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PRODUCTION OF PYROLYSIS OIL FROM PINE SEEDS THROUGH FIXED BED PYROLYSIS PROCESS AND ITS COMPARISON WITH FOSSIL OIL

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Abstract- *The conversion of pine seeds into pyrolytic oil by fixed bed reactor has been taken into consideration in this study. A fixed bed pyrolysis system has been designed and fabricated for obtaining liquid fuel from biomass solid wastes. The major components of the system are: fixed bed reactor, liquid condenser and liquid collectors. The pine seeds in particle form are pyrolized in an externally heated 7.6 cm diameter and 46 cm high fixed bed reactor with nitrogen as the carrier gas. The reactor is heated by means of a cylindrical biomass source heater. Rice husk, cow dung and charcoal are used as the energy source. The products are oil, char and gas. The parameters varied are reactor bed temperature, running time and feed particle size. The parameters are found to influence the product yields significantly. The maximum liquid yield is 51 wt% at 500^0C for a feed size of <1.18 mm at a gas flow rate of 5 liter/min with a running time of 90 minute. The pyrolysis oil obtained at these optimum process conditions are analyzed for some of their properties as an alternative fuel. The higher heating value of pine seed-oil was found as 24.22 MJ/kg. The heating value of the oil is moderate.*

Keywords: Pine seeds, Pyrolytic oil, Fixed bed reactor, Fossil oil, Biomass

1. INTRODUCTION

Biomass has been recognized as a major renewable energy source to supplement declining fossil fuel sources of energy. It is the most popular form of renewable energy and currently biofuel production is becoming very much promising. Transformation of energy into useful and sustainable forms that can fulfill and suit the needs and a requirement of human beings in the best possible away is the common concern of the scientists, engineers and technologists. From the view point of energy transformation, fixed bed pyrolysis is more attractive among various thermo chemical conversion processes because of its simplicity and higher conversion capability of biomass and its solid wastes into liquid product.

In South Asian developing countries, especially in Bangladesh the generation of biomass waste is quite high. Along with other residues these waste accumulated is creating disposal problems. Also direct burning of these wastes creates a serious environmental problem. As carbonaceous solid wastes are the source of energy, therefore, the potential of recovering these wastes into useful form of energy by pyrolysis into liquid fuel should be considered. In this way the waste would be more readily useable and environmentally acceptable. This liquid of high heating value can easily be transported, can be burnt directly in the thermal power plant; can easily be injected into the flow of conventional petroleum refinery, can be burnt in a gas turbine or upgraded to obtain light hydrocarbon transport fuel. The solid char can be used for making activated carbon. The gas has high calorific value, sufficient to be used for the total energy requirements of the pyrolysis plant. Recently some work has been carried out with biomass solid waste as feedstock at the Fluid Mechanics Laboratory of Mechanical Engineering Department of Rajshahi University of Engineering & Technology (RUET), Rajshahi, to obtain liquid fuel using fixed bed pyrolysis technology.

2. PYROLYSIS TECHNOLOGY: A BRIEF OVERVIEW

2.1. Pyrolysis Technology

Pyrolysis is an attractive method to recycle scrap tires has recently been the subject of renewed interest. Pyrolysis of tires can produce oils, chars, and gases, in addition to the steel cords, all of which have the potential to be recycled. Tire pyrolysis liquids (a mixture of paraffins, olefins and aromatic compounds) have been found to have a high gross calorific value (GCV) of around 41-44 MJ/kg, which would encourage their use as replacements for conventional liquid fuels [1, 2, 3]. In addition to their use as fuels, the liquids have been shown to be a potential source of light aromatics such as benzene, toluene and xylene (BTX), which command a higher market value than the raw oils [4, 5]. Similarly, the liquids have been shown to contain monoterpenes such as limonene [1-methyl-4-91-methylethenyl) -cyclohexene] [6, 7].

