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Effect of Operational Parameters on the Products from Catalytic Pyrolysis of Date Seeds, Wheat Straw, and Corn Cob in Fixed Bed Reactor

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Abstract – Pakistan depends heavily on imports for its fuel requirements. In this experiment, catalytic pyrolysis of a blend of feedstock's consisting of date seed, wheat straw, and corn cob was conducted in a fixed bed reactor to produce oil that can be used as an alternative fuel. The main focus was to emphasize the outcome of important variables on the produced oil. The effects of operating conditions on the yield of bio-oil were studied by changing temperature (350-500 ℃), heating rate (10, 15, 20 ℃/min), and particle size (1, 2, 3 mm). Moreover, ZnO was used as a catalyst in the process. First, the thermal degradation of the feedstock was investigated by TGA and DTG analysis at 10 ℃/min of different particle sizes of 1, 2, and 3mm from a temperature range of 0 to 1000 ℃. The optimum temperature was found to be 450 ℃ for maximum degradation, and the oil yield was indicated to be around 37%. It was deduced from the experiment that the maximum production of bio-oil was 32.21% at a temperature of 450 ℃, a particle size of 1mm, and a heating rate of 15 ℃/min. When using the catalyst under the same operating conditions, the bio-oil production increased to 41.05%. The heating value of the produced oil was 22 MJ/kg compared to low-quality biodiesel oil, which could be used as a fuel.

Key words: Thermo-gravimetric analysis (TGA), Thermal degradation, Heating rate, Particle size, Temperature

1. Introduction

Pakistan is heavily dependent on imports for its fuel requirements. According to the latest available data from the Pakistan Bureau of Statistics, Pakistan's total consumption of petroleum products in the fiscal year 2020-2021 was 21.78 million tons, which is an increase of 10.6% compared to the previous fiscal year. The majority of this consumption is in the form of diesel, petrol, and furnace oil. The demand for fuel in Pakistan is driven by several factors, including economic growth, transportation [1], and electricity generation. It is important to note that Pakistan faces challenges in meeting its energy needs due to different reasons, including a lack of domestic oil and gas resources, a reliance on expensive imported fuel, and an aging infrastructure.

These challenges have led to frequent energy shortages and load shedding, which can have significant economic and social impacts. Similarly, Pakistan produces a significant amount of organic waste, which includes biodegradable waste such as food waste [2], agricultural waste, and other organic materials. According to the United Nations Development Program (UNDP) and the Ministry of Climate Change in Pakistan, the country generates around 48.5 million tons of solid waste annually, out of which 40% is organic waste. This means that Pakistan produces approximately 19.4 million tons of organic waste each year [3]. The report further highlights that the management of solid waste, including organic waste, is a major challenge. A significant portion of the waste is either not collected or improperly disposed of [4], leading to environmental pollution and health hazards. Several initiatives are being taken by the government and non-governmental organizations to address this issue, including the promotion of composting and biogas production from organic waste. However, much more needs to be done to effectively manage the organic waste generated and convert it into a resource. Until this point, a few scientists committed their endeavors to examine the co-pyrolysis of different organic waste, including date seeds, olive stones, wheat straw, rice husk, and corn cob to get biofuel as a vital asset. A portion of these investigations has been talked about in this segment as pursued. Abdel-rahman (2021) [5] did the co-pyrolysis of the blend of date pits and olive stones: This research investigated the potential of utilizing a mixture of date pits (DP) and olive stones for the production of bio-oil and bio-char via pyrolysis [6].

The results showed that the co-pyrolysis of the mixed feedstock at a temperature of 500 ℃, with a feed particle size of 60 meshes, for 80 minutes, and a heating rate of 20 ℃/min, resulted in the highest yield of liquid products. Similarly, Hossain (2017) conducted a study on the co-pyrolysis of rice husk and solid tire waste in Japan, using a modified co-pyrolysis reactor. The suitability of the feed was assessed based on ultimate and proximate analysis as well as TGA. The study involved processing various compositions of rice husk and solid tire waste at 450 ℃ to produce oil, char, and gas. The results showed that

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the maximum yield of 52% oil was obtained from a 50% by-weight mixture of the two organic materials without N_2 gas flow. The optimal size for rice husk was between 1800-2300 μm, while the dimension for tire waste was 211 cm^3. The liquid oil produced from co-pyrolysis was found to be comparable to conventional petroleum products.

