

PYROLYSIS OF COCONUT SHELL FOR BIO-OIL

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ABSTRACT

The conversion of coconut shell into pyrolytic oil by fixed bed fire-tube heating reactor has been taken into consideration in this study. The major components of the system were fixed bed fire-tube heating reactor, liquid condenser and collectors. The raw and crushed tamarind seed (in particle form) was pyrolyzed in an electrically heated 10 cm diameter and 27 cm high fixed bed reactor. The products are oil, char and gases. The parameters varied were reactor bed temperature, running time, gas flow rate and feed particle size. The parameters were found to influence the product yields significantly. The maximum liquid yield was 34.3 wt% at 450°C for a feed size of 0.6mm at a gas flow rate of 6 liter/min with a running time of minute. The pyrolysis oil was obtained at these optimum process conditions were analyzed for physical and chemical properties to be used as an alternative fuel.

Keywords: Pyrolysis, Fixed Bed, Coconut Shell, Renewable Energy, Biofuel

1. INTRODUCTION

Agricultural waste is one of the members of biomass, which is an attractive renewable energy resource because it is widely dispersed and could contribute zero net carbon dioxide emission to the atmosphere [1]. Biomass can be used as raw material for pyrolysis to generate liquid, gaseous and solid fuels. Pyrolysis conversion technology for biomass has been investigated over the last three decades and is used commercially [2]. Pyrolysis produces gas, vapor that can be collected as liquid and solid char. The yields of each of these products depend on process conditions [3]. Solid char has a good gross calorific value (GCV) of 17-36 MJ/kg [4] and may be used to provide heat for pyrolysis process itself. Solid char can also be used as a fuel either directly as briquettes or as char-oil or char-water slurries or it can be used as feedstocks to prepare activated carbon. The pyrolysis gas fraction contains high concentrations of CO₂, CO, H₂, CH₄, C₂H₄, C₃H₆, and other hydrocarbons with a GCV of 6.4-9.8 MJ/kg and can be used to provide process heat, circulated as an inert carrier gas or exported for applications such as feed drying. The usages of char and gas products in the pyrolysis process itself reduces production costs for the heating system. Bio-oil derived from agricultural wastes has moderate GCV ranging from 15-38 MJ/kg with some advantages in transportation, storage, combustion, retrofitting and flexibility in production and marketing [5]. The liquid product, is useful as a fuel, may be added to petroleum refinery feedstocks or upgraded by catalysts to produce

petroleum grade refined fuels. The bio-oil is a mixture of about 300 types of major and minor organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds [6]. Bio-oil has several environmental advantages over fossil fuels as a clean fuel. It is CO₂/GHG neutral. Therefore, bio-oil can generate carbon dioxide credits. No SO_x emissions are generated, because plant biomass contains insignificant amounts of sulfur. Thus, bio-oil would not be subjected to SO_x taxes. Bio-oil fuels generate more than 50% lower NO_x emissions than diesel oil in a gas turbine. The agro-based biomass is usually produced in the rural area where a large scale pyrolysis plant can be installed. Due to the decoupling nature of the pyrolysis plant, the bio-oil based small scale power generation plant can be installed in the remote area where the bio-oil can be supplied. The coconut palm, *Cocos nucifera*, is a member of the family *Arecaceae* (palm family). It is the only accepted species in the genus *Cocos* [7]. The conditions required for coconut trees to grow without any care are: mean daily temperature above 12–13 °C (53.6–55.4 °F) every day of the year. mean yearly rainfall above 1000 mm (39.37") ,no or very little overhead canopy, since even small trees require a lot of sun The main limiting factor is that most locations which satisfy the first three requirements do not satisfy the fourth, except near the coast where the sandy soil and salt spray limit the growth of most other trees[8]. Coconut palms are grown in more than 80 countries of the world, with a total

