

Catalytic pyrolysis of *Sweet Sorghum* plant by using fixed-bed reactor; Effect of different temperatures on the pyrolytic bio-oil yield and FT-IR characterization

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Pyrolysis of sweet sorghum, lignocellulosic graminaceous plant has been conceded using the fixed bed tubular reactor. Temperature plus catalyst are the important factors which effect the pyrolysis process. Here catalytic pyrolysis has been done by the catalyst ZnO-Fe₂O₃/Al₂O₃ at different temperatures. We have done our pyrolysis reactions on 3 changed temperatures i.e. 250 °C, 350 °C, 450 °C. By using catalyst, we obtain the pyrolytic products at a very low temperature and it is proved very efficient method for biofuel production. From different temperature experimentation, we concluded that the best optimal temperature along with catalyst for pyrolysis is 350 °C for the yield of bio oil. Maximum yield can be obtained at this temperature.

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1. Introduction

Energy requirement around the world presently is encountered mostly by non-renewable energy sources like rough oil, natural gas and coal. Following sources of energy are inadequate (Yorgun et al., 2003). Utmost of the situations aimed at upcoming energy source recommend unconventional biomass energy is the most important part in the 21st century. The usage from biomass by way of an energy resource stays a problem of large significance, such as it creates portion of an alternate answer for the additional of fossil oils (Şensöz et al., 2008). The requirement for renewable energy has directed to enlarged study on transformation of alternate (non-conventional) biomass to oils, like bio-ethanol (Guigou et al., 2011). The worldwide production as well as utility of bio oils have enhanced intensely in latest years, from 2000 to 2007 is 18.2 billion liters to 60.6 billion liters respectively, which includes 85% of bioethanol (Saini et al., 2014). Biomass is single from the past as well as the greatest hopeful energy causes also comprises organic and animal trashes, waste water also energy yields, farming and industrialized remains which could be utilized for the making of biofuels. There are numerous energy transformation technologies mistreatment for biomass i.e. straight ignition (97% of the world's bioenergy is produced by this process), pyrolysis, gasification, as well as living dealing. Biomass could be biologically altered to fluid or gasiform fuels for example ethanol, methanol, methane as well as hydrogen, which existed in recent times categorized as the fuel of the upcoming (Antonopoulou et al., 2008). Lignocellulosic plants comprises constituents (cellulose, hemicellulose and lignin) having different physical and chemical attributes that could be altered separately into different things for different aims (Kurian et al., 2015). Sweet sorghum goes to the family of Graminae, having local name as jawar as well as it is cultivated as food crop in Pakistan. This crop has several uses; having grains, food as well as different sugar forms. This plant grows in kharif period and is of double purpose crop. It's a hot weather and short day yearly crop. Bioethanol is produced from the stem of sweet sorghum and it is assumed as alternate fuel in near future (Ban et al., 2008). This is a great biomass as well as sugar yield crop which consisting

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almost the same quantities of insoluble and soluble compounds like hemicellulose, cellulose, sucrose and glucose, well thought to be an encouraging alternate biofuels feedstock (Cai et al., 2013). Stem of sweet sorghum contains high sugar content similar to sugar cane. However sweet sorghum is a brilliant plant to be used as biomass feedstock by thinking its high sugar amount in stem juice (Yesuf et al., 2014).