Here is a study by Yangyang Ma (2021) [7], using surplus biomass as a renewable and sustainable feedstock for biofuels and chemicals is an attractive option. However, the high oxygen content in biomass poses a challenge to its use as fuel. Catalysts are needed to improve the quality of bio-oil in the production process. Therefore, the study investigated the catalytic fast pyrolysis of rice straw (RS) and wheat straw (WS) using basic (MgO and CaO) and acidic (ZSM-5 and Y-zeolite) catalysts at varying reaction temperatures. The composition of the feedstock and catalysts used affected the pyrolysis products. RS produced a higher amount of carbonyls (62.91%) at 400 ℃, while WS without any catalysts produced a lower amount (57.72%). Y-zeolite catalysts resulted in a higher amount of aromatic hydrocarbons (52.9%) for RS, while CaO catalysts produced a higher amount of phenolics (48.5%) for WS (walnut shells) [8]. The flash-pyrolysis technique converts the entire biomass matter, excluding the ash. In this method the powdery biomass is converted into three components: bio-oil (the yield is typically 70% on an energy basis, a powdery biomass feed at a moisture content of 10%); pyrolysis gas (typical yield 14%) and char (typical yield 16%) [9].

Pakistan is one of the major producers of dates in the world, with a large share of its production coming from the Khairpur district in the Sindh province [10]. According to the latest available data from the Pakistan Bureau of Statistics, Pakistan produced approximately 631,000 metric tons of dates in the fiscal year 2020-2021. Pakistan is a major producer of corn. However, it corn cobs can be a significant source of agricultural waste, and their disposal can pose environmental challenges.

However, the objective of this present research is to reduce greenhouse gas emissions: Pyrolysis can help to reduce greenhouse gas emissions by converting organic waste materials into biochar, which is a carbon-rich solid that can be used to sequester carbon in the soil [11], reduce waste disposal. Pyrolysis can help reduce waste disposal by converting organic waste materials into valuable products, such as bio-oil, biochar, and syngas and reduced reliance on fossil fuels. Pyrolysis can help reduce the reliance on fossil fuels by producing bio-oil and syngas that can be used as renewable energy sources [12]. Also, studying soil improvement, biochar produced by pyrolysis can be used as soil improvement to enhance soil fertility, water preservation, and nutrient intake.

2. Materials and Method

Feedstock used is a blend taken from Kherpur dates, seeds local wheat straw, and Corn cob. First, size reduction of feedstock was done in a steel grinder, then sizing was done using different sieves having meshes no. 18, 10, and 6 so that the feedstock could be classified into average sizes of 1 mm, 2 mm, and 3 mm. For each experimental run, a 21g sample was used.

The proximate analysis and elemental analysis of the feedstock were done in NFC lab where separate feedstock of date seed, wheat straw, and corn cob was analyzed, and then a blend of these three was also analyzed the results are shown in Tables 1 and 2.

2-1. Thermogravimetric Analysis

The TGA of feedstock as a blend was studied in the Environmental Engineering Department of Punjab University.

In TGA, the following values are typically studied: Weight loss: The change in weight of the sample is monitored as a function of temperature or time. This provides information on the thermal stability, decomposition temperature, and reaction kinetics of the sample Differential weight: The rate of weight loss, or differential weight, is calculated by taking the derivative of the weight loss curve. This can provide additional information on the reaction kinetics and the effect of various experimental parameters on the sample. Temperature: The temperature of the furnace is controlled and monitored during the experiment. This provides information on the thermal stability of the sample and the temperature at which it undergoes decomposition. Atmosphere: The atmosphere in the furnace can be controlled, usually

Table 1. Proximate analysis of feedstock

Proximate analysis	Sample-A	Sample-B	Sample-C	Sample-D
	Wheat straw	Corn Cob	Date seed	Blend feedstock
Ash (%)	8.8	4.33	4.04	5.08
Volatile Matter (%)	83.77	86.26	83.03	84.26
Moisture (%)	1.6	0.98	0.6	0.97
Fixed Carbon (%)	5.83	8.43	12.33	9.69

Table 2. Elemental analysis of feedstock

		Carbon %	Hydrogen %	Nitrogen %	Sulfur %
Ultimate analysis	Sample-A	48.23	6.27	0.97	0
	Sample-B	52.65	8.14	0.63	0.02
	Sample-C	51.32	6.89	0.88	0.01
	Sample-D	49.47	5.65	0.59	0.04

by using an inert gas such as nitrogen or argon, or by using a reactive gas such as oxygen. This allows the study of the effect of different atmospheres on the thermal behavior of the sample. Time: The duration of the experiment is also recorded. This provides information on the rate of the reaction and the time required for complete decomposition [13,14].

In Fig. 1, moisture removal starts in the first phase up to 90 ℃ to 100 ℃. After that cracking and decomposition of feedstock started in which large polymers are reduced into small polymers. At around 300 ℃ a rapid conversion of feed stock is seen and around 450 ℃ maximum oil yield is predicted. Further heating converts it to gases. Similarly, Fig. 2 shows the maximum yield of 1 mm average particle size.

