Evaluating Pyrolysis of Cypress Tree Residues (Stems and Leaves) in a Continuous Thermal Reactor

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ABSTRACT

Pyrolysis is a thermochemical process by which biomass is decomposed by heating in the absence of oxygen and the resulting emitted gases and settled bio-char are used for energy supply. Cypress pruning residues due to their gums content are a good source for pyrolysis. In this study, a reactor equipped with a screw conveyor was built and used for pyrolysis of stems and leaves of cypress tree. Then the effects of temperature and residence time of the reactor on their thermal decompositions was investigated using factorial experiments based on a completely randomized design. In these experiments, temperature was set at 5 levels from 300 to 500°C, with 50 degrees intervals and the residence time was set from 5 to 30 minutes with 5 minute intervals. The results showed that, at 1% significant level, both resident time and reactor temperature and their interaction had significant effects on bio-char yields for both stem, and leaves. The analysis of TG/DTG diagrams showed that the bio-char was formed from 200 to 500°C. The highest rate of decomposition of hemicellulose was at 340°C, and it was 450°C and 580°C for cellulose and lignin, selectively. The final rich carbon content of bio-char was formed after 750°C which resulted 23% for the stems and 28% for the leaves. The pyrolysis experiments with different retention time in the reactor indicated that, in general, the amount of bio-char decreases as the retention time increased.

INTRODUCTION

Increase in consumption of fossil fuels, non-renewability of these resources and multiple energy crisis are every day challenges to the world energy supply. Thus, investigations on alternative resources of energies have been the main subject of many energy research in the past two to three decades. Crop residues are a good alternative and renewable source of energy that can supply part of the word energy demands (Tripathi *et al.*, 2016). Traditionally, plant residues are burned and used for heating and cooking. The energy content of these materials, depending on the type of plant, is between 15 to 19 Mega Joules per kilogram (Channiwala and Parikh, 2002).

Plant residues can be transformed to more valuable energy sources using various processes. For example, charcoal and pellets made from plant residues are used as solid biomass fuel (Ramezanzade and Ghazanfari Moghaddam, 2018). On the other hand, biomass liquid fuels such as biomethanol, bioethanol and biodiesel have been considered by many researchers as alternates for liquid fossil fuels (Amini-Niaki and Ghazanfari, 2013; Vasudevan *et al.*, 2005). Biogas generation from various biomass has also been used for many years and it has gained special attention along other alternative biomass energy sources (Doaguie *et al.*, 2012). Another way to use the energy of biological materials, especially plant residues, is to simultaneously convert them into gaseous and oil by pyrolysis of these materials (Pattiya and Suttibak, 2012; Yorgun and Yıldız, 2015).

Pyrolysis is a thermochemical process in which biomaterials are heated in the absence of oxygen at high temperatures. In this processes most of biomass is converted to char or combustible gases. The emitted gases can be distilled and converted into bio-oil for biofuel usage (Yorgun and Yıldız, 2015; Zhao *et al.*, 2018). Pyrolysis temperature and resident time of biomass within a reactor have great effects on thermal decomposition and process efficiency. As the temperature rises, more gas is produced and less char is formed (Williams and Besler, 1996). In addition, the quality of the char produced is a function of the operational parameters of thermal decomposition (Aysu and Küçük, 2014).

Plant residues have different percentages of various organic matter, but the main constituents of these residues are cellulose, hemicellulose and lignin. The amount of these contents varies in different parts of plants, such as leaves, roots, and stems (Chen *et al.*, 2019). Pine and cypress residues contain volatile substances (essential oils) and gum (Iwasaki *et al.*, 2014). Gums are polysaccharide compounds that are normally solid and combustible. Essential oils are composed of terpenoid compounds or phenols that are easily dissolved in alcohol, ether and chloroform. These compounds are volatile and easily converted to gas during combustion. The presence of gums and