production of 61 million tones per year [9]. The husk and shells can be used for fuel and are a source of charcoal. Activated carbon manufactured from coconut shell is considered superior to those obtained from other sources, mainly because of small macrospores structure which renders it more effective for the adsorption of gas and vapor and for the removal of color, oxidants, impurities and odor of compounds. Characterization studies on coconut shell have been carried out through proximate, ultimate and thermo gravimetric (TG) analysis. The result of these analyses showed that coconut shell has high potentials to produce liquid fuel by pyrolysis conversion process. Although pyrolysis of biomass has achieved commercial status, there are still many aspects of the process which are largely empirical and require further study to improve reliability, performance, product consistency, product characteristics and scale-up. A quite number of the previous research groups worked for the potential recovery of fuels and chemicals from different agricultural residues and by-products including rice straw [4], guayule bagasse, sesame stalk, hazelnut shells, rice husks, jute stick, sugarcane bagasse [5], olive bagasse, sweet sorghum bagasse, cotton stalk, olive husk, corncob and tea waste [1] have already been studied, but most of them have focused on the effect of reactor temperature on product yields and product compositions. Ablative, circulating fluid bed, fixed bed, cyclone, fluid bed, and entrained flow reactors [10], but not fixed-bed reactors with fire-tube heating have been studied. Therefore, the objective of this study was to develop a new heating system for pyrolysis for recovery of liquid hydrocarbons from biomass solid wastes. A fixed-bed fire-tube heating pyrolysis reactor system was designed and fabricated considering all the process parameters. The abundantly available agricultural waste, coconut shell, was pyrolyzed in the internally heated fire-tube heating reactor system under N₂ atmosphere. The effects of operating temperature, feed size and vapor residence time on the product yields were investigated. The whole pyrolysis liquids obtained at optimum operating conditions were characterized by physical properties.

2. MATERIALS AND METHODS

2.1 Materials

The ripe coconut shell fruits were collected locally in Rajshahi and seeds were separated.

The seeds were crushed and sieved to the sizes 0.6-6.0 mm and oven dried to remove moisture for 12 hours at 110°C prior to pyrolysis. The proximate and ultimate analysis and gross calorific values of the coconut shells are presented in Table 1.

Table 1. Proximate and ultimate analysis, and gross calorific values of solid coconut shell

Biomass samples	Proximate Analysis (wt%,)			Ultimate analysis (wt%,)					GCV (MJ/Kg)
	Combustible matter	Moisture	Ash	C	H	O	S	N	
Coconut shell	85.36	11.26	3.38	63.45	6.73	28.27	0.17	0.43	22.83

2.2 Experimental Set-Up And Procedure

Coconut shell is pyrolyzed in an externally heated stainless steel fixed bed reactor system. The main components of the system are fixed bed reactor, liquid condenser and ice cooled liquid collectors. The effective length of the reactor is 46 cm and the diameter is 7.60 cm. The schematic diagram of the experimental set-up is presented in Fig. 1. The geometric features of the fixed-bed fire-tube heating reactor and fluid dynamics study on its cold model are presented elsewhere [11]. The experimental unit consists of a fixed-bed fire-tube heating reactor chamber, a gravity feed type reactor feeder, two ice-cooled condensers, N₂ gas cylinder, N₂ gas pre-heater, an air compressor, char collection bag and thermocouples with temperature controller. The reactor chamber was heated internally by fire-tubes containing insulated electric coil. In each pyrolysis run, by the action of gravity force a quantity of 500 (±2.0) gm of coconut shell sample was supplied from the feeder into the reactor chamber by opening the feed control valve as shown in Fig.1

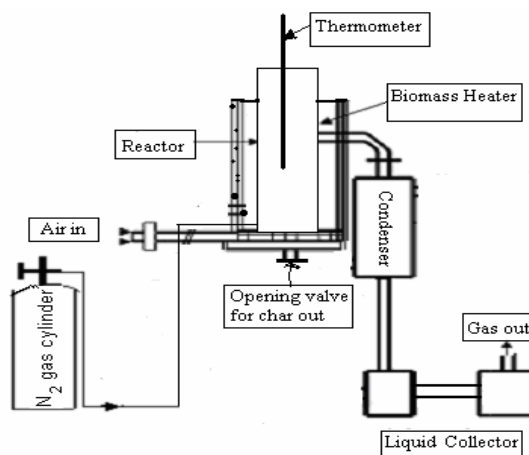


Fig 1. Schematic diagram of fixed bed pyrolysis system

Then the reactor was purged before experiments by the flow of N₂ gas of 6 l/min for 5 min to remove the

