Influence of Reaction Temperature and Water Content on Wheat Straw Pyrolysis

N.Ibrahim, Peter A. Jensen, K. Dam-Johansen, Roshafima R. Ali, and Rafiziana M. Kasmani

Abstract—The aim of this study was to investigate the influence of reaction temperature and wheat straw moisture content on the pyrolysis product yields, in the temperature range of 475-575 °C. Samples of straw with moisture contents from 1.5 wt % to 15.0 wt % were fed to a bench scale Pyrolysis Centrifuge Reactor (PCR). The experimental results show that the changes in straw moisture content have no significant effect on the distribution of pyrolysis product yields. The maximum bio-oil yields approximately 60 wt % on dry ash free feedstock basis) was observed around 525 °C - 550 °C for all straw moisture levels. The water content in the wet straw bio-oil was the highest. The heating value of bio-oil and solid char were measured and the percentages of its energy distribution were calculated. The energy distributions of bio-oil, char and gas were 56-69 %, 24-33 %, and 2-19 %, respectively.

Keywords—Flash pyrolysis, moisture content, wheat straw, bio-oil.

I. INTRODUCTION

The flash pyrolysis process has been subject of intense research in the last decades mainly with the objective to maximize the organics liquid yields [1], [2]. During pyrolysis, biomass is thermally decomposed without an oxidizing agent to produce a solid charcoal, liquid oil and gases. High heating rates of the biomass particles and a short gas residence time at temperature of 450 – 600 °C are required to obtain the highest possible liquid yield [3]. Depending on the feedstock and operating conditions, the flash pyrolysis of wood produces 50-75 wt % of liquid bio-oil (including water), 15-25 wt % of solid char and 10-25 wt % of non-condensable gases [4], [5].

The process is a promising thermal conversion route of biomass to produce a nearly ash-free liquid fuel with a high volumetric energy density. The char contain most of the inorganic components and it can be used as an energy carrier or as a soil fertilizer [6], [7]. The pyrolysis gas can be used to generate electricity or to provide heat for the pyrolysis process. The pyrolysis gas consists mainly of carbon monoxide, carbon dioxide and light hydrocarbons [8], [9]. Also, the liquid oil can be directly used without any upgrading as a fuel oil in many combustion applications such as boilers. Upgrading is probably needed if the bio-oil shall be applied to smaller engines. The liquid oil is composed of a large variety of higher molecular weight species, organic acids, aldehydes, alcohols, phenols and other oxygenates. This oil is also known as a pyrolysis liquid, bio-oil or tar and has a lower heating value of 15-20 MJ/kg, about half that of conventional fuel oil [10]. Bech and co-workers [11], [12] measured the heating value of bio-oil produced from wheat straw at a reactor temperature of 550 °C and the value was determined to approximately 15 MJ/kg (dry basis). The pyrolysis oil can undergo secondary reactions to be further broken down into gas, refractory tar and water [13], [14]. The distribution and the yield of the pyrolysis products depend on several operating parameters including biomass characteristic, feedstock particle size, temperature, heating rate, and reactor configuration, as well as the extraneous addition of catalysts [15].

Over the last two decades, extensive studies have been conducted to understand the flash pyrolysis process and to obtain the optimal conditions for producing high quality bio-oil. The effect of biomass properties has been a research area, but only little attention has been focused on the effect of feedstock moisture content on wood flash pyrolysis [16] and none wheat straw moisture influence studies has been found. The presence of water in biomass could influence the pyrolysis behaviour and affects the physical properties and quality of the bio-oil. Previous studies [16]-[19] indicate that moisture may change the product composition or enhance some pyrolysis reactions. Shafizadeh [17] found that the decomposition rate of wet cellulose was much faster than that of dry cellulose when subjected to the same conditions in a closed system at 200 °C. Gray and co-workers [16] found that the presence of moisture increased the char yield by as much as 5 yield wt % (relative to dry sample). A recent study investigated the effect of wood moisture content on the flash pyrolysis oil yield [18]. They found that, as the wood moisture content increases, the char and gas yield increase and the produced water decreases but the liquid organics yield remains constant. In contrary, another researcher [19] found that the pyrolysis oil yield produced from conventional pyrolysis at a low heating rate of 0.1-1.0 c/s, was increased with increasing fuel moisture content and the oil obtained from dry feedstock was very viscous especially at higher temperatures. This paper reports results of a study on the effect of straw moisture content on wheat straw pyrolysis yield and the obtained product distribution.
II. MATERIALS AND METHOD