Pyrolytic char may be used as a solid fuel or as a precursor for the manufacture of activated carbon [8, 9]. It was found that another potentially important end use of the pyrolytic carbon black (CBp) may be as an additive for crude bitumen [10]. Some of the previous research group studied the composition of evolved pyrolysis gas fraction and reported that it contains high concentration of methane, ethane, butadiene and another hydrocarbon gases with a GCV of approximately 37 MJ/m^3, a value sufficient to provide the energy required by the pyrolysis process [11].

There are four main thermo chemical methods of converting biomass. Such as (1) pyrolysis (2) liquefaction (3) gasification (4) direct combustion. Pyrolysis is one of the most important thermo-chemical conversion processes. So direct conversion of feed material (tire) by using pyrolysis system. Pyrolysis can be presented by the following equation

$$CaH_bO_c + Heat \longrightarrow H_2O + CO_2 + H_2 + CO + CH_4 + C_2H_6 + CH_2O + \ldots\ldots\ldots + Tar(liquid\ oil) + Char$$

2.2. Selected Biomass Waste

Pine seeds were selected as the feed material for this study. *Polyalthia longifolia* in the genus Swietenia, is extensively cultivated in India, Sri Lanka, Bangladesh etc as avenue tree. It is a semi evergreen tree, about 30-35m tall. Fruit shape is oval, fruit length is 1 to 3 inches, fruit covering dry or hard, the fruit color is brown.

2.3. Reasons for Selecting Pine Seeds as Biomass Waste

1. A large amount (250000 tons/yr) of pine seeds are not utilized which is grown in Bangladesh

2. The production of oil from pine seeds may provide the use of a renewable resource, and at the same time adding value to agricultural products.

Table 1: Approximate composition of pine seeds [12]

Moisture	5%
Crude Protein	31.6%
Oil	10-12%
Soluble sugar	5.15%
Fat	44.9%
Ash	4.5%

2.4. Fixed Bed Pyrolysis System

Pyrolysis may be either fixed bed pyrolysis or fluidized bed pyrolysis. In fixed bed pyrolysis, a fixed bed pyrolyser is used. The feed material in the reactor is fixed and heated at high temperature. As the feed is fixed in the reaction bed (reactor), it is called fixed bed pyrolysis. In this process, the feed material is fed into the reactor and heat is applied externally. Liquid petroleum or other inert gas is used for making inert condition and for helping the gaseous mixture to dispose of the reactor. The losses in fixed bed pyrolysis are relatively less than fluidized bed pyrolysis. Moreover, fluidized bed pyrolysis is more complex. This project work is based on fixed bed pyrolysis.

2.5. Feed Preparation

The pine seeds were collected and dried. It was then crushed into smaller sizes. These are <1.18mm, 1.18mm, 2.36mm, and 4.75mm in dia. It was dried with the help of oven. Thus the feed material is prepared.

3. EXPERIMENTAL PROCEDURE

The following procedures are employed for experimental operation:

(1) Feed material was weighed and filled into the reactor.

(2) The experimental set-up was assembled.

(3) High temperature adjustable gaskets were used to seal the joints and fittings of the hot parts of the connecting pipe, reactor and condenser.

(4) Ice was placed into the condenser.

(5) The reactor was heated externally by a biomass heater at different temperatures and these temperatures were measured by thermometer.

(6) The N2 gas was passed through reactor through a heated pipe and this flow was controlled by the use of a gas flow meter valve.

(7) The operation time was recorded by means of a stopwatch.

(8) When the operation was completed a small flow of N2 gas was allowed to pass through the system to prevent back flow of air which might react with hot gases when the reactor was still hot.

(9) It is dismantle when the rig was cooled enough to be handled. The char was collected from the reactor bed and weighed. All data are recorded in tabular form.

(10) All the parts of the system were cleaned and the heating value of the liquid and char was measured by a bomb calorimeter before reassembling for the next run.

4. PHYSICAL PROPERTY

Physical properties of pine seeds oil is given below in table.

Table 2: Physical characteristics of pine seed oil.

