

Torrefaction of wheat straw

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ABSTRACT: *Wheat straw is an agricultural by-product available in large quantities in Syria, and, if utilized efficiently, can provide appropriate feedstocks for competitive energy production with consequent reduction of dependence on fossil fuels. Torrefaction of wheat straw is an important technology that transforms the straw into solid, liquid and gaseous biofuels. The torrefied solid fuel produced is a coke-like biomass or charcoal fuel known as biochar. In this paper the biochar formed as a result of the torrefaction of wheat straw was analysed and its properties were determined. The results indicate that the torrefied biochar may be used as a suitable alternative to coal and other fossil fuels reducing thereby the dependence of the economy on fossil fuels and utilizing an agricultural waste product that is otherwise of little commercial value.*

KEYWORDS: *Torrefaction, wheat straw, biochar.*

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I. INTRODUCTION

1. Torrefaction or mild pyrolysis is a slow pyrolysis or an irreversible thermochemical treatment process of complex solid or fluid chemical substances. Thermochemical treatment processes are generally classified according to their equivalence ratio (ER), which is defined as the amount of air added relative to the amount of air required for stoichiometric combustion. The equivalence ratio for torrefaction and other pyrolysis processes is 0 ($ER = 0$), whereas the equivalence ratio for combustion is equal to or greater than 1 ($ER \geq 1$), and the equivalence ratio for gasification varies between 0.25 and 0.50 ($Er = 0.25 - 0.50$) [1].

Torrefaction of biomass is a mild form of pyrolysis carried out under atmospheric conditions and at temperatures typically ranging between 200-320°C, where the onset of primary pyrolysis occurs at 200°C. For the low temperatures applied in torrefaction, the warm-up period is relatively short, even for the low heating rates commonly applied in torrefaction.

Torrefaction serves to improve the properties of biomass in relation to thermochemical processing techniques for energy generation such as combustion, co-combustion with coal or gasification. Torrefaction also eliminates all biological activity reducing the risk of fire and stopping biological decomposition. About 10% of the energy content in the biomass is lost as a result of the torrefaction process, but this energy of the volatiles can be used as a heating fuel for the process itself. During torrefaction, moisture and low weight organic volatile components are removed and the biomass loses typically 20% of its mass (dry bone basis). In addition, torrefaction partly depolymerises the biopolymers (cellulose, hemicellulose and lignin) and the long polysaccharide chains, producing a hydrophobic, dry, blackened solid product as "torrefied biomass" or "bio-coal" with an increased energy density (on a mass basis) and greatly increased grindability. As a result, significantly lower energy is required to process the torrefied fuel and it no longer requires separate handling facilities when co-fired with coal in existing power stations. Torrefied or so-called roasted wood has found applications as a barbecue fuel and firelighter. Finally, it has been suggested that torrefied biomass is a suitable feedstock for systems previously not considered feasible for raw biomass solid fuels such as entrained flow gasification. This is because torrefied biomass forms more spherical-shaped particles during grinding or milling [1-4].

Torrefaction of wood and other biomass materials may be used as a pretreatment technology prior to gasification. Torrefaction increases the relatively low energy density and the carbon content of the biomass and lowers its moisture content [1].

Torrefaction temperature is one of the most important parameters in torrefaction pretreatment process [9]. To achieve good physical properties with a relatively high energy yield, lower temperatures and shorter residence times are applied.

Other advantages of the torrefaction pretreatment process include lowering the O/C ratio of the treated material and improving its hydrophobicity, homogeneity, and grindability properties [1]. Satpathy et al. found that the torrefied wheat and barley straw are more hydrophobic and the moisture uptake is reduced by 61–68% under suitable torrefaction conditions [8].

II. STRAW

Straws are agricultural by-products available in large quantities. They include in general both grain and grass straws. Grain straws are the dry stalks of cereal plants, after the grain and chaff have been removed. Straws make up about half of the yield of cereal crops such as barley, canola, corn, oats, rice, rye, sorghum and wheat. Of these straws rice and wheat straws are abundant agricultural residues with low commercial value [15].

Straw is a lignocellulosic material consisting predominantly of lignocellulose (80 per cent or more), water-soluble substances (5 to 12 per cent) and mineral matter or ash and proteins which are usually present in very small amounts (2.2 to 3.0 per cent) [13].

