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RESEARCH ARTICLE - CHEMICAL ENGINEERING

Bio-Oil Production from Fast Pyrolysis of Cotton Stalk in Fluidized Bed Reactor

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Abstract Fast pyrolysis was used to convert waste biomass into bio-oil, which has a benefit of storage and transportation with the potential as a fossil oil substitute. Pakistani cotton stalk was pyrolyzed in a bench-scale bubbling fluidized bed reactor. The effect of reaction conditions such as temperature and feed size on the bio-oil, char and gas yields was investigated. The optimal pyrolysis temperature for the production of bio-oil was 490 °C which gave the maximum yield (36 wt%) of product at feed size of 1.0 mm. Bio-oil yield increased with the increase in temperature, while the yield of char decreased. The various properties of bio-oil attained under these pyrolysis conditions were defined. Chemical composition of bio-oil was determined using FTIR and GC–MS analysis, and major chemical compounds were phenols, carboxylic acids, ketones, aldehydes, furans and sugars.

Keywords Fast pyrolysis · Cotton stalk · Fluidized bed reactor · Bio-oil · Temperature · Biomass particle size

1 Introduction

Renewable energy is of increasing importance responding to the present concerns over the depletion of fossil fuel reserves and environmental threats [1,2]. Biomass is one of the most viable renewable energy sources which has the highest potential to contribute in the energy needs for the developed as well as the developing countries in the world [3]. Wood, energy crops, agricultural residues and forestry wastes are some of the key renewable energy sources available [4–7]. These resources can supply the liquid, solid and gaseous fuels [8].

Pakistan is an agriculture-based country which produces agricultural wastes such as wheat straw, rice straw, cotton stalk, maize stalk, sugar cane trash, corn stover and tobacco stalk in huge volume [9]. The production of these residues is about 84 million tonnes per year, and their conventional use is for heating, cooking and animal fodder [10,11]. This agricultural waste is an alternate potential resource for energy production. Consequently, the agricultural wastes which are useless and produce environmental problems can be made into more valuable energy-rich products which are environment friendly.

Biomass residues can be converted into renewable energy through thermal, biological and physical processes [12]. Thermal processes include combustion, gasification and pyrolysis, and among these processes, fast pyrolysis has more attraction due to the production of liquid fuel with advantages of transportation, storage and versatile potential applications [13–16]. Fluidized bed fast pyrolysis is considered as one of the most promising technologies among the thermochemical conversion processes to convert waste biomass into liquid fuels due to high biomass conversion efficiency [17,18].

Fast pyrolysis is thermal decomposition of biomass at moderate temperature in the absence of oxygen and produces liquid (bio-oil), solid (charcoal) and incondensable gas [19]. The key objective of this technology is to convert solid biomass into liquid fuel [20]. The proportions of three products depend on the process conditions and feedstock used. The pyrolysis product fractions of liquid, charcoal and incondensable gas are reported in the ranges as, respectively, 60–75,

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15–25 and 10–20 wt% [21]. Pyrolysis gas mainly consists of carbon monoxide (CO), methane (CH_4) and carbon dioxide (CO_2). Bio-oil consists of the oxygenated compounds having functional groups such as carboxyl, carbonyl as well as phenolic. The main components of the liquid bio-oil are water, insoluble lignin fractions, aldehydes, carboxylic acids, carbohydrates, phenols, ketones, alcohols and furfural [22]. Fast pyrolysis of biomass can be performed with a variety of reactors such as entrained flow reactors, vacuum furnace reactors, vortex reactors, rotating cone reactors, circulating fluidized bed reactors and fluidized bed reactors [23]. Fluidized bed reactors are considered the most suitable for fast pyrolysis of biomass [24] due to high heat and mass transfer rates, rapid devolatilization, easy control and ready scale-up. Various biomasses like eucalyptus wood, pine sawdust, miscanthus, mallee bark jatropha oil cake and sugarcane bagasse have been investigated in fluidized bed pyrolysis reactor.