essential oils in plant residues can affect the pyrolysis status of these residues (Sharma *et al.*, 2011). In a study on thermal decomposition of pine stems in a temperature range of 250 to 600°C showed that by decrease in the size of the stems particles, the processing time was reduced. Also, by increasing the temperature of thermal decomposition temperature, the process time and residual mass can was significantly reduced (Iwasaki *et al.*, 2014). Thermal decomposition tests require a well-equipped device that can control all or some of the parameters affecting the process. Different devices have been used in the research (Dalluge *et al.*, 2014). The common feature of all these devices is having a reactor with controllable temperature and residence time. Heating rate is also an important factor for proper operation of a reactor (Iwasaki *et al.*, 2014; Yorgun and Yıldız, 2015). Therefore, for a proper pyrolysis, it is necessary to build a reactor that adequately control both temperature and the residence time of the material within the reactor.

Cypress and pine residues are produced worldwide as these trees are the prevailing plants of many forest and they are also grown in many around the cities. Many studies have been devoted to combustion and pyrolysis of pine and cypress residues. The purpose of this study was to design and build a reactor equipped with a screw conveyor device with the ability to control temperature, residence time and heating rate for the pyrolysis process of stem and leaves of cypress tree residues. The pyrolysis characteristics of the stems and leaves were also compared

MATERIALS AND METHODS

Building the Reactor

The reactor chamber used for the experiments was a cylindrical tube made of galvanized iron with a length of 600 mm and a diameter of 140 mm and a thickness of 10 mm was used. The screw conveyor of the reactor was designed in SoildWorks software. The main shaft of the conveyor was a 580 mm length hollow CK45 alloy steel having 40 mm diameter and a thickness of 5 mm. To make the spiral on the shaft, a steel metal sheet with a thickness of 4 mm was used. The reactor design specification and its schematic diagram are shown in Fig. 1.

In order to supply the required heat of the thermal decomposition process, four parallel 1000 W thermal elements were wrapped around the screw conveyor chamber for heating the materials at different heating rates. A K-type thermocouple having a temperature range of 0 to 800°C was used for measuring the temperature inside the reactor. To prevent heat loss, a 5 cm thick wool fiber isolation was wrapped around the heating elements. A 400-watt electric motor was used to drive the helix. The rotation speed of this motor was adjusted using a variable frequency AC inverter. To perform the pyrolysis process in the absence of oxygen, nitrogen was used as carrier gas with a flow rate of 100 ml / min.

Characterization of the Materials

Samples of cypress plant residues were obtained from Kerman region, Kerman, Iran. The samples were divided into leaves and stems and spread in sun dried for 20 days. The final moisture content for stem was 11.6% and for the leaves was 7.8%. They were then used separately for proximate analysis, TGA and pyrolysis experiments. Elemental analyses of leaf and stem samples were determined using a CHNS analyzer and an electric furnace was used to measure their ash content. Using the data obtained from elemental analysis, high heating value (HHV) and low heating value (LHV) were calculated for samples using the following equation (Channiwala and Parikh, 2002):

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \tag{1}$$

$$LHV = HHV - 0.2182H \tag{2}$$
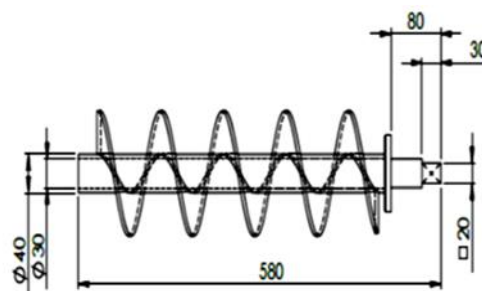
(a)
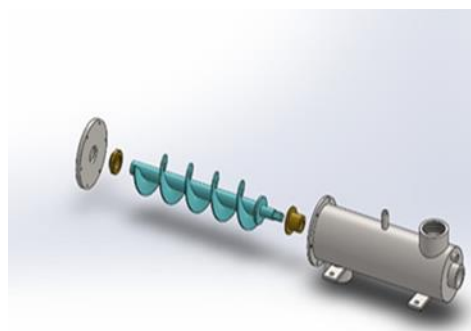
(b)

Fig.1. The dimension (a) and the schematic diagram (b) of the screw conveyor.