DTG curves are examined to obtain valuable thermophysical characteristics of materials. The primary DTG peak is typically associated with cellulose degradation, accompanied by a lower-temperature shoulder, indicating hemicellulose degradation and a higher-temperature tail suggestive of lignin degradation. Stage I is characterized by a minor mass loss attributed to water and volatile compound evaporation. In Stage II, a substantial mass loss occurs as hemicellulose, cellulose, and lignin decompose, consistent with findings in other studies on biomass. Stage III involves the slow-rate decomposition of carbonaceous matter over a wide temperature range.

2-2. Experimental Setup

In NFC IE&FR students conducted their pyrolysis experiments using a fixed bed reactor made of 0.2-inch thick stainless steel, capable of withstanding temperatures up to 750 ℃. The reactor was designed with a flange and head for secure sealing, with an inlet for nitrogen purging and an outlet for fumes. A stainless steel capsule, measuring 12.5 inches, was placed in the middle of the reactor to hold the thermocouple. The inlet point extended 11 inches into the reactor to ensure proper fume flow through the outlet. The thermocouple capsule made direct contact with the sample to ensure accurate temperature readings. Rubber rings or silicon tubing were used to seal the reactor. The stainless steel reactor used in the pyrolysis process was placed inside an electrically heated cylinder that contained 2 inches of fiberglass insulation. The reactor was not permanently fixed in the heater but could be easily removed for cooling. The heater assembly included a control panel with temperature readings and heater voltage panels. Two glass condensers were also included

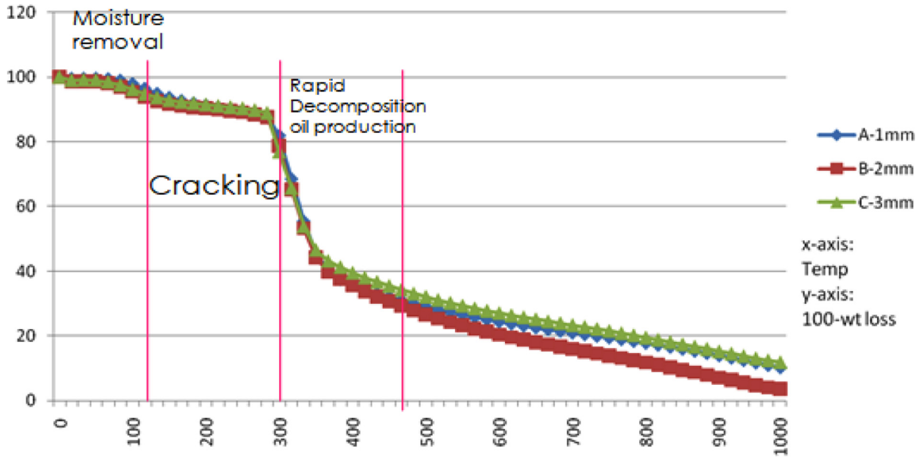

Fig. 1. TGA of feedstock of 1 mm, 2 mm, and 3 mm at 10 ℃/min and max temp 1000 ℃.

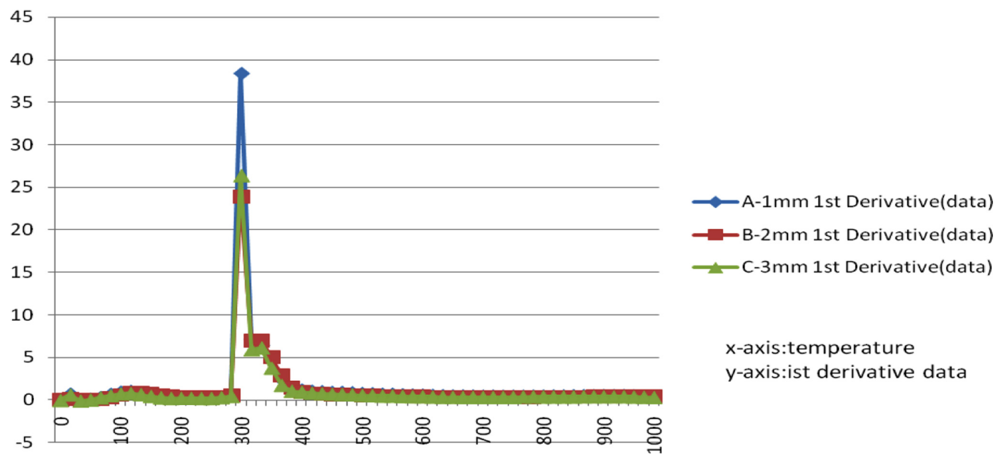

Fig. 2. Graph b/w rate of change of weight loss and temperature of different average sizes.