Sweet sorghum has great photosynthetic capability energy crop, and it is altered to rising in low nutrient territories, to form this plant great encouraging energy-crop for production of bio-ethanol. Stem and grain of sweet sorghum has great biomass and sugar content so that's why they are the brilliant rough material for bioethanol production (Cao et al., 2012). Now comparison to sugarcane this plant is a reasonable crop. As compared to sugarcane sweet sorghum is a cheaper crop because it can be grown less amount of water as well as rainfall. The extract obtained from sugar cane contains 16-23% of sugar content. Growing duration of sweet sorghum is about four months and it requires four times less water as compared to sugarcane therefore in India there is enhanced awareness in bioethanol production from sweet sorghum in latest years. Sugarcane is three times more costly than sweet sorghum. Furthermore, due to the presence of high reducing sugar content it is suitable for ethanol production. Reducing sugars prohibits crystallization as well as 90% fermentation can be done easily (Reddy et al., 2005). Pyrolysis, is an encouraging thermochemical alteration and it plays important character in biomass alteration. Although it's a very complicated process and affected by many parameters (Yang et al., 2007). Conditional operating parameters can give us a useful assortment of products as well as yields (Collard et al., 2014). The energy can be recovered through the thermochemical and biochemical reactions (Demirbas, 2001). The biomass alteration into different gas and liquid products is a charming choice, although, this includes many difficulties (Hussain et al., 2012). Thermochemical reactions could be divided into gasification, pyrolysis, carbonization, as well as direct-liquefaction (Demirbas, 2001). Pyrolysis is the most attentive process and high amount of bio oil can be yield by optimizing the conditions along bio gas and bio char. Bio oil can be used in turbines and engines also in the form of feedstock in refineries. Reaction conditions from the pyrolysis process. For pyrolysis of biomass the physical conditions like temperature, residence time and heating rate have very intense consequence upon the product quantity and compositions (Demiral et al., 2006).

Composite material like wood and other biomass of plant is composed of organic polymer containing oxygen (Shun et al., 2013). Product obtained from the pyrolysis is of acidic nature, viscous and is unstable to heat as well as comprises great quantity of oxygenated compounds. In the latest years to improve the pyrolysis oils many techniques are used like hydro deoxygenation, emulsification, steam reforming and catalytic cracking. The one improvement in bio-oil quality could be done by adding the catalyst in pyrolysis process. The important intentional purposes of utilizing a catalyst are to (i) Decrease the viscosity of bio oils during pyrolysis (ii) Decrease the corrosiveness of bio-oil by producing less carboxylic acids (iii) Increase the production of wanted useful products for example hydrocarbons which enhances the calorific values. Various scientists have broadly utilized catalytic pyrolysis, which is the reliable process of alteration of many plant feed stocks straight into great excellence bio-fuels (Aysu et al. 2016). Catalyst is utilized for specifically obtain the desired compounds as well as consequently the required use (Auta et al., 2014). Catalytic pyrolysis includes the two stages: first bio-mass pyrolysis secondly alteration of pyrolysis gases through catalyst. Bio-mass is heated first and changed in pyrolysis gases, bio-oils as well as bio-char. Then, later oxygenated compounds changed into aliphatic as well as aromatic hydrocarbons through deoxygenation process when the pyrolysis gases are in contact with the outer layer of the catalyst (Aysu et al. 2016). Oxygenated compounds existence within the bio oil mostly adds to its harmful aspects, larger viscosity, less volatility, great acidity as well as causing corrosiveness and great uncertainty (Imran et al., 2014). As for as our information concerned here exists no described work upon pyrolysis of sweet sorghum at a very low temperature. Therefore, in this study we used sweet sorghum as a biomass source. Here we are going to study the pyrolysis of sweet sorghum with catalyst by using fixed bed pyrolysis reactor. Pyrolysis reaction will be conducted at lower temperature along with use of catalyst. Here we are using the Fe₂O₃-ZnO/Al₂O₃ catalyst. A very small quantity of catalyst is used in this pyrolysis reaction.

Table 1. Typical features of biomass.

Properties	Sweet sorghum
Crop season (months)	3.5
Number of cycle/year	Two
Yield (t/ha/year)	60
Brix (% juice)	11-13
Fiber (% cane)	13

2. Experimental details

2.1 Materials

All the materials were purchased from sigma Aldrich. All the chemicals are of standard analytical grades. Sweet sorghum plant crop collected in the summer season near about May and it remained till September. Sweet sorghum plant stem was separated from other parts of plant like leaves, seeds and flower. Then stem was cut into small pieces and then dried into the oven at 100 °C for about ten days after washing with distilled water. Finally, the stem become dry, then they crushed and converted into powder material. The cellulose, hemicellulose and lignin content in sweet sorghum is 45%, 27% and 21% respectively and 5,804 kg per ha is the theoretical yield of ethanol from sweet sorghum. Fixed bed reactor apparatus was arranged along the tubular furnace. N₂ gas cylinder also connected for gas supply into the furnace chamber. A condenser system was also used to condense the gases coming from biomass during the pyrolysis.