inside air. The temperature of the reactor was increased to a desired value of 400, 450, 500, 550°C or 600°C. During pyrolysis of coconut shell a reddish brown visible vapor usually flared into the atmosphere. When the decomposition was completed colorless (no visible) N₂ gas came out from the reactor. The colorless flaring was the significance of the completion of the thermal decomposition of the coconut shell. The reaction time was 100 min for every of all pyrolysis runs after which usually no further visible vapor product came out. Nitrogen gas was supplied in order to maintain the inert atmosphere in the reactor and also to sweep away the pyrolyzed vapor product to the condensers. Pyrolysis vapor product was passed through two sets of condenser pipes to quench into liquid and then collected in the reagent bottles. The uncondensed gases were flared to the atmosphere. The bottles were completely filled up with liquid so that no air could be trapped into the bottles. When pyrolysis of the feed material in the reactor was completed, the vapor exit port was closed and the reactor heater and LPG burner were switched off. N₂ gas supply was also stopped. After cooling down the system, the char product was pushed out from the reactor chamber with the aid of compressed air supplied from the air compressor by opening char exit port. Char was collected in the char collection bag and weighted. The liquid was then weighted and gas weight was determined by subtracting the liquid and char weight from the total weight of feedstock. Afterwards, the system had been made ready for the next run just repositioning the valves. Initially the pyrolysis were performed by varying the temperature within the range of 400–600°C at every 50°C for a particular feed size and vapor residence time. Once the temperature of maximum liquid yield (450°C) was selected, additional tests were conducted at the optimum temperature by varying the feed size and the vapor residence time to find out the optimum process conditions.

2.3 Pyrolytic product liquid analysis

Pyrolytic liquids obtained under the maximum liquid yield conditions were well mixed and homogenized prior to analysis being made. Some physical properties of pyrolytic liquids including density, viscosity, flash point, pour point and GCV were determined by using the standard methods ASTM D189, ASTM D445, ASTM D92, ASTM D97, and ASTM D240, respectively. Elemental analysis (C, H, N and S) of liquids was determined with an elemental analyzer of model EA 1108, which followed the quantitative "dynamic flash combustion" method.

3. RESULTS AND DISCUSSIONS

3.1 Pyrolysis product yields

3.1.1 Effect of reactor temperature on the product yields

The percentage yields of the pyrolysis products, liquids, solid char, and gases obtained from at a temperature range between 400-600°C, feedstock size of 0.6 mm and gas flow rate of 6 L/min are presented in

fig.2. The figure shows that when the temperature increased from 400 to 450°C, the yield of liquid increased first to a maximum value at 450 °C, and then decreased to a minimum value at 600 °C. The gas yield increased over the whole temperature range, while char yield decreased over the whole temperature range. It is apparent that a fairly sharp temperature optimum exists at which maximum yield of liquid was achieved probably due to strong cracking of the selected crushed coconut shells at this temperature. The coconut shell sample was not totally decomposed at a temperature less than 450 °C. The thermal decomposition of the sample increased (*i.e.* solid yield decreased) up to a temperature of 450 °C and hence increased the liquid and gas yields. Solid char consists of a small amount of volatile hydrocarbons, solid hydrocarbons, and inorganic compounds. Therefore, there is no obvious mechanism for char loss with increasing temperature; only higher temperatures volatilize some of the solid hydrocarbons of the char. In competition with char loss reactions, a certain amount of char- or coke-like carbonaceous material is formed due to secondary reactions among the polymeric compounds, derived primarily from depolymerization and fragmentation reactions of three key biomass building blocks: cellulose, hemicellulose, and lignin [12]. The decrease in liquid yields and increase in gas yields above a temperature of 450 °C is probably due to decomposition of some oil vapors into permanent gases, and secondary carbonization reactions of oil hydrocarbons into char. The increase in gas yields at higher temperatures

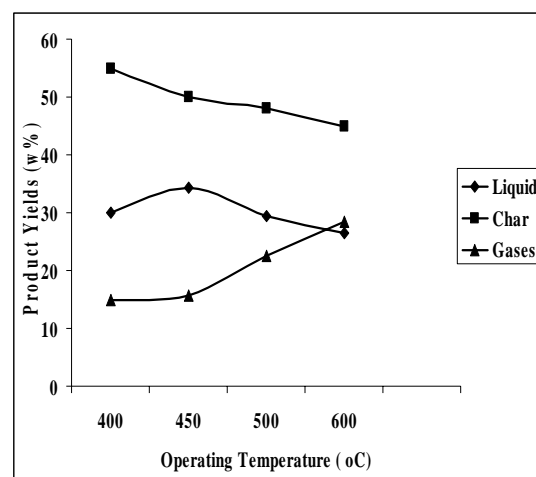


Fig 2. Effect of temperature on product yields

is also caused by char loss reactions. Thus, at higher temperatures the gas yields gradually dominated; however, 450 °C seems to be the optimum temperature to obtain liquid products from thermochemical conversion of solid coconut shell by pyrolysis, since decomposition is complete and liquid yields become maximized. Pyrolysis product yields and their distributions over the whole range of temperature depend not only on feedstock composition and operating temperature, but also on the specific characteristics of the system used, such as size and type of reactor, efficiency of heat transfer from the