Proximate analysis that gives some ideas about bulk components of a biomass was done and the percentage of volatile matter, ash content, moisture content and fixed carbon were determined. In brief, a) Moisture content of the samples was found using oven drying method; b) The percentage ash was determined by separately heating 2 g of each sample in the furnace at a temperature of 550°C for 4 h. The weight of remained sample (ash) was determined; c) Volatile matter was determined by weighting 5 g moisture free sample and heating them in an oxygen free crucible at 900°C for 7 minutes. The loss in mass, (less that due to moisture), is the amount of volatile matter. d) Fixed carbon was obtained by subtracting the mass of moisture, ash and volatile matter from the initial weight of the sample

Thermo-gravimetric Analysis (TGA)

For TGA tests, about 100 g of each group was ground and then about 1 g of each sample was analyzed using a thermal analysis device (TGA). TGA diagrams can provide useful information about thermal decomposition at different temperatures and heating rates. This method of analysis helps to study the behavior of the material under heat more accurately and will avoid errors in graphs that appear to have only one step. The intensity of the peaks is proportional to the slope of the weight changes in the TGA diagram. Narrower and more intense

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peaks are associated with higher weight changes and greater slope. Also, by observing the level below the peaks, the amount of changes in the sample mass can be compared. If a thermal decomposition event is short or two consecutive events are very close to each other, it is difficult to detect them in the TGA diagram, and in these cases the derivative of the TG diagram, the DTG diagram, is used. In the DTG diagram, all the deflection points of the TGA diagram appear as peaks. The TGA tests were performed using a TGA device in the temperature range of 25 to 900°C, with a heating rate of 10°C per minute and in a nitrogen atmosphere with a flow rate of 100 mm per minute.

Testing the Reactor

In order to investigate the temperature and residence time of the reactor on the thermal decomposition of stems and leaf samples, experiments based on factorial tests based on a completely randomized design with three replications were performed. In these experiments, based on the results of thermal analysis tests, the reactor temperature was considered at 5 levels from 300 to 500°C, with 50 degree intervals and the sample retention time in the reactor, from 5 to 30 minutes and at 5 minute intervals.

In each test, the desired temperature was first set on the electronic board connected to the reactor so that the reactor was heated at that temperature and the desired temperature remained constant during the test using an electronic relay. After the reactor reached the desired temperature, 10 g

sample was placed in the reactor and the pyrolysis experiments were performed. It should be noted that the experiments related to each time level were performed separately. At the end of each test, the sample were collected from the reactor outlet and were weighted. The weight percentage of bio-char was determined.

RESULTS AND DISCUSSION

The results of statistical analysis for the effect of temperature and residence time in the reactor on bio-char yield for stems and leaves samples are shown in Table 1 (a) and (b), respectively. According to this table, the effect of both temperature and time factors and their interaction on the

Yield of bio-char produced are significant ($\alpha=0.01$). Thus, in the pyrolysis experiments the levels of these two factors should be considered.

Proximate Analysis

The results of proximate and ultimate analysis for stem and leaves of cuprous residues are given in Table 2. The moisture content for the stem sample is 11.60% and for leaves it is 7.19%. Moisture content which represents the quantity of water in a sample, affects the heating characteristics of a material. In fact, as the percentage of moisture in a material increases it lowers the carbon burn rate and consequently lowers the energy value of a biomass. Thus, stem should have lower burn rate that leaves of cypress residues.

Table 2 shows the ash content of the stem (3.5%) and leaves (3.81%). The ash content shows the amount of the inorganic residue in biomass. The primary components of ash are oxides of silica, aluminum, iron, calcium, magnesium, titanium, sodium and potassium (Cavalaglio *et al.*, 2020). Knowledge of amount of ash in a biomass aids in estimating both its tendency to form deposits in the reactor and the composition of the char produced during pyrolysis which in turn influences the heating values. The lower percentage of ash content for the leaves indicates that the leaves have better combustion quality.