A. Material

The wheat straw pellets used in this study were manufactured by compressing straw and extruding it to pellets in a ‘Pellet Mill’. The pellets were crushed in a roller mill and were further screened into a fraction with a particle diameter < 1.40 mm. The particles appeared to have a more or less spherical shape. An analysis of the wheat straw is shown in Table I. Straw samples with moisture contents of 1.5 % wt (‘dry’), 6.2 % wt (‘as received’) and 15.0 % wt (‘wet’) were used for the experiments. Wet straw samples were prepared by sprinkling water on it to achieve a moisture content of 15.0 ± 1 % wt and storing it for 3 to 4 days to ensure that the water had been fully distributed. Dry straw samples were prepared by drying at 105 °C for at least 24 hr.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Wheat straw</th>
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<tr>
<td>Proximate</td>
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<tr>
<td>Volatile matter, %db</td>
<td>74.7</td>
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<tr>
<td>Ash, %db</td>
<td>5.9</td>
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<tr>
<td>Moisture, %wt</td>
<td>5.9</td>
</tr>
<tr>
<td>HHV (MJ/kg, dry basis)</td>
<td>18.75</td>
</tr>
<tr>
<td>Ultimate (wt %, dry ash free basis)</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>49.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.2</td>
</tr>
<tr>
<td>Nitrogen</td>
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<tr>
<td>Sulphur</td>
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</tr>
<tr>
<td>Oxygen (by difference)</td>
<td>43.12</td>
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<tr>
<td>Ash Composition (wt %)</td>
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<tr>
<td>Cl</td>
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<tr>
<td>Si</td>
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<td>Al</td>
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<tr>
<td>P</td>
<td>2.37</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>18.89</td>
</tr>
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</table>

B. Apparatus and Procedure

The flash pyrolysis experiments were conducted in a bench scale Pyrolysis Centrifuge Reactor (PCR) as depicted in Fig. 1 [11], [12]. The set-up consists of a screw type feeder, an ablative centrifuge reactor, an electric heater, a cyclone, a condenser, a coalescer, a gas dryer and a pump. The biomass was introduced by the screw feeder into the horizontally oriented Ø 82 x 200 mm tubular reactor. Here, a three-blade rotor with a clearance of 2 mm to the reactor wall rotate at a fixed speed of 14800 rpm creating a centrifugal force at the pipe wall of approximately 1.0 x 10⁴ g (acceleration), and thereby provides rotation of the gas and the biomass particles. The reactor wall was heated electrically by four independent heating zones located on the outer surface of the reactor tube. While undergoing reaction, the particles moved down the reactor pipe before leaving suspended in the gas through the tangential outlet. Larger char particles were removed by a change-in-flow separator whereas fines were collected by the cyclone. Vapors were condensed in a direct water cooled condenser (bubble chamber) filled with previously produced bio-oil. The temperature in the condenser was controlled to be 55 to 75 °C by means of a pipe coil cooled by tap water. Aerosols that were not retained by the condenser were collected in a coalescer filled with ROCKWOOL® (fibers). In the coalescer aerosols were removed and the bio-oil was collected in a conical flask. The gas was pumped to the preheater and heated to 400 °C before it is recirculated to the reactor in order to maintain a desired gas residence time of 0.2-0.3 s and avoid condensation of liquid products within the reactor. The amount of produced gas was measured by a temperature compensated gas meter and a sample was collected in a gas bag. Before the gas volume was measured, it was cooled to ambient temperature in order to remove water. The gas residence time in the reactor was calculated based on the experimental data obtained (from pyrolysis product yield). Details about the reactor are presented in previous work [12], [20]-[21].