hot reactor surface to and within the biomass, feed particle size, and vapor residence time. Therefore, results from different studies are difficult to compare. Studies on fluidized-beds and fixed-beds [13] resulted in product distributions similar to those of the presented study. Solid yield decreased and gas and liquid yields increased up to an intermediate temperature. At increasing temperatures, solid yields remained almost constant, gas yields increased and liquid yield decreased. The liquid yields obtained in the presented study are slightly lower and char yields are higher compared to those of previous studies [14]. These variations are mainly due to compositional differences (moisture, volatile, fixed carbon and ash content) in biomass feeds and quality of pyrolytic product liquids. A higher volatile content of feedstock with lower amounts of fixed carbon and ash is desirable for higher percentage of liquid yields in the pyrolysis process. Higher amount of fixed carbon and ash content of a feedstock contribute to char formation. Moreover, water in bio-oils originates from the original moisture in the feedstocks and dehydration reactions occurring during pyrolysis [15]. Feedstock used in the presented study was of a lower volatile and moisture and a higher fixed carbon and ash content compared to that used in earlier studies.

3.1.2 Effect of feed size on the product yields

The effect of feed size on product yields under optimum reactor temperature and for a N_2 gas flow rate of 6 L/min is presented in Figure 3. The figure shows that the maximum value of liquid yields for feed sizes of 0.6 mm and then decreased for larger feed size while the char yield increased and gas yield decreased for all particle sizes above 0.6 mm. The thermal conductivity of biomass is very poor ($0.1 \text{ W/m}^2\text{ }^\circ\text{C}$ along the grain, $0.05 \text{ W/m}^2\text{ }^\circ\text{C}$ cross grain), and hence biomass particles have to be very small to allow rapid heating to achieve high liquid yields. Theoretically, particle size has a great effect on pyrolysis product yields. It is generally assumed that a decrease in particle size will tend to generate higher liquid product yields [16]. 6 L/min.

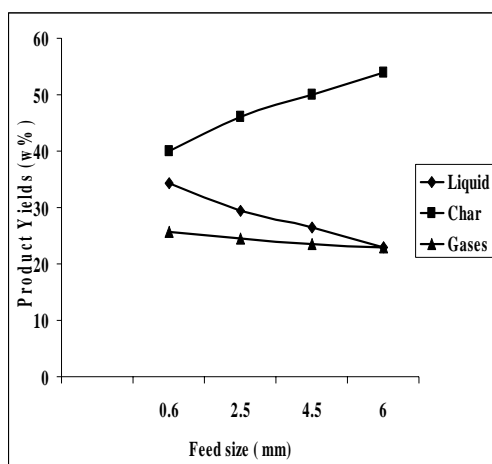


Fig 3. Effect of feed size on product yields

During pyrolysis, a high heating rate (up to $1000 \text{ }^\circ\text{C/s}$) may be achieved with a thin reaction layer but the lower thermal conductivity of biomass prevents such a heating rate through the whole particle. Smaller feed sizes provide more reaction surface and allow a high heating rate, but the decomposition of the biomass feed occurs too quickly. There is sufficient time for secondary reactions in the oil vapors and consequently gas yields increase and liquid and char yields decrease. In contrast, the heating rate in larger feed particles is low due to their lower thermal conductivity, and heat can flow only to a certain depth in the available pyrolysis time. Thus, the cores of the larger particles become carbonized and/or cannot be decomposed completely resulting in an increase in char yield and a decrease in liquid and gas yields. Pyrolysis experiments performed by Putun et al. [16] in a fixed-bed reactor suggested that particle size had little effect on product yields. In our study, we observed the same. For particle size 0.6 mm decomposition proceeds to completion and there is less of a chance for secondary cracking at the optimum reactor temperature and a gas flow rate

3.1.3 Effect of running time

The variation of product yields with respect to running time at optimum reactor temperature 450°C for feed particle of size 0.6 mm are shown in Figure 4. The maximum liquid product is 34.3 wt% of biomass feed while the solid char product is 37 wt% for running time 100 minutes. It is observed that for running time less than that of 100 minutes the liquid yield is not optimum that may be due to incomplete pyrolysis reaction of the whole feed. For the running time above 100 minute the liquid yield is almost constant with slight increase in gases and decreases char yield. Thus it may be