Westerhof et al. [25] studied the fast pyrolysis of pine wood as feedstock in fluidized bed reactor and established the trends for the yields of pyrolysis products with temperature. Heo et al. [26] studied the pyrolysis of miscanthus and found that char yield decreases by increasing the reaction temperature, whereas the yield of bio-oil decreases gradually after optimum pyrolysis temperature. Pattiya et al. [27] probed the fast pyrolysis of cassava rhizome (CR) and cassava stalk (CS), in a fluidized bed fast pyrolysis reactor. The maximum yields of bio-oil from CR and CS were obtained at temperatures of 472 and 469 °C, respectively. Mourant et al. [28] investigated the effects of temperature on the fast pyrolysis of mallee bark in fluidized bed reactor. Kim et al. [29] explained the effect of temperature on the pyrolysis products of chicken litter and turkey litter in a fluidized bed reactor. Montoya et al. [30] considered the effect of pyrolysis temperature on sugarcane bagasse in fluidized bed reactor.

Scott et al. [31] carried out many tests to study the effect of particle size on yields of pyrolysis oil, char and gas for aspen popular wood in bench-scale fluidized bed flash pyrolysis. Raja et al. [32] conducted the jatropha oil cake flash pyrolysis experiments in fluidized bed reactor to determine the effect of biomass particle size on yield of pyrolysis liquid. Heidari et al. [33] studied the effect of particle size on the pyrolysis of eucalyptus wood in fluidized bed reactor. By the increase in particle size, the bio-oil and char yields reduced and gas yields increased. Park et al. [34] investigated the variation of feed size on the product distribution for japanese larch. Choi et al. [35] compared the effect of three different sizes in cylindrical bubbling fluidized bed reactor. Heo et al. [26] investigated the effect of particle size on miscanthus fast pyrolysis under fluidized bed conditions. Garcia et al. [36] described the effect of particle size on the yield and quality of pyrolysis oil in fast pyrolysis of oil mallee woody biomass in a novel bench-scale fluidized bed reactor.

At present, there is no inclusive research about the fast pyrolysis of cotton stalk as well as effect of temperature and biomass particle size on yield of pyrolysis products in the fluidized bed reactor. In this experimental study, the effect of temperature and particle size on the yield of bio-oil and coproducts is investigated. In addition, composition of the bio-oil obtained under optimum pyrolysis conditions is determined by FTIR and GC/MS analysis.

2 Experimental Methods

2.1 Feedstock

Cotton stalk used as feedstock was collected from Burewala, District Vehari, Pakistan, and shredded into coarse particles using rotary cutting mill. The samples were finally ground in grinding mill into particle sizes of 1.0, 1.5 and 2.0 mm and were air-dried having moisture content of <10 %. Silica sand was used as bed material in the fluidized bed reactor to perform experiments with size of −40 mesh and 2600 kg/m^3 density. Nitrogen was used as fluidizing gas in the silica sand bed.

Ultimate and proximate analysis of the cotton stalk was carried out at GC University, Lahore, and NFC IET, Multan, Pakistan (Vario Micro CHNS Serial No.15071001 analyzer, Leco TGA701 analyzer).

The higher heating value (HHV) was determined by auto-bomb calorimeter (Leco AC 500) and chemical composition by standard TAPPI method. Table 1 shows the results of CHNS, proximate analysis, heating value and chemical composition of the cotton stalk.

The proximate analysis results are presented on dry basis. Cotton stalk was dried in an oven at 105 °C for overnight to reduce the moisture in product prior to the experiments. Chemical composition of bio-oil was determined using GC–MS (Gas chromatography–mass spectrometry) analyzer, and FTIR (Fourier transform spectroscopy) (Agilent CARY 630) was applied to identify the functional groups and bonds in bio-oil liquid. GC/MS analysis of bio-oil was performed on a Shimadzu GC/MS-QP2010 plus equipped with an Agilent 5973 mass selective detector (MSD). The GC column used was a DB-WAX 122-7032, 30 cm long with 0.25 mm ID and 0.25 μm film. The oven was programmed to hold at 40 °C for 5 min, ramp at 5 °C/min to 250 °C and hold there for 20 min. The injector temperature was 220 °C, and the injector split ratio was set at 30:1. Carrier gas helium flow rate was 1 mL/min. The bio-oil samples were prepared as 10 % solution in acetone. Karl Fischer Titrator was used to determine the water contents in the bio-oil using hydranal as titrant. Composition of incondensable gas obtained from the pyrolysis of cotton stalk was found using GC analyzer (Cp-3800/3300 Netherland).