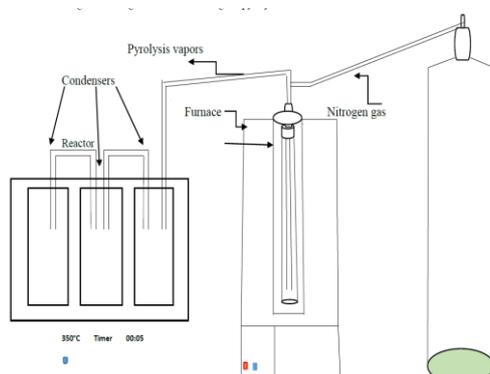


Fig. 1. Fixed bed reactor for the pyrolysis of sweet sorghum.

Table 2. Sweet Sorghum Composition.

Constituents (dry weight)	Percentage
Cellulose	44.6
Hemicellulose	27.1
Lignin	20.7
Ash	0.4
Fiber	13

2.2. Procedure

Tubular fixed bed reactor has been used for pyrolysis experiment. Biomass was dried for 7-8 days at 100 °C before pyrolysis experiment starts. To prevent the introduction of oxygen and to create inert environment nitrogen gas was introduced at very slow rate in reactor tube also to avoid gas pressure. Reaction tube contains 5g of biomass sweet sorghum and small amount of catalyst. Catalyst is

prepared by co-precipitation method. Plaster of Paris was used to make all the connections of glass tubes airtight. Thermo-couple was used to control the temperature in electric tubular furnace. When glass tube was sealed firmly with introduction of nitrogen gas pipette the bio oil collecting bottles were also linked firmly with the output tubes. After the reaction started the temperature increased slowly i.e. 20°C/ min and the desired temperature was achieved. Whole reaction took 30 minutes after attaining the desired temperature. Three collecting bottles were placed in ice bath for bio oil. Bio oil, bio gas and bio char were collected successfully and their quantity was measured by the following procedure. Biogas was discharged but can be calculated by subtracting the attained product bio char and bio oil.

The total conversion and quantity of the product was calculated by using following formula:

$$\begin{aligned} \text{Conversion (\%)} &= \frac{W_{\text{biomass}} - W_{\text{biochar}}}{W_{\text{biomass}}} \\ \text{Liquid (\%)} &= \frac{W_{\text{liquid}}}{W_{\text{biomass}}} \\ \text{Solid (\%)} &= \frac{W_{\text{biochar}}}{W_{\text{biomass}}} \\ \text{Solid (\%)} &= \frac{W_{\text{biochar}}}{W_{\text{biomass}}} \times 100 \\ \text{Gas (\%)} &= 100 - (\text{liquid\%} + \text{biochar\%}) \end{aligned}$$

We carried out the pyrolysis reactions at three different temperatures. These three temperatures are 250°C, 350°C and 450°C. We collected three different bio products in each pyrolysis experiment.

2.3. Product analysis

The Products obtained from different pyrolysis experiments were analyzed by GC-MS and FT-IR techniques. FT-IR test has been accomplished utilizing Perkin Elmer Spectrophotometer system to identify the distinctive peaks as well as their functional groups.

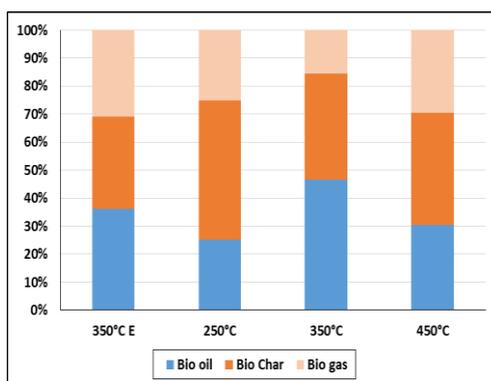


Fig. 2. Distribution of energy products of sweet sorghum in catalytic and non-catalytic pyrolysis.