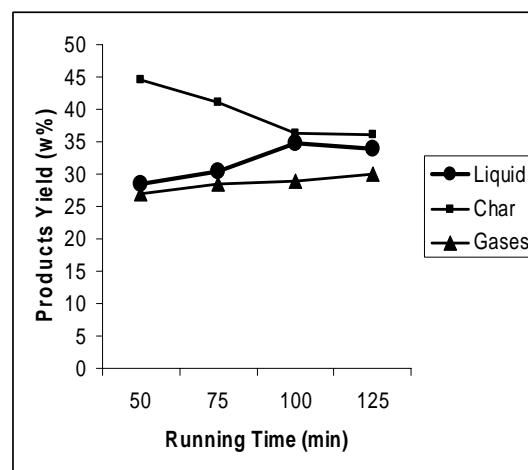


Fig 4. Effect of running time on product yields

concluded that the pyrolysis of solid biomass feed is completed within 100 minute of running time. Through the experimental investigation it is found from paper waste fixed bed pyrolysis for bed temperature 450°C , feedstock size of 2-3 cm with a running time of 45 min, the maximum liquid yield was 54 wt% of solid feedstock.

A number of research works [17] have been carried out for running time on product yields and their results are approximately similar to those of the presented study.

3.2 Analysis of product liquids

3.2.1 Fuel properties of the pyrolytic liquids

Bio-crude oils obtained from pyrolysis of coconut shell were homogeneous and no phase separation took place in the storage bottles. The derived liquids were characterized in terms of fuel properties and chemical compositions and compared to other pyrolytic derived fuel from date seed and Heavy fuel oil. in Table 2.

Table 2: Comparison of coconut shell pyrolysis oil with biomass derived pyrolysis oil and petroleum fuel

Properties	Coconut shell seed oil	Date seed oil [18]	Heavy fuel oil [19]
Kinematic viscosity at 30°C (cSt)	1.99	6.63	200 [#]
Density (kg/m ³)	1095.5	1042.4	980 [*]
Flash Point (°C)	>100	126	90-180
GCV (kJ/kg)	21400	28636	42000

N.B.: # at 50°C * at 20°C

It is found that the density of pyrolytic liquids was higher than that of commercial diesel fuel, which corresponds to a higher energy content. Viscosity plays an important role in design and operation of the fuel injection system as well as in atomization quality and subsequent combustion properties of the fuel. The viscosity of liquid products from jute stick sample was higher than that of No. 2 diesel but considerably lower than that of heavy fuel oil (200 cSt at 50°C). A low viscosity of 1.99 cSt at 30°C is a favorable feature in the handling and transportation. The viscosity of bio-oils usually vary over a wide range (35-1000 cP at 40 °C) depending on the feedstock and process conditions, and especially on the efficiency of collection of low boiling components [16]. The flash point of the selected biomass-derived liquids was >70 °C. This flash point is not too high when compared with petroleum-refined fuels; for example, kerosene has a required minimum flash point of 23 °C, diesel fuel of 55 °C and light fuel oil 79 °C. The high flash points of biomass-derived liquids are not surprising since the product liquids represent un-refined liquids with a mixture of components having a wide distillation range. The flash points of bio-oils usually vary in the range of 40-70 °C or above 100 °C,

depending on the contents of light organic volatiles . The pH value of the pyrolytic liquids was about 4. Bio-oils usually contain about 7-12 wt% acids, and have a pH of 2-4 [20]. Thus, storage and handling of the liquids can be problematic in industrial usage as corrosion can occur .

4. CONCLUSIONS

The pyrolytic product yields and liquid product composition of the presented study prove that “fire-tube heating” in fixed-bed pyrolysis technology is an efficient and effective method of heating. The optimum liquid yields conditions for the reactor system are: operating temperature 450 °C, feed size 0.6 mm and gas flow rate 6 L/min with the running time 100 min .The physical properties analysis showed that the oil is heavy in nature with moderate viscosity. The heating value of the oil is moderate.

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6. NOMENCLATURE

Symbol	Meaning	Unit
T	Temperature	(K)
GCV	Gross Calorific Value	(kJ/kg)
wt%	Weight percentage	

7. MAILING ADDRESS

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