Fig. 1 Schematic diagram of the ablative pyrolysis bench scale reactor system

In this work, samples of straw with different moisture contents (1.5 wt %, 6.2 wt % and 15.0 wt %) were treated to investigate the moistures effect on the pyrolysis products distribution of bio-oil, char, water and gas. To start an experiment, a 500.0 g
A sample of straw was placed in the feeder and the system was purged with nitrogen. The heat tracing of the reactor outlet tube was turned on and after the reactor reached the selected temperature, the rotor speed was adjusted to about 14800 rpm. The obtained straw feed rate was approximately 23 g/min. The experiment was run for 14-20 minutes and stopped just before the coalescer pressure meter reading reached a pressure of -400 mbar. The pressure was decreasing due to blocking of the condenser nozzle that has an inner diameter of 4.0 mm. Therefore, the experiment was stopped to avoid a decreased gas flow in the system. After the system had cooled, liquid and char yield in addition to spend raw material was determined gravimetrically. The gas yield was calculated on the basis of the measured gas volume and a molecular weight measurement obtained immediately after the run in order to minimize the potential effect of light gasses diffusing out of the gas bag. Liquid samples were filtered through a Whatman #4 filter paper on a Buchner funnel to remove char from the bio-oil. The char left on the filter was washed thoroughly using ethanol and acetone and dried under an infrared light bulb for 10 minutes. Then the residual mass of char was determined. The water content in the liquid products from the condenser (bubble chamber) and the conical flask below the coalescer filter was determined by refractive index measurements [21]. The liquid left in the coalescer was assumed to be similar in composition to the liquid collected in the condenser and the amount was determined by weighing the coalescer before and after the run. Overall, the yield of pyrolysis oil was determined from the condensed liquid in the condenser and coalescer. The char yield was determined from the char collected in the direct char separator, the cyclone and the char in the oil (char left on the filter). The mean values and standard deviations of the mean values for each yield of pyrolysis products were determined by making two to three experiments at each condition. All yields shown in Figures are given on a dry ash-free feedstock basis (daf). All data points presented are average values and the range indicates a 95 % confidence interval.

C. Higher Heating Value and Energy Distribution in Pyrolysis Products

The higher heating value (HHV) of bio-oil and char was measured by a bomb calorimeter IKA C200 using the standard DIN 51900-1, whereas the heating value of the pyrolysis gas was calculated by difference [22].

\[
HHV_{\text{gas}} = \frac{HHV_{\text{biomass}} - (HHV_{\text{oil}} \times Y_{\text{oil}}) - (HHV_{\text{char}} \times Y_{\text{char}})}{Y_{\text{gas}}}
\]

where HHV represents the higher heating value in J/g and Y is the yield of each pyrolysis product. The energy distribution of the pyrolysis products were calculated as:

\[
\% \text{ Energy distribution} = \frac{HHV_{a} \times Y_{a}}{HHV_{\text{biomass}}} \times 100
\]

Where a is the pyrolysis products (bio-oil, char and gas).

III. RESULTS AND DISCUSSIONS

A. Mass Balance

Fig. 2 shows an example of mass balance closures of the pyrolysis products distribution from as received straw at different reactor temperatures. The pyrolysis products are char, gas and bio-oil and the latter is subdivided into the liquid organics and produced water. The product yields were determined on a dry ash free (daf) basis, taking into account the ash and moisture content of the feedstock. Therefore, the water yields presented is the water generated by the pyrolysis reaction excluding the water input of the feed. The overall mass balance closures for all investigated straw moisture levels were between 89 and 103 wt %, in the temperature range of 475-575 °C.

B. Bio-oil

Fig. 3 presents the obtained bio-oil yields as a function of feedstock moisture contents and pyrolysis temperatures. The presented bio-oil yields are the liquid organics plus the water generated during the pyrolysis process. The bio-oil yield obtained is in the range of 40-60 wt %, for all straws within the investigated temperatures. Maximum bio-oil yields of approximately 60 wt % for all straw moisture levels occurred at the temperature range from 525 °C to 550 °C. The yields of bio-oil produced from another type of wheat straw (moisture content: 5.8 wt % and ash content: 6.8 % db) done by previous study [11] was around 50-57 wt % within the similar temperature range. The maximum bio-oil of approximately 57 wt.% also occurred around 525 °C. The level of bio-oil yields obtained is comparable to the current results.

Further increasing of reactor temperatures, cause a lower of bio-oil yield due to conversion of tar to gases. It can be seen on Figure 3 that similar bio-oil yields were obtained with different straw moisture content.