Table 2. Indicates that the percentage of volatile matter for stems is lower than that for leaves, 72.3% and 75.5%, respectively. The amount of volatile matter in a biomass is mainly combustible gases that are released when biomass is heated up to 900°C. The presence of volatile matter in a biomass influences the fuel reactivity (Cavalaglio *et al.*, 2020). Samples with higher amount of volatile matter have more flame when they are combusted. Volatile matters are the kinds of components which are readily burnt in the presence of oxygen. They are a mixture of aromatic compounds which are gasified during heating. High volatile matter in the fuel is undesirable as it produces more tar and smoke during combustion. Thus, in this case stems have better burning quality. The amount of fixed carbon content of the samples are also shown in Table 2. Fixed carbon is the combustible portion of the solid residues that remains after biomass is heated up to 900°C.

Higher value of fixed-carbon content indicates that the sample requires longer combustion time. As indicated in the table, leaves have higher amount of fixed carbon.

Ultimate Analysis

Ultimate analysis is mainly focused on carbon, hydrogen and nitrogen content. These elements are the major component of biomass and determine the fuel efficacy and the possible pollutant behavior (Cavalaglio *et al.*, 2020). Since pollutants are more related to nitrogen and sulfur contents, both of these elements are lower in the stem samples, thus stem results in lower pollution during a burning process. The HHV and LHV that were calculated using Equation 1 and 2 are also presented in this table. The HHV of any fuel is the energy released per unit of mass per unit of volume of the fuel when it is completely burned. The HHV refers to the condition where water is condensed out of the combustion products and represents the gross calorific value. The HHV of a lignocellulose fuel is a function of its lignin content, it can be compared the HHVs with the chemical composition data. The HHVs of these lignocellulose feedstock increase with increase of their lignin contents, demonstrate that the HHV is highly correlated with lignin content. More carbon and hydrogen elements in a sample contribute to a higher heating value. On the other hand, as moisture content, oxygen, nitrogen and ash content of a material increases its heating value decreases (Channiwala and Parikh, 2002). As indicated in the table, both HHV and LHV calculated for leaves are higher than the values calculated for stems. The table indicates that the moisture and oxygen content of stem are higher than those of leaves these will contribute to the lower heating values for stem.

Table 1 (a). The analysis of variance for yield if bio-char from stems**.**

Source of variation	Degrees of freedoms	Sum of squares	Mean squares	P
Time	4	3001.41	750.35	0.00
Temperature	4	8639.55	2159.89	0.00
Time x Tempe	16	3554.59	222.16	0.00
Error	32	28	0.875	

Table 1 (b). The analysis of variance for yield if bio-char from leaves.

Source of variation	Degrees of freedoms	Sum of squares	Mean squares	P
*Time	4	2089.791	521.45	0.00
*Temperature	4	6651.65	168.91	0.00
Time × Temp.*	16	1832.39	114.52	0.00
Error	32	30	0.937	

*significant at 1% level

Table 2. Proximate and ultimate analysis, and heating values for samples

Component	stem	leaf
Ash (%)	3.50	3.81
Moisture (%)	11.6	7.19
Volatile Matter (%)	72.3	75.5
Fixed Carbon (%)	12.6	13.5
C (%)	45.1	46.1
H (%)	4.9	5.5
N (%)	1.8	2.2
O (%)	44.3	42.1
S (%)	0.3	0.4
HHV (MJ/kg)	17.08	18.37
LHV (MJ/kg)	16.01	17.16

Thermo-gravimetric Analysis

TGA and DTG diagrams for cypress stems and leaves are shown in Fig. 2 (a) and (b), respectively. These diagrams show similar trends for thermal degradation and decomposition of various compounds within both stems and leaves. In general, the two TGA diagrams can be divided into six weight loss sections. The first stage which is dehydration and volatilization stage, the starting temperature is around 30°C and ends at 130°C. In Fig. 2 (a) and 2(b) this stage show 5.12% for stems and 4.43% for leaves indicating leaves have less moisture.