Table 1 Characteristics of cotton stalk

Proximate analysis (wt% db)		Ultimate analysis (wt% db)		Chemical composition (wt%)	
Volatile matter	65.05	Carbon	44.47	Cellulose	27.5
Fixed carbon	31.18	Hydrogen	3.77	Hemicellulose	25.4
Ash	3.77	Oxygen	51.14	Lignin	21.7
HHV (MJ/kg)	16.75	Nitrogen	0.62		

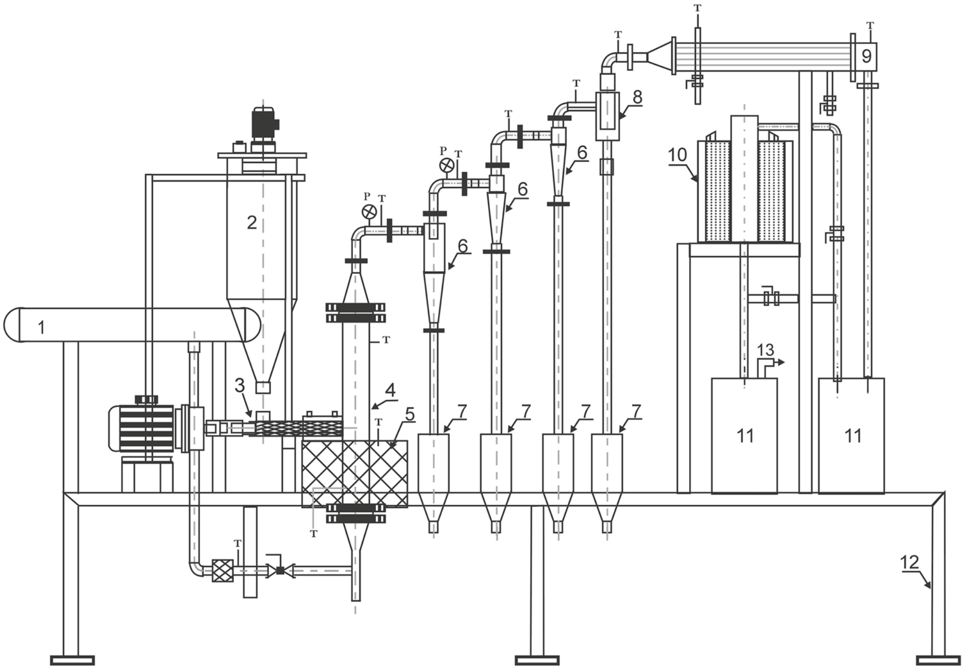


Fig. 1 Pyrolysis apparatus. *1* Nitrogen header, *2* feed hopper, *3* biomass feeder, *4* fluidized bed reactor, *5* reactor heater, *6* cyclones, *7* char collector, *8* strainer, *9* water condenser, *10* dry ice condenser, *11* pyrolysis liquid collector, *12* frame, *13* vent gas

2.2 Pyrolysis Apparatus

Fast pyrolysis bench-scale plant (Fig. 1) with feed capacity of 2 kg/h was designed, fabricated and operated at the Institute of Chemical Engineering and Technology, University of the Punjab, Lahore, Pakistan. The major components of the system were biomass feeding system, fluidized bed reactor, heating system, gas solid separation system, pyrolysis vapors condensation system and instrumentation and control system. In the fast pyrolysis process, screw feeder was used to transport the regulated biomass feedstock into the fluidized bed reactor, and preheated inert nitrogen gas at about 350–400 °C was passed through the bottom of the reactor as a fluidization gas for the sand bed. Pyrolyzed volatiles along with charcoal left the reactor from the top. The solid char particles were separated from the gas in the cyclone separators, and pyrolysis gas was first condensed in the water-cooled condenser and then in dry ice condenser to obtain pyrolysis liquid. The non-condensable gas was passed through a filter to remove fine solids, and then samples of gas were taken after every 15 min for analysis. The remaining gas was either burnt in the flare or vented out. The fluidized bed reactor was made of stainless steel SS 316 L and has diameter of 100 mm and height of 750 mm. The reactor was heated indirectly with carbide heating rods to maintain the pyrolysis reaction temperature.