Analysis	Pine seeds oil
Kinematic viscosity at 350C (cSt)	12.15
Density(kg/m3)	1240
Flash Point(0C)	60
Fire Point (0C)	76
HHV of liquid(MJ/kg)	24.22
HHV of char(MJ/kg)	22.5
HHV of feed material(MJ/Kg)	20.7

5. EFFECT OF FEED PARTICLE SIZE

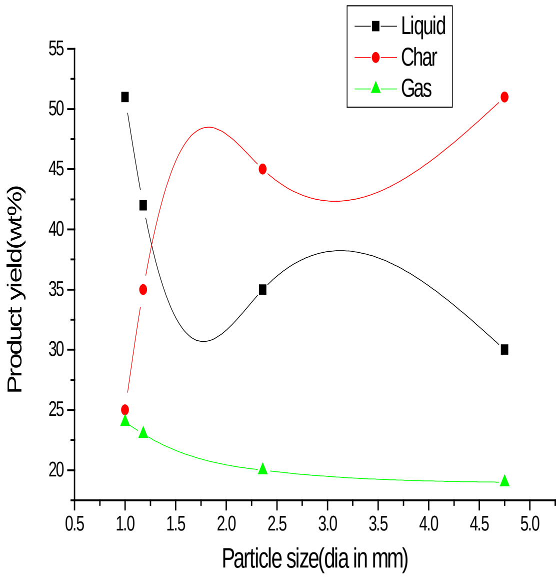

Fig.1: Effect of feed particle size on product yield (<1.18 mm, 1.18 mm, 2.36 mm and 4.75mm) for reactor temperature 450~550oC.

Figure 1 represents the percentage weight of liquid and solid char products for different particle size of feed at a bed temperature of 500oC and an operating time of 90 minutes. It is observed that at 500oC the percentage of liquid collection is a maximum of 51% of total biomass feed for particle size of <1.18 mm .A less amount of liquid is obtained from the larger particle size feed. This may be due to the fact that the larger size particles are not sufficiently heated up so rapidly causing incomplete pyrolysis that reduced liquid product yield.

6. EFFECT OF REACTION TEMPERATURE

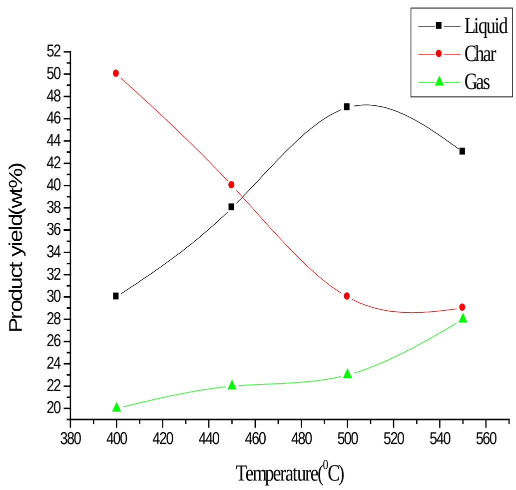

Fig.2: The effect of operating temperature on product yield.

Figure 2 shows the variation of percentage weight of liquid, char and gaseous products at different bed temperature with particle size of < 1.18mm. From this it is found that the maximum liquid products yield is obtained at a temperature of 500^{o}C, and this is 47%wt of total biomass feed. At lower temperature the liquid product yield is decreasing while with the increase of temperature above 500^{0}C, the liquid product yield is again deteriorating. With the increase of temperature the solid char yield is decreasing above 500^{0}C and increasing below 500^{0}C. It may be caused at lower temperature less than 500^{0}C , complete reaction cannot be taken place.