The dehydration stage is an energy demanding process due to high latent heat vaporization of water.

The second weight loss which is 2.08% for stems and 1.51% for leaves is mostly related to evaporation of bound water. , Ay this stage, the heat added to the residues is used to increase their temperature. This stage ranges between 130 and 200°C. During this short stage no significant decomposition occurs, buy only the bound water and very light volatiles are expelled.

The third weight loss period appears occurs between 200 and 375°C. In this stage decomposition of hemicellulose takes place. The weight loss in this stage is 46.84% for stems and 43.49% for leaves. By the end of this stage, almost all hemicellulose is decomposed, and small fractions of cellulose starts to decompose. If the temperature does not exceed 350°C for extended period, a torrefied product (charcoal) with high energy density and low fixed carbon content is obtained.

The fourth stage occurs between 375 and 430°C for leaves and up to 500°C for leaves, indicating leaves have higher lignin than stems, since decomposition of lignin starts at about 450°C During this stage, both hemicellulose and cellulose completely decompose, and the lignin starts to degrade. The biomass structure keeps breaking and decomposing to produce slightly richer fixed carbon content compared to torrefaction. The weight loss in this stage is 8.77% for stems and 15.05% for leaves.

The fifth stage of weight loss occur at temperature above 450°C for stems and above 500°C for leaves and they end at about 650°C. If heating continues over 400°C, a very-high-carbon-rich charcoal is obtained. At the end of this stage lignin is completely decomposed and a very high fixed carbon contents are obtained. The total weight loss in this stage is 9.83% for stems and 3.7% for leaves.

The last stage is for a process called bio-coking. At the end of this stage, a large amount of pure carbon is formed. This carbon is suitable for metal ore extraction. This final carbon content is 23% of the initial weight in the stem and about 28% of the initial weight for the leaf.
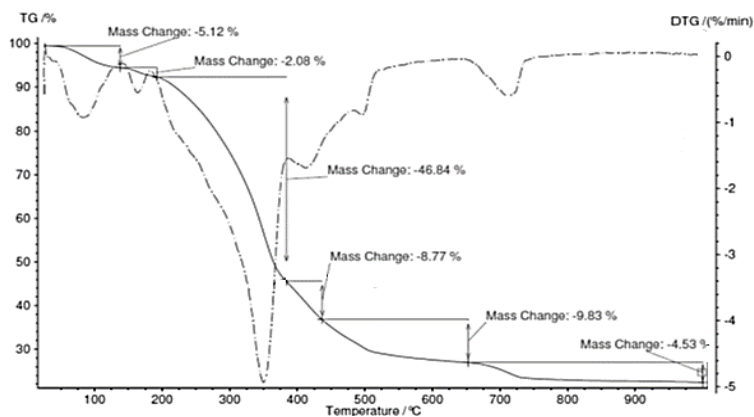
(a)
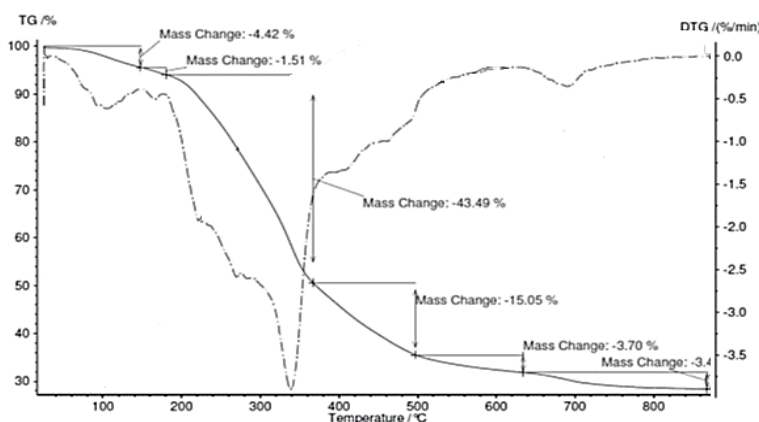
(b)

