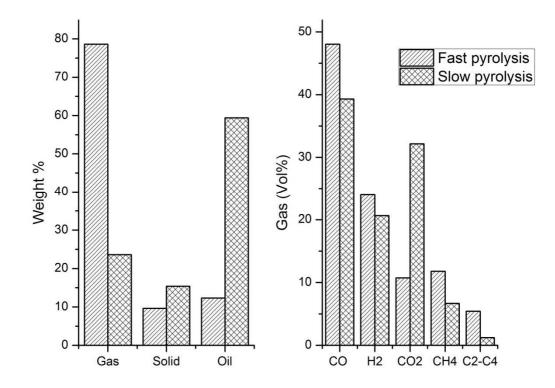


Figure 3 - Comparison of product yield and gas composition from slow and fast pyrolysis of wood at 850°C

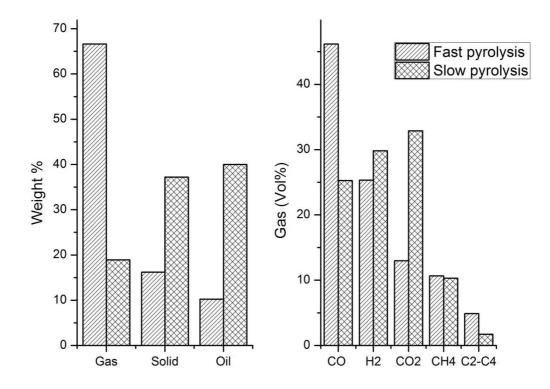


Figure 4 - Comparison of product yield and gas composition from slow and fast pyrolysis of rice husk at $850^\circ C$

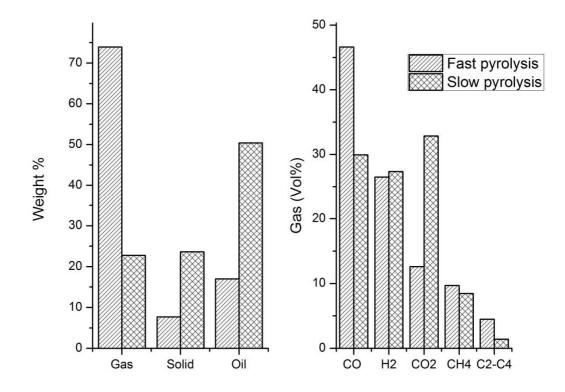


Figure 5 - Comparison of product yield and gas composition from slow and fast pyrolysis of forestry residue at 850°C

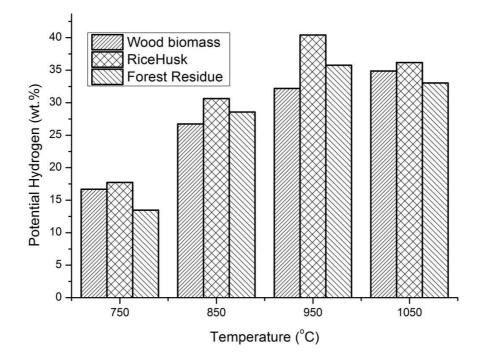


Figure 6 Potential hydrogen production from the various biomass samples