3. Results and discussion

3.1. Effect of temperature

Temperature has a major effect on biomass conversion in bio oil biogas and bio char during pyrolysis reaction. Biomass decomposition occurs at high temperature in inert environment. Hydrolysis, fragmentation and repolymerization are the three stages of pyrolysis. Yield of biomass

is maximum at medium temperature because of catalyst. Using catalyst reaction can be carried out at low temperature. After the reaction twitches bio oil manufacturing starts, as the temperature is increased yield of bio oil is also increased but after a certain high temperature the bio oil yield decreases because of secondary decomposition and bio gas starts to form. Bio oil yield lowers as the temperature rises and gaseous product starts to produce. The conversion and product from the pyrolysis at different temperature is found to be different. At intermediate temperature bio oil yield is maximum and at highest temperature biogas yield is maximum. In our experiment pyrolytic products calculated. Three bio products obtained in each experiment and all products are beneficial for many applications.

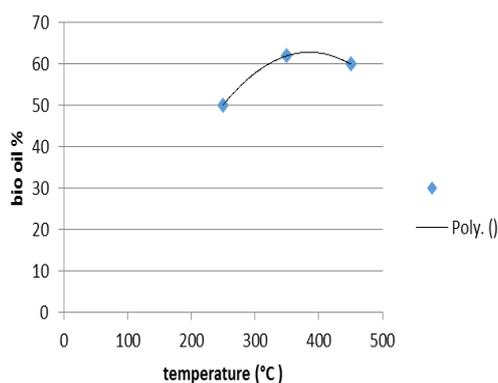


Fig. 3. Temperature effects upon product yields of sweet sorghum pyrolysis.

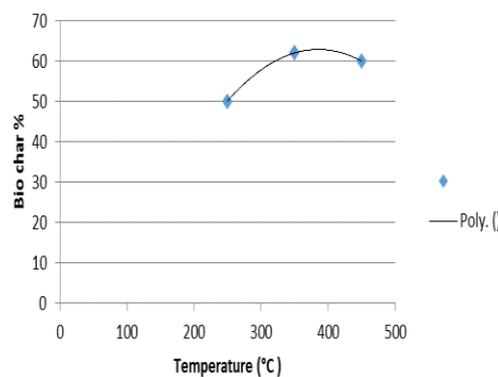


Fig. 4. Temperature effects upon product yields of sweet sorghum pyrolysis.

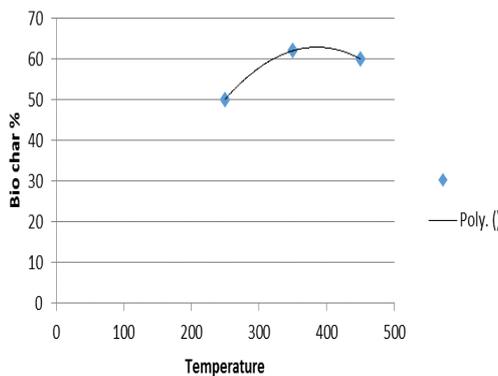


Fig. 5 Temperature effects upon product yields of sweet sorghum pyrolysis.

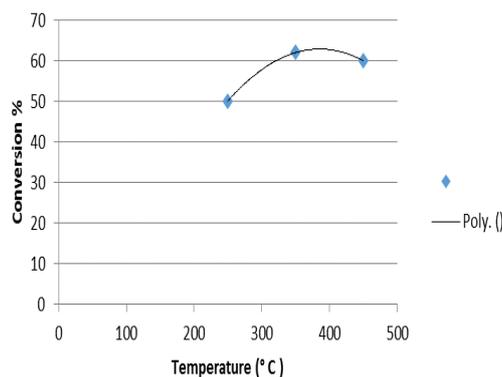


Fig.6. Temperature effects upon product yields of sweet sorghum pyrolysis.