Lignocellulosic materials are the most abundant renewable biomass resources on earth [5]. In general lignocellulosic (woody and herbaceous) biomass has a fibrous structure and it contains approximately 70-80% carbohydrates. It consists of three main carbon-based polymeric structures, known collectively as lignocellulose. These three natural constituents of biomass are cellulose (40-50%), hemicellulose (25-35%) and lignin (15-20%). Lignin is an aromatic and optically inactive amorphous heteropolymer. Of the three constituents of biomass, only lignin has a mole ratio of C : H : O (1 : 1.3 : 0.3) close to that of crude petroleum (1 : 1.6 : 0.05) [1].

Of the agricultural by-products available in large quantities, straws can provide if utilized efficiently appropriate feedstocks for competitive energy production with consequent reduction of dependence on fossil fuels [10]. In China alone, it is estimated that 400 million tonnes of wasted straw could be used as a substitute for 200 million tonnes of coal [11].

Straws can be used either as a solid fuel of high calorific value and reduced pollutants emission or they may be converted into coke-like biomass or charcoal fuel. Straws may also be mixed with other ligneous and waste materials such as paper mulberry, sawdust and livestock excretions to provide biomass material suitable for energy production [10, 15]. The use of straw in large-scale biomass power plants is becoming widespread in countries of the European Union, with several facilities already online, particularly in Denmark where straw is the most abundant biomass resource [10]. A new generation of small scale (less than 20 MWe) biomass-fuelled power plants has also been developed based on a gas turbine (Brayton cycle) prime mover. These power plants were expected to increase the efficiency and lower the cost of generating power from straws and other biomass fuel [12].

Needless to say, uses for straw other than energy production have been suggested, for example, the conversion of straw into a substance having the properties of stable manure. Furthermore, adsorbents made of rice straw, barley straw and wheat straw can be used for water treatment and the used adsorbent reused after re-treatment as a fuel or fertilizer [13, 14].

III. TORREFACTION OF STRAW

Studies on the thermal decomposition of biomass lignocellulosic materials showed that the hemicelluloses, which are the most reactive components, decompose first, at 200-260°C, followed by the celluloses at 240-350°C and finally by the lignin at 280-500°C [6, 7]. Pyrolysis causes the cellulose, hemicellulose, and part of the lignin in the biomass to disintegrate to smaller molecules that condense to form bio-oil, while the remainder of the original mass (mainly the remaining lignin) is left as solid biochar and noncondensable gases. In the relatively low temperature range of torrefaction, the hemicelluloses are the components that are mainly decomposed [1].

Experiments at different torrefaction conditions in nitrogen were undertaken by Bridgeman et al. to examine optimization of the process for wheat straw. Progress of torrefaction was also followed by chemical analysis (C, H, N, O, ash), and it was seen that the characters of the straw fuel begin to resemble those of low rank coals in terms of the van Krevelen coal rank parameter. In addition, the results indicated that the volatile component of straw is both reduced and altered producing a more thermally stable product with higher calorific value. The difference between the mass and energy yield was shown to improve for the higher torrefaction temperatures investigated. The combustion behaviour of raw and torrefied fuels was studied further by differential thermal analysis. It was shown that both volatile and char combustion of the torrefied sample become more exothermic compared to the raw fuels, and that depending on the severity of the torrefaction conditions, the torrefied fuel can contain up to 96% of the original energy content on a mass basis [3].

Torrefaction of straw with pelletisation is gaining attention, because it increases its energy density, making it possible to transport it still further. This processing step also makes storage much easier, because torrefied straw pellets are hydrophobic. Because the torrefied straw pellets have superior structural, chemical and combustion properties to coal, they can replace all coal and turn a coal plant into an entirely biomass-fed power station [1].

In this work, wheat straw was used because of its availability, as wheat is one of the most important agricultural products in Syria,

Experimental work

Wheat straw was collected from the field towards the end of the rainy season. This was done in order to make use of field or natural leaching reducing thereby the alkali metal contents of the straw. The straw was then left to dry in the sun to reduce its moisture content. The moisture content of the dried straw was 16%. Finally the straw was crushed to reduce its particle size. Table 1 shows the properties of the dried straw used in this study. As can be seen from Table 1, the oxygen and carbon contents of the dries wheat straw are higher than in other types of straw whereas the ash content is lower.