Fig. 2. The TG and DTG diagrams for cypress a) stems, b) and leaves

Evaluation of Pyrolysis Process

The weight loss diagram of the leaf samples at different retention times is presented in Fig 3. As can be seen in this Fig. the rate of weight loss of the sample at 300°°C is significantly lower than for the other levels and at the end more bio-char is left in the samples. But from a temperature of 350°C onwards (up to 500°C) the changes in the weight of the sample will be almost the same and the sample will reach weight stability after 5 minutes in the reactor. Thus, 300°C is low for pyrolysis of these residues and there is no significant difference when pyrolysis is done from 350 to 550°C. But a slight increase in the weight loss is noticed as the temperature rises from 350 to 550°C.

As shown in Fig. 3, the amount of residual solid (coal) decreases as the sample retention time in the reactor increases. At a temperature of 300°C, there is a significant difference between a stay time of 5 and 10 minutes compared to higher times. At the temperature level of 350 to 400°C, the weight difference between each time level decreases so that except for the difference between the time of 5 and 10 minutes, the amount of solid matter will not change and from 15 minutes onwards. The sample reaches weight stability.

At temperatures of 350 and 400°C, the amount of bio-char remaining at different residence times were almost equal. In other words, at these temperature levels from 5 minutes onwards, increasing the residence time of the sample in the reactor has an effect on the amount of charcoal formation. The highest amount of solid residue was obtained during a 5-minute residence time at 300 ° C. Also, the lowest amount of coal was reported from 25 minutes onwards at a temperature of 450°C and 15 minutes onwards at a temperature of 500°C.

CONCLUSIONS

In this study, a reactor equipped with a screw conveyor was built and used for pyrolysis of cypress residues. Based on results, the following conclusions are made:

- The effect of temperature and retention time of the reactor and their interaction had significant impact on the yield of bio-charcoal.
- The HHV and LHV of leaves were higher than those of stems.
- The amount of produced bio-char decreased as the retention time in the reactor increases.
- The final pure carbon left after pyrolysis at 750°C was 23% of the initial weight for the stems and about 28% of the initial weight for the leaves.

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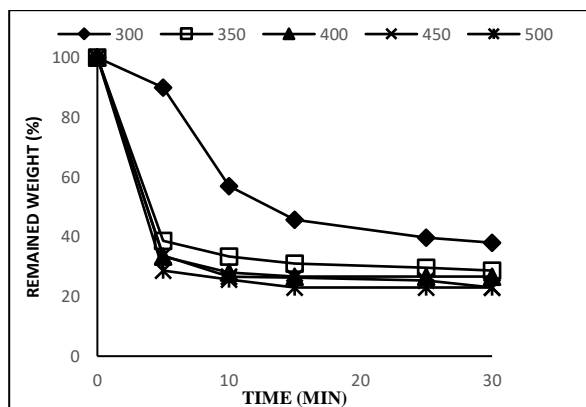
(a)
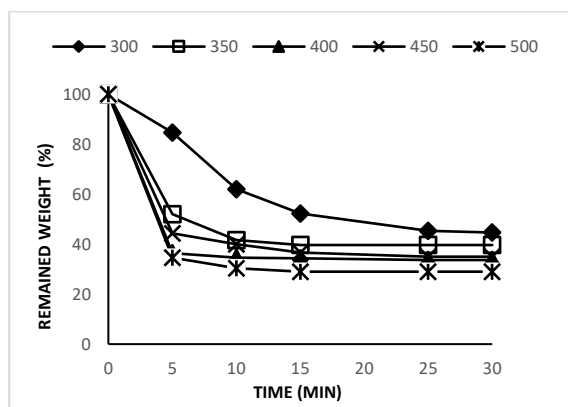
(b)

Fig. 3. The weight loss diagram of the samples at different retention times and temperatures (a) stems, (b) leaves.

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