7. EFFECT OF RUNNING TIME

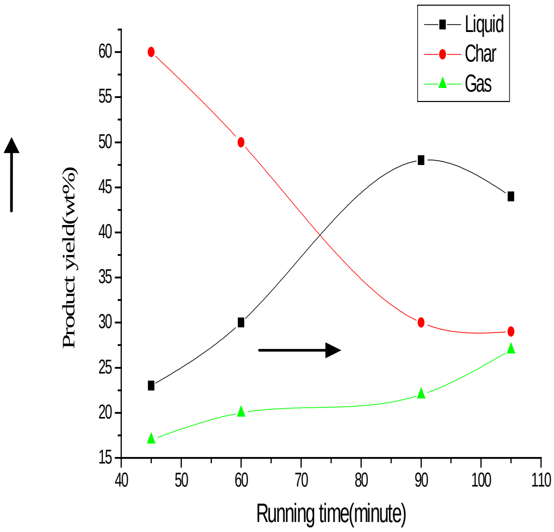

Fig 3: Effect of running time on product yield for reaction bed temperature 450~500^{0}C and for feed particle size 1.18 mm.

Figure 3 shows the variation of product yield (wt%) of liquid, solid char and gas products at a temperature of 500^{0}C for feed particle of size of < 1.18mm. The maximum liquid product is 48 wt% of biomass feed while the solid char product is 30wt% of dry feed at 90 minutes. It is observed that lower and greater running time than of that of 90 minutes the liquid product yield is not optimum that may be due to insufficient pyrolysis reaction and higher rate of gas discharge respectively. Secondary cracking reaction taken place by which the amount of permanent gas product is increased. So at temperature higher than 500^{0}C liquid product is decreased.

8. COMPARISON OF PINE SEEDS OIL WITH PETROLEUM PRODUCTS AND BIOMASS DERIVED PYROLYSIS OIL

The comparison of physical characteristics of pine seeds oil with other biomass derived pyrolysis oil and petroleum products is shown in Tables 3 and 4.

Table 3: Comparison of pine seeds pyrolysis oil with biomass derived pyrolysis oil

Analysis	Pine Seed oil	Date Seed oil [12]	Waste paper oil [13]	Sugarcane bagasse oil [14]	Jute stick oil [15]
Kinematic viscosity at 35^0C (cSt)	12.15	6.63	2.00	89.34	12.8
Density (kg/m^3)	1240	1042.4	1205	1198	1224
Flash Point (^{0}C)	60	126	200	105	>70
HHV(MJ/kg)	24.22	28.636	13.10	20.072	21.091

Table 4: Physical characteristics of the pine seeds pyrolysis oil and its comparison

Analysis	Pine Seed oil	Fast Diesel [16]	Diesel [17]	Heavy Fuel Oil [18]	Wood Waste [17]
Kinematic viscosity at 35^0C (cSt)	12.15	1.3-3.3.3$^{\#}$	2.61*	200$^{\#}$	66.99
Density (kg/m^3)	1240	780	827.1*	980*	1180.2
Flash Point (^{0}C)	60	75	53	90-180	59
HHV(MJ/kg)	24.22	45-46	45.18	42-43	19.80

#at 50^0C *at 20^0C

From the comparison it is shown that the viscosity of pine seeds oil is favorable than other pyrolysis oils. It has HHV of 24.22 MJ/kg.

9. CONCLUSION

The objectives of the study are fulfilled by using the biomass waste in the form of pine seeds with fixed bed pyrolysis system made of stainless steel pipes and sheets. The fixed bed pyrolysis of solid pine seed has a maximum oil yield of 51wt% of biomass feed particle size of <1.18mm at a reactor bed temperature of 500^{o}C and a gas flow of 5 liter/ minute with the running time of 90 minute. With increasing reactor bed temperature, percentage weight of char production is decreasing and the gas production is increasing. The physical properties analysis showed that the oil is heavy in nature with moderate viscosity. The oil possessed favorable flash point. The heating value of the oil is moderate.

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11. NOMENCLATURE

Symbol	Meaning	Unit
BTX	benzene, toluene and xylene	Dimentio-nless
CBp	pyrolytic carbon black	Dimentio-nless
GCV	gross calorific value	(J/kg)
HHV	higher heating value	(J/kg)