![Fig. 2 Pressure Overall mass balance closures for as received straw](6.2 wt. % water)
Fig. 3 Total bio-oil yields as a function of pyrolysis temperature

C. Water Content

The water content in the bio-oil was analyzed. The water in the bio-oil originates from the original moisture in the feedstock and dehydration reactions occurring during the pyrolysis process [23]. It is reported in many studies that the water content in bio-oil varies over a wide range 15 – 35 wt % (dry basis), depending on the feedstock and process conditions [24], [25]. However, for rice straw, the water content measured in the bio-oil is rather high, typically in between 50-60 wt % (dry basis) [26]. In this work the analysis of water content in bio-oil seen in Fig. 4 showed that in wet straw oil, the water content was 33-44 wt.% 24-32 wt.% in as received straw oil and 19-22 wt % in dry straw oil. If no water were formed during the pyrolysis process, the wet straw oil would contain 24-35 wt % water and the dry straw oil would contain 10-13 wt % water. It can be concluded that the water in bio-oil mostly originates from the original moisture in feedstock. Therefore it is an advantage to dry the biomass before pyrolysis, to less than 10 % water in order to minimize the water in the bio-oil.

D. Liquid Organics Yield

Fig. 5 shows the liquid organics produced at different straw moisture contents. In the temperature range of 475 - 575 °C, the liquid organics yields were similar at all straw moisture levels. The maximum liquid organic yields appear at 525 °C to 550 °C and the maximum yields were approximately 50 wt.% At these temperatures also, approximately 40 wt.% of liquid organic yields was produced using another type of wheat straw (moisture content: 5.8 wt.%) in a PCR unit [12]. The difference is due to the different characteristics of feedstock used but the pyrolysis operating conditions remains the same. The current study shows that the effect of straw moisture on the liquid organics distribution is insignificant and the yield remains constant at each reactor temperature. These results are in line with experimental results reported by Westerhof et al. [18]. In their work, they pyrolysed the pine wood with different moisture contents ranged between 0 wt.% to 20 wt.%, in a fluidized bed reactor by applying the flash pyrolysis concept and an approximately 46 wt % of liquid organics yields (on a dry feedstock basis) was obtained for all wood moisture levels at a reactor temperature of 480 °C [18].

E. Char Yield

As seen in Fig. 6, a decreasing char yield with temperature is observed for all straw moisture levels, with a minimum char yield of approximately 18 wt.% at 575 °C. A significant difference in char yield for the different straw moisture levels was only observed at 475 °C. The maximum char yields were observed at 475 °C; 41 wt.% (dry straw), 47 wt.% (as received straw) and 51 wt.% (wet straw). The high char yield with high straw moisture at 475 °C could be explained by a slow particle surface temperature rise because of water evaporation. The low particle heating rate cause an increased char yield.

F. Pyrolysis Gas Yield

Generally the temperature has a dominant effect on the pyrolysis gas yield as seen in Fig.7. The gas yield increases as temperature increase for all straw moisture levels. The high gas yield at high temperatures are causes by the pyrolysis oil vapor being converted into gases through secondary cracking [29]-[31]. However, the straw moisture content does not influence the formation of the gases. The current results are in good agreement with previous study [16] although they used a woodex material in a batch fluid-bed reactor at a heating rate of 300 °C/min. In the present work, the gas yields obtained are in the range of 5-20 wt % for all straw types and it can be concluded that the gas formation was not affected by the presence of fuel moisture contents.

Fig. 4 Water content in bio-oil as a function of temperature
G. Water Yield

The water yield discussed here is referring to the water that formed from the dehydration reactions throughout the pyrolysis process. The water produced by reaction for all straw moisture levels was measured as shown in Figure 8. The curves showed that the change in feedstock moisture content and reactor temperature has no significant effect on the water yield, and that a mean yield of 9 wt.% water was produced. The similar water yield of approximately 9.9 wt.% was obtained from forest-residue pyrolysis done at the VTT laboratory [32].