Table 1. Properties of the dried wheat straw

Elemental analysis Wt. %	Carbon	44.0
	Hydrogen	5.8
	Oxygen	42.4
	Nitrogen	0.4
	Sulphur	0.3
Chemical formula		CH _{1.57} O _{0.72} N _{0.01}
Ash (Wt. %)		7.1
Fixed carbon (Wt. %)		31.3
Volatile Matter (Wt. %)		61.8
Calorific Value (MJ/kg)	Nett Calorific value	16.1
	Nett Calorific value, calculated	16.4
	Gross Calorific value	17.4
	Gross Calorific value, calculated	17.7
Available chemical energy (MJ/kg)		18.3

Small samples of wheat straw (2-10 mg) were heated in an electric tube furnace heated by silicon carbide elements. The furnace tube has an external diameter of 59 mm and the length of the heated section is 250 mm. A Pt-Rh thermocouple was placed in the middle of the heated section. The straw samples were placed in a crucible inside the furnace tubes and were heated in an atmosphere of nitrogen gas with a flow rate of 0.8 litres per minute. The heating of the straw samples was carried out in two stages. In the first stage the samples were heated to a temperature of 200-300°C at a slow heating rate of 10-100° per minute. In the second stage the temperature was kept constant for specified periods of time to allow for the completion of the pyrolysis reactions. At the end of the experiments the samples were left in the furnace and were cooled to a temperature of 50°C by a stream of compressed air at 25°C. Finally, the samples were removed and weighed. It was observed that heating the samples led to some weight loss depending on the heating temperature and the residence time. When the samples were heated to a temperature of 250°C and a residence time of 30 minutes the weight loss was 18% and the weight percentage of the biochar formed was 82%. This is slightly less than the calculated value of 0.83.

$$\frac{M_{C_{\infty}}}{M_0} = 0.90 - 0.0014 (T(^{\circ}\text{C}) - 200) = 0.90 - 0.0014 (250 - 200) = 0.83$$

The volatiles percentage was 12%.

$$\frac{M_{V_{2\infty}}}{M_0} = 0.13 + 0.001 (T(^{\circ}\text{C}) - 260) = 0.13 + 0.001 (250 - 260) = 0.12$$

And the overall loss = 100 - 82 - 12 = 6%

Analysis and properties of the torrefied biochar

The biochar formed was darkish in colour. Table 2 shows the properties of the biochar formed. A bomb calorimeter was used to determine its calorific value and sulphur content. It is apparent from table 1 that the nett calorific value (18.5 MJ/kg) was greater than the corresponding nett calorific value of the raw straw (16.1 MJ/kg). This is due to the fact that the torrefaction reactions remove materials such as water and carbon dioxide which have no calorific value. The difference between the gross and nett calorific values is small because the hydrogen content of the biochar is small.

Table 2. Properties of the biochar

		Measured	calculated
Elemental analysis	Carbon	55.8	51.9
	Hydrogen	5.8	5.0
	Oxygen	29.5	33.5
	Nitrogen	0.5	0.5
	Sulphur	0.4	0.4
Ash (Wt. percent)		8.0	8.7
VM (Wt. percent)		49.1	51
Moisture (Wt. percent)		2.8	4
Fixed carbon (Wt. percent)		40.1	36
Bulk Density (Kg/m ³)		26.8	-
Chemical formula		CH _{1.23} O _{0.53} N _{0.01}	CH _{1.14} O _{0.48} N _{0.01}
Calorific value MJ/kg	Nett CV	18.5	19.4
	Gross CV	-	20.6

The ash content was measured by placing a weighed sample of the biochar in the furnace at a temperature of 650°C for 90 minutes and weighing it after being cooled to room temperature. The ash content was calculated from the weight difference.

Similarly, the volatile matter of the biochar was determined by heating the samples to a temperature of 900°C for seven minutes. The volatile matter content may also be calculated using the following equation:

$$\frac{VM_{solid}}{VM_{raw}} = -0.0122 T (^{\circ}C) + 3.88$$

$$\frac{VM_{solid}}{VM_{raw}} = -0.0122 \times 250 + 3.88 = 0.83$$

$$\text{Volatile matter content} = 0.83 \times 0.618 = 0.51$$

The difference between the measured and calculated values is small

$$\left(\frac{51-49}{49}\right) = 4.8 \%$$

For the determination of the moisture content a sample of 1 g of the biochar was heated in a drying oven at temperature of 96°C for thirty minutes and the measuring the weight loss. The moisture content obtained was 2.8%. According to Garba et al. [16], it would be possible to eliminate moisture completely by increasing the torrefaction temperature to 300°C.