The feeding system was comprised of a hopper with nominal capacity of 0.03 m^3, stirrer to entrain the biomass and screw feeder having the variable speed to drive the feedstock into the reactor. The distributor plate was made of stainless steel with hole size of about 100 μm to retain the silica sand bed. Nitrogen gas was heated into the preheater at 350–400 °C to establish the temperature in the reactor. The biomass was directly fed to the bed in the reactor after achieving the designated temperature. The temperature at the cyclones was maintained at about 400 °C to avoid the condensation of pyrolysis vapors in order to minimize the secondary cracking reactions responsible for producing surplus gas. More detail of pyrolysis system was explained in the research article [37].

The cotton stalk pyrolyzed in the fluidized bed reactor at temperature of 360–540 °C with standard deviation of around 5.0 °C was solids from cyclones as charcoal and the gas from the vent. Condensed liquid from water and dry ice condensers was referred as bio-oil. Bio-oil and charcoal were weighed, and gas mass was taken by difference. The standard operating procedure for fast pyrolysis has been adopted for the experiments.

3 Results and Discussion

The pyrolysis was carried out at flow rate of nitrogen above the minimum fluidization velocity calculated from Kunii and Levenspiel equations [38]. Silica sand with known size (−40 mesh) and weight of about 1000 g was used as fluidized bed material. The temperature of pyrolysis reaction was measured using thermocouples at three points in the reactor, and value was averaged. The various pyrolysis reaction conditions are shown in Table 2. The temperature from the exit of the reactor to inlet of condenser was maintained at 350-400 °C in order to avoid condensation of tar in the lines. The condensable was rapidly cooled down in the water and dry ice condensers, respectively.

3.1 Effect of Temperature on Pyrolysis Products Distribution

Fast pyrolysis of cotton stalk (Fig. 2) was carried out in fluidized bed reactor. Bio-oil and charcoal (Fig. 3) were collected after each experiment and yield of individual product calculated from the mass balance. The pyrolysis oil produced from the fast pyrolysis reaction was due to the fast heat-up of biomass and simultaneous fragmentation and depolymerization of the cellulose, hemicellulose and lignin present in the feedstock. The produced bio-oil is a complex mixture of hundreds of compounds with varying molecular weights. The yield of bio-oil was affected by the parameters such as biomass, reactor type and process conditions. The bed temperature was the most important parameter which affected the yield of bio-oil, char and gas in the pyrolysis process.

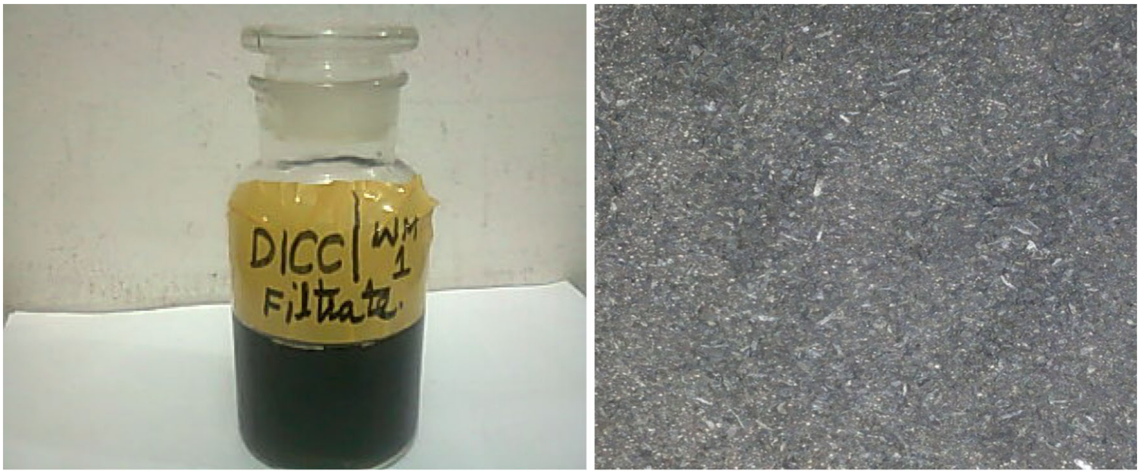
Figure 4 illustrates the effect of pyrolysis temperature on the distribution of pyrolysis products of cotton stalk. It is learned that bio-oil yield first increases from 28 to 36 wt% with the increase in reactor temperature from 360 to 490 °C and then decreases to 33 wt% at a temperature of 540 °C. The maximum bio-oil yield is 36 wt% at temperature of 490 °C. The amount of char yield decreases from 28 to 16 wt% at the same pyrolysis temperature. The mass balance was calculated by taking mass of input feedstock and output products by weighing individual masses from different units such as bio-char from cyclones 1, 2, 3 and strainer, whereas bio-oil from condensers (water and dry ice) and then adding these values. The total mass closure was always less than 100 wt% due to some tar and char always trapped into the pipe lines of pyrolysis system which was physically difficult to recover. The bio-oil yields were reported on wet basis because water might be present in the pyrolysis liquid. The yield of bio-oil seems low because in the literature [39] yields were reported after applying the optimization model which compensated the yield losses in pipe lines of pyrolysis system.