The no existence of oxygen in presence of high temperature becomes the reason of wide depolymerization/fragmentation from the macromolecular structures of the wood. Primary products could promote fissure to yield lower molecular mass products. Cross-linking through condensation reactions as well as water loss, consequence in bio-char production. If we increase the temperature increase rate, then bio-char yield is decreased because of fast volatilization and reduced second-order polymerization rates. Extended gas residence times at pyrolysis temperatures allow greater secondary vapor-phase breaking to gases, water, formic as well as acetic acids, also further low-molecular-weight products. Hence, fast gas quenching decreases the degree of cracking [20].

3.2. Catalyst effect on product yield

Pyrolysis of biomass at higher temperatures leads to the production of only smaller amounts of bio-oil due to the presence of oxygen containing compounds, higher acid amounts and poor calorific value. However, for the higher yield production of bio-oil and beneficial compounds, catalytic pyrolysis has come out to be a very efficient methodology [21]. Hence, during the process of pyrolysis, it is of utmost importance to reduce the oxygen containing compounds and there are only two reactions that are capable of eliminating this oxygen content i.e., dehydration and decarboxylation. Former removes H_2O and latter causes the breakage of large chain compounds into smaller ones. Hence, with the help of right catalyst, the content of oxygenated compounds can be effectively reduced thus enhancing the yield and the quality of oil [17].

3.3. Characterization of pyrolysis product by FT-IR

The bio oil elemental analysis at different temperatures gives information about functional compounds present in the pyrolytic product. In viewing spectra of bio oil at $450^\circ C$ major peak is observed at 3333.54cm^{-1} indicate the presence of primary aliphatic amide. Tertiary olefin compounds at 1643cm^{-1} , tertiary alcohols and phenols at 1393cm^{-1} and a methylene peak in $1445\text{-}1485\text{cm}^{-1}$ range is also confirmed. Ether compound presence is also indicated near about 1016cm^{-1} . FT-IR spectra at $350^\circ C$ has the almost same peaks like at 3330.54cm^{-1} primary aliphatic amide, Tertiary olefinic compounds at 1643cm^{-1} and tertiary alcohols and phenols at 1395cm^{-1} . Now the spectra at $250^\circ C$ has nearly same peaks like 3317.54cm^{-1} primary aliphatic amide, Tertiary olefinic compounds at 1642cm^{-1} and tertiary alcohols and phenols at 1395cm^{-1} . If we talk about the spectra of biochar of all three different temperatures, common peaks observed in all these are near about 2600cm^{-1} , 1600cm^{-1} , near 1416cm^{-1} , 1315cm^{-1} , near about 1100cm^{-1} , and 873cm^{-1} , and 779cm^{-1} (See Figure 7)

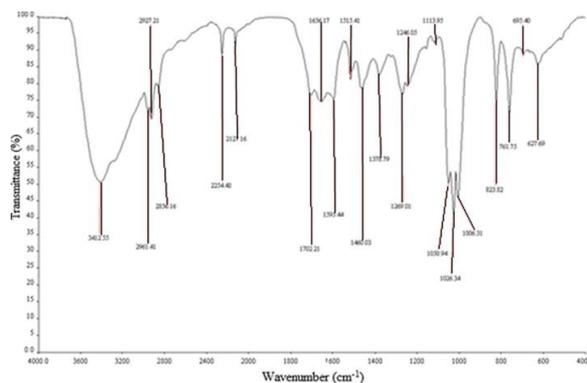


Fig.7.FTIR of sweet sorghum

4. Conclusion

In this study, fixed-bed pyrolysis reactor was employed to achieve the pyrolysis of stem of sweet sorghum. Suitable catalyst was used at different temperatures and bio-oil and bio-char were obtained. Bio-oil is the mixture of many useful compounds. The catalyst was prepared by coprecipitation method. ZnO-Fe₂O₃/Al₂O₃ was found to be very efficient catalyst and the maximum bio-oil yield was obtained at 350°C. Moreover, FT-IR characterization was also carried to confirm the presence of useful compounds needed for the bio-fuel production.

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