The amounts of sulphur, nitrogen and ash in the raw straw are expected to remain unchanged in the biochar formed. The ash content of the biochar can therefore be easily calculated from the ash content of the straw as follows:

Ash weight percent in the raw straw = 7.1 (Table 1)

Weight percentage of the biochar = 82

Ash percent in the biochar = $7.1 \div 82 = 8.7$ (Table 2).

Finally, the fixed carbon content was calculated by subtracting the moisture, VM and ash:

Fixed carbon = $100 - (49.1 + 8.0 + 2.8) = 40.1$

The fixed carbon content may also be calculated using the following equation:

$$\frac{FC_{solid}}{FC_{raw}} = -0.0003 T^2 (^{\circ}C) + 0.1762 T (^{\circ}C) - 24.149$$

$$\frac{FC_{solid}}{FC_{raw}} = -0.0003 \times 250^2 + 0.1762 \times 250 - 24.149 = 1.15$$

Fixed carbon = $1.15 \times 0.313 = 0.36$

The difference between the two values = $\frac{40-36}{40} = 10\%$

For the determination of hydrogen and carbon, the simplest procedure is by burn a biochar sample in a closed crucible in an atmosphere of oxygen and using a weighed amount of cupric oxide to absorb the water of

combustion and then calculating the hydrogen content from the weight difference of the cupric oxide. For the carbon content, sodium hydroxide is used to absorb the carbon oxide formed.

The weight percentages of the different elements may also be calculated as follows:

$$\frac{C_{char}}{C_{raw}} = -0.00014 T (^{\circ}C) - 0.010 \frac{t (s)}{3600} + 1.22$$

$$\frac{C_{char}}{44.0} = -0.00014 \times 250 - 0.010 \frac{30 \times 60}{3600} + 1.22 = 1.18$$

$$\text{Carbon} = 44.0 \times 1.18 = 51.9$$

$$\frac{H_{char}}{H_{raw}} = -0.0040 T (^{\circ}C) - 0.020 \frac{t (s)}{3600} + 1.87$$

$$\frac{H_{char}}{5.8} = -0.0040 \times 250 - 0.020 \frac{30 \times 60}{3600} + 1.87 = 0.86$$

$$\text{Hydrogen} = 5.8 \times 0.86 = 5.0$$

$$\frac{O_{char}}{O_{raw}} = -0.0050 T (^{\circ}C) - 0.015 \frac{t (s)}{3600} + 2.05$$

$$\frac{O_{char}}{42.4} = -0.0050 \times 250 - 0.015 \frac{30 \times 60}{3600} + 2.05 = 0.79$$

$$\text{Oxygen} = 42.4 \times 0.79 = 33.5$$

$$\frac{C}{H} = \frac{55.8}{5.8} = 9.6$$

$$\frac{C}{O} = \frac{55.8}{29.5} = 1.9$$

These ratios are closer to the corresponding ratios in coal which means that this biochar may be used a substitute for coal or in a char-coal mixture (Table 3).

Table 3. Ratio of carbon to hydrogen and oxygen in fossil and bio fuels

	wood	Straw	Biochar	Peat	coal	Petroleum
carbon	49.5	44.0	55.8	58.0	66.9	85.4
Hydrogen	6.0	5.8	5.8	6.3	3.6	12.7
Oxygen	43.0	42.4	29.5	35.0	10.1	0.4
C/H	8.3	7.6	9.6	9.2	15.5	6.7
C/O	1.2	1.0	1.9	1.7	6.6	213.5

For the density determination, a beaker was filled with deionised water and weighed. The weighed dried biochar sample was then placed in the water and completely immersed in the water. The volume of the sample was then measured from the volume of displaced water and its density calculated assuming a density of 1.0 kg/m³ for the water.

IV. CONCLUSION

The analysis and properties of the biochar formed by the torrefaction of wheat straw demonstrates clearly that the biochar is a viable alternative to fossil fuels reducing thereby the dependence of the economy on fossil fuels and utilizing an agricultural waste product that is otherwise of little commercial value.

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