Table 2 Pyrolysis conditions

Parameter	Temperature (°C)	Gas flow rate (m^3/h)	Feed rate (g/min)	Pressure	N_2 Preheater temperature (°C)
Range	360–540	2.5–3	10–15	Atmospheric	350–400


(a) (b)

Fig. 2 **a** Cotton stalk coarse particles. **b** Cotton stalk fine particles



(a) Bio Oil **(b)** Charcoal

Fig. 3 **a** Bio-oil. **b** Charcoal

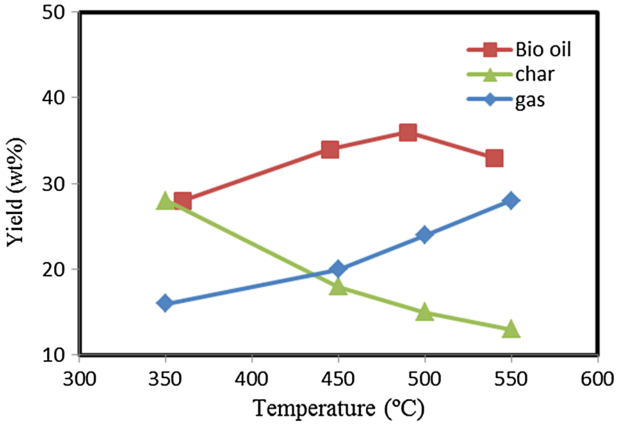


Fig. 4 Effect of temperature on yield of bio-oil, char and gas for the pyrolysis of cotton stalk

The decrease in the liquid yield and increase in gas yield are due to secondary vapor cracking reactions, whereas decrease in bio-char yield is due to the greater primary decomposition of biomass or char [34,40,41]. The similar results are reported in the literature by Sulaiman et al. [42], Garcia et al. [36] and Heidari et al. [43] for fast pyrolysis of eucalyptus wood, mallee woody biomass and eucalyptus grandis.

FTIR absorbance spectra peaks of pyrolysis liquid obtained from cotton stalk are shown in Fig. 5. The functional groups or bonds present in the pyrolysis liquid are shown in Table 3. The alcohols and phenols in the pyrolysis liquid are specified by the broad absorbance peak of O–H stretching vibration of 3353 cm^{-1} in the range between 3500 and 3200 cm^{-1}. It is important to note that bio-oil was not dried before IR spectrum so the peak around 3353 cm^{-1} may contain some contamination of water content. Alkanes are found