H. Gas Molecular Weight

Fig. 9 shows the effect of straw moisture contents and reactor temperatures on the pyrolysis gas molecular weight. It is seen that the gas molecular weight was not significantly affected by straw moisture content or temperature. The gas molecular weight was in the range of 31-35 g/mol. Bech et al. (2007) found the pyrolysis gas molecular weight from wheat straw to be approximately 37 g/mol and not affected by reactor temperatures [12], [21]. It was slightly higher probably due to the different characteristic of the used wheat straw.
I. Gas Residence Time

The gas residence times in the reactor was calculated based on the performance curve of the positive displacement gas pump and the yield data obtained from the experiments. The molecular weight of tar was taken to be 350 g/mol [11], [33] and it was assumed that the straw was instantaneously pyrolyzed when subjected to the reactor entrance. It was found that the gas residence time only changed a little with varying straw moisture content as seen in Fig. 10. In this experimental series, the hot gas residence time varied between 0.19 and 0.23 s. It can be concluded that within this range the yields of products at different moisture content of feedstock were probably not affected by the small gas residence time changes seen in Fig. 10.

J. Heating Values and Energy Distribution of the Pyrolysis Products

The higher heating value of bio-oil and char were determined and their energy distributions were calculated as shown in Fig. 11. Bio-oils have a medium heating value in the range of 15-17 MJ/kg (as produced or wet basis), approximately half that of conventional fuel such as gasoline, kerosene and diesel [34]. However, the heating value of bio-oil is very close to those of methanol and ethanol [34]. Char has a higher heating value of about 19-21 MJ/kg (as produced) and it is comparable with lignite and bituminous coal [34]. The energy distribution of bio-oil, char and gas for all straw types were around 56-69 %, 24-33%, 2-19 %, respectively, as seen in Fig. 11. At higher temperatures, the energy content of bio-oil and char reduce while the energy content in the pyrolysis gas increases. It is seen that an increased gas heating content can be obtained at high temperatures. This is important if the gas shall be used to supply energy for the pyrolysis process.

IV. CONCLUSIONS

The influence of straw moisture content and reactor temperature on the flash pyrolysis product yield has been experimentally investigated. In the current study the fraction of bio-oil, char and gases produced from pyrolysis of straw were in the range of 40-60 wt %, 18-50 wt.% and 5-22 wt.%, respectively, regardless of the straw moisture levels. The straw bio-oil yields obtained are slightly lower than the 50-75 wt.% that reported in the literatures for woody material [4], [5]. However the yield is reasonable due to the different feedstocks used. The optimal reaction temperature for the production of bio-oil was around 525 °C to 550 °C for all straw moisture contents. The presence of moisture in the feedstock has shown no significant effect on the pyrolysis product distribution. The liquid organics yields were similar for all straw types and the yields were almost constant at each reactor temperature. The similar observation was discovered by another study [18]. The gas and water yields were neither affected by the feedstock moisture level. The effect of straw moisture on char yield only can be observed at the lower temperature, 475 °C. At this temperature, wet straw produces the highest char yield followed by as received straw and finally dry straw. Gray et al. [16] and Westerhof et al. [18] also found that more moisture in the feedstock results in an increased char yield.

Apparently, the pyrolysis temperatures have a dominant effect on the pyrolysis product yield. In general, the yield of liquid organics increased with increasing pyrolysis temperature from 475 °C to 550 °C and then decreases at higher temperatures. The gas yield kept increasing with reactor temperature due to secondary cracking takes place at higher temperatures, which in turn lead to a reduction of the liquid organics yield and an increased production of light hydrocarbon gases. There were no affect on produced water yield with increasing temperatures.

Regardless of straw moisture contents, the maximum liquid organics yield occurred around 525 °C to 550 °C with the yield ranging from 45 to 53 wt.% (Fig. 5). The yields of liquid organics were comparable for all straw moisture levels at each reactor temperatures. The yields of reaction water and pyrolysis gas also were not affected by the moisture content of the feedstock.

Overall, the change in straw moisture content has no significant effect on the distribution of pyrolysis product yields except for char.

The water content in bio-oil increases with increasing of straw moisture content. The water content in dry straw oil was 19-22 wt.%, 24-32 wt.% for as received straw oil and 33-44
wt.% for wet straw oil. It can be concluded that the water in bio-oil mostly originates from the original moisture in feedstock. The high water content in bio-oil may cause a phase separation and lowers the heating value of the oil. The presence of water in bio-oil with higher amount also limits its utilization as a fuel, especially in combustion, as it reduces the combustion rates, delay the ignition and lower the adiabatic flame temperatures during combustion. Therefore it is an advantage to use a relatively dry feedstock in order to have a better quality of the bio-oil.

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REFERENCES