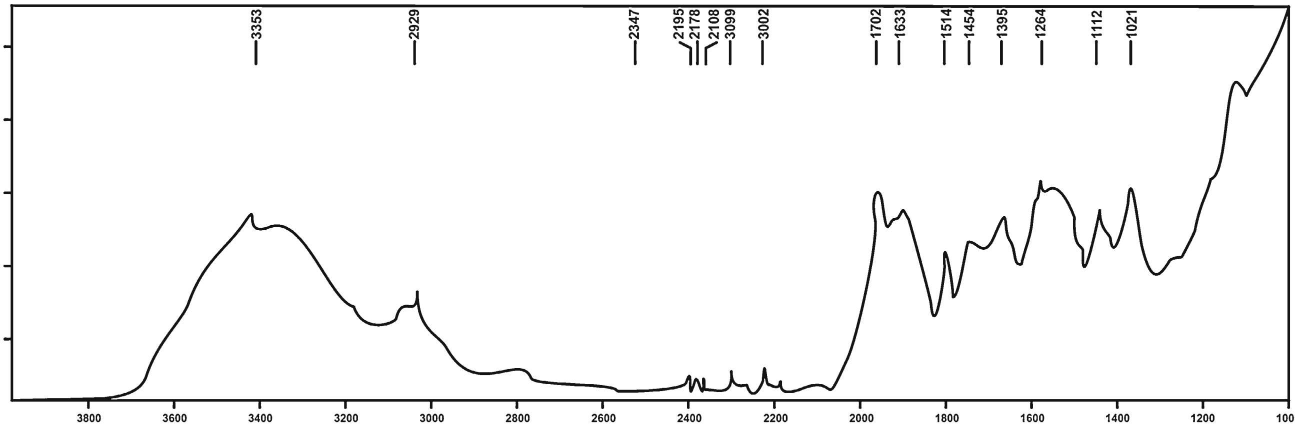


Fig. 5 FTIR absorbance spectra of pyrolysis liquid

Table 3 Functional groups characterized in Fig. 5

Wavenumber (cm^{-1}) experimental	Wavenumber (cm^{-1}) range	Functional group	Bond
3353 (s, b)	3500–3200	Phenols, alcohols	O–H
2929 (m, n)	3300–2500	Carboxylic acids	O–H
1702 (s, n)	1725–1680	Carboxylic acids/ketones	C=O
1639 (m, n)	1680–1620	Alkenes	C=C
1454 (m, n)	1470–1450	Alkanes	C–C
1365 (m, n)	1370–1350	Alkanes	C–C
1021 (s, s)	1300–1000	Alcohols, carboxylic acids, ethers, esters	C–O
747 (m, s)	680–860	Aromatic	C–H

in the medium absorbance peak of C–H asymmetric stretching with wavelength of 2929 cm^{-1}. The presence of ketones and aldehydes is characterized by the strong and medium narrow absorbance peaks of C=O between the frequency range of 1625–1750 cm^{-1}. The methyl and dimethyl groups are indicated by the medium narrow absorbance peaks of C–C vibrations of 1454 and 1365 cm^{-1}, respectively. The peak at 1454 cm^{-1} represents the bending vibration of aliphatic C–H, while the peak at 1365 cm^{-1} represents the parallel vibration of C–H. The possible absorbance peak of C–O of wave number 1021 cm^{-1} in the range of 1000–1300 cm^{-1} represented alcohols, carboxylic acids, ethers and esters. The aromatic compounds are categorized by the presence of the absorbance peak of 747 cm^{-1} wavenumber in 680–860 cm^{-1} range. The similar functional groups and bonds were found in the bio-oil derived from rice husk and sunflower pressed bagasse by Islam et al. [44] Gercel [45] and Zhou et al. [46] in the literature.

The bio-oil obtained from the fast pyrolysis of cotton stalk is in the homogenous phase and dark brown in color. The total acid number (TAN) of bio-oil obtained is 64 (mg KOH/g of oil). The water content in the condenser bio-oil varies from 24 to 35 wt% which might be due to original moisture in the feedstock and dehydration reactions in the pyrolysis process [47]. It may be reduced by adding electrostatic precipitator (ESP) in the pyrolysis system which removes moisture and aerosols from the liquid product. The decrease in bio-oil yield and increase in the water content in the bio-oil depend upon several pyrolysis parameters such as temperature, feed particle size and vapor residence time [26,33]. As the temperature increases from 450–650 °C, water content in the bio-oil increases and decreases at a temperature of 300–450 °C [36], whereas bio-oil yield also decreases at higher temperature (>500 °C) due to secondary cracking reactions [48,49].

The fractions (area %) of chemical compounds in the bio-oil are shown in Table 4 which presents quantitative detail of various aliphatic hydrocarbons, aromatics, alcohols, aldehydes and oxygenates.

Table 4 GC–MS analysis of obtained bio-oil

Compound	Area %
Acetic acid	30.57
2-Propanone, 1-hydroxy-	21.16
Phenol	3.78
2-Propanone, 1-(acetyloxy)-	2.16
1-Hydroxy-2-butanone	2.07
3-Furaldehyde	1.96
2-Cyclopenten-1-one	1.86
1,2-Cyclopentanedione, 3-methyl-	1.62
2,3-Butanedione	1.42
Levoglucosan	1.31
2-Butanone, 3-hydroxy-	0.75
Phenol, 4-methyl-	0.69
2-Butanone	0.68
2-Cyclopenten-1-one, 3-methyl-	0.66
Propanoic acid	0.65
2(5H)-Furanone	0.62
Phenol, 3-methyl-	0.59
Phenol, 2-methyl-	0.55
2-Cyclopenten-1-one, 2-methyl-	0.54
2-Amino-1,3-propanediol	0.48
Phenol, 4-ethyl-	0.33
2-Butanol, 3-methyl-, acetate	0.3
2-Furanmethanol	0.29

3.2 Effect of Particle Size on Pyrolysis Products Distribution

Feed particle size is also one of the significant constraints controlling the yield of pyrolysis oil including water. The amounts of water content with particle size of 1.0, 1.5 and 2.0 mm are 24, 29 and 35 %, respectively. Almost similar trends in results for water content from fast pyrolysis of pine sawdust and apricot stone are found by Wei et al. [50]. Water content in the bio-oil increases with the increase in

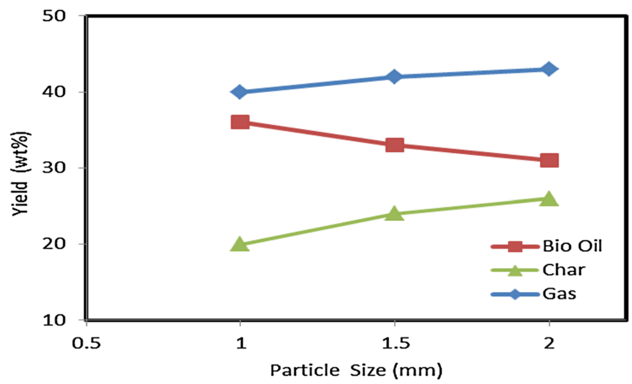


Fig. 6 Effect of feed particle size on yield of bio-oil, char and gas for the pyrolysis of cotton stalk

particle size due to the heat and mass transfer as well as on account of secondary cracking reactions inside the biomass particle. The polymerization secondary reactions of some volatile constituents may deposit in the form of large molecules on the walls of pores resulting in the increase in yield of char and decrease in release of volatiles which takes place in large size biomass particles [51]. The increased water content in the bio-oil indicates secondary cracking reactions during pyrolysis [52].

In Fig. 6, the effect of feed sizes such as 1.0, 1.5 and 2.0 mm is shown on yield of pyrolysis product distribution. It is revealed from the graph that the bio-oil yield decreases by increasing the feed size of cotton stalk, whereas char and gas yields increase. Bio-oil yield decreases from 36 to 31 wt%, char yield from 20 to 26 wt% increases, and gas yield increases from 40 to 43 wt% by the increase in particle size. Shen et al. [53] and Park et al. [34] reported the similar results of effect of particle size on the yield of pyrolysis products for oil mallee woody biomass and japanese larch. This effect of particle size of biomass is conceived due to the heating rate [54]. By increasing size of the feed particle, distance from the surface of particle to its center increases which impedes the rapid heat transfer, indicating the incomplete pyrolysis reaction there and hence the pyrolysis volatiles are cut down which decreases the pyrolysis oil yield [55].

Gas chromatograph is used to analyze non-condensable gas shown in Fig. 7. The qualitative analysis of pyrolysis liquids is carried out by GC using acetone as a solvent. Test 1 chromatogram yields about 10 number of peaks with different retention times leading the chemical composition of liquid oil included acetone, benzene, 3-methyl pentane, 2,2-dimethylbutane, 3,5-dimethyloctane, 2-methylhexanoic acid and 1,2-benzene dicarboxylic acid, whereas test 2 chromatogram gives one significant peak with retention time of 47.475, indicating the compound as 1,2-benzene dicarboxylic acid, Bis(2-ethylhexyl) phthalate. The similar chemical compounds are found for the bio-oil in the literature [56,57]. There may be more than hundred compounds in the bio-oil, but due to pyrolysis conditions, especially reactor temperature and long vapor residence time, only few compounds are present in liquid, resulting in lower bio-oil yield.

It is observed that there are three peaks of indicating significant peak of H_2 and minor peak of CO_2 gas and third one of n-butane, isobutane. The literature [58,59] on fast pyrolysis reported that CO_2 was the product of primary pyrolysis, whereas CO and CH_4 were produced from secondary cracking reactions of volatiles followed by the reduction of CO_2. The secondary cracking also yields H_2 and CO.

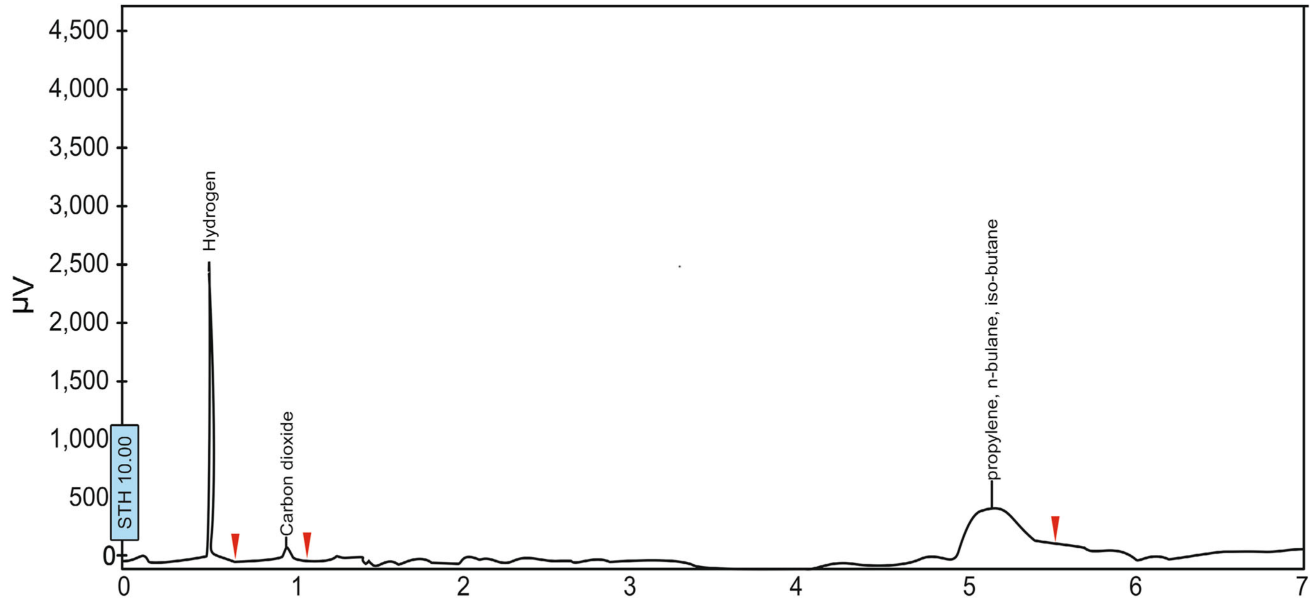


Fig. 7 Run 2 Gas chromatograph of non-condensable gas

4 Conclusions

Fast pyrolysis of cotton stalk is conducted in the bubbling fluidized bed reactor at temperatures of 360–540 °C, and influence of pyrolysis temperature and feed size on the yield of bio-oil and coproducts is investigated. The yield of bio-oil increases with the increase in temperature, whereas yield of charcoal decreases with increasing the temperature and yield of gas also increases with rise in the temperature. The maximum bio-oil yield obtained is 36 wt% at temperature of 490 °C at feed size of 1.0 mm. The major chemical compounds of bio-oil obtained at the optimum reaction conditions are 2,3-butanedione, 2-propanone,1-hydroxy, acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-butanone, 2-cyclopenten-1-one, 2(5H)-furanone, phenol, 1,2-cyclopentanedione, 3-methyl- and levoglucosan.

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