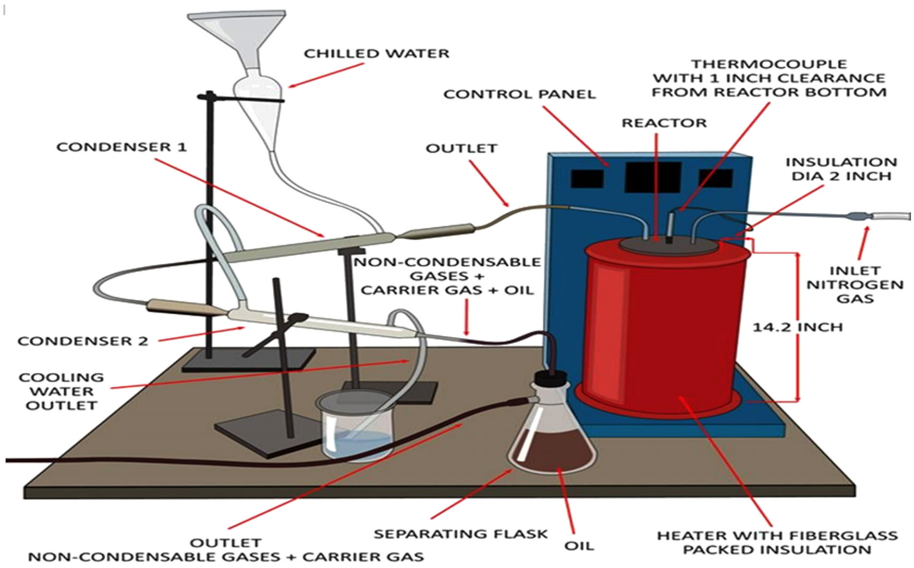

Fig. 3. Schematic diagram of the fixed-bed pyrolysis reactor.

in the assembly to condense pyrolysis fumes continuously, which were collected in a flask. Any non-condensable gases were released into the air. A nitrogen cylinder and flow meter were used to ensure continuous purging of nitrogen through the reactor as shown in Fig. 3.

2-3. Experimental Procedure

The objective of this experimental work was to assess how variations in operating parameters, such as temperature, heating rate, and particle size, affect the yield of bio-oil produced from the pyrolysis of feedstock, i.e., date seed, wheat straw, and corn cob. The experiments were conducted using particle sizes ranging from 1mm to 3mm and maximum operating temperatures changing from 350 ℃ to 500 ℃. The impact of heating rates was also analyzed at 10 ℃/min, 15 ℃/min, and 20 ℃/min. A total of 45 experiments were conducted to investigate the impact of these variables on bio-oil yield. The experimental procedure is explained in detail as shown in Fig. 4.

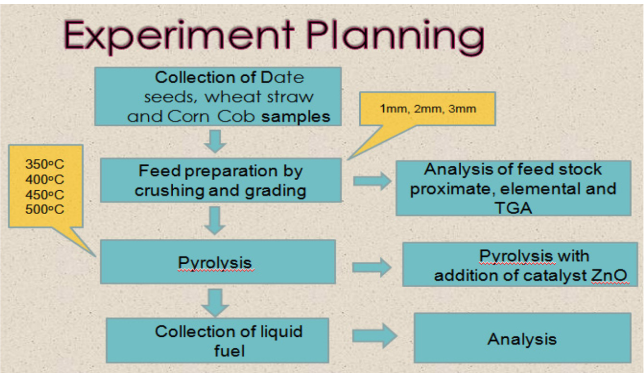

Fig. 4. Layout plan of the Experimental Procedure.

2-4. Experimental Runs

A 21g sample was taken for each experimental run, containing an equal amount of 7 grams of each feedstock. The sample was loaded in the rig of a fixed bed reactor. Nitrogen purging was done for 2 minutes to remove oxygen. Then the reactor was heated by turning on an electric heater. The temperature for the experiment was set by the control panel. Each experimental run was operated at a different heating rate. Continuous water flowed through the condenser so that condensable gases could be condensed and the liquid was collected in a flask. On-condensable gases were disposed of in an open atmosphere. At the final desired temperature the heater was put off to be cooled down. After concluding the experiment, nitrogen purging was done till the reactor was cooled to 200 ℃ to remove any remaining condensable and non-condensable gases. The derived fuel (liquid oil) and black char readings were noted and collected in separate containers. The flask along with the bucket for feedstock was cleaned before proceeding to the next experimental run. The same procedure was followed for catalytic pyrolysis in which 5% ZnO was added as a catalyst in 21g feedstock to check the yield of oil.

2-5. Biofuel Processing

After the pyrolysis process, the resulting oil underwent derived fuel processing, which involved three steps: moisture removal, acid treatment, and basic treatment. First, the oil was heated to 120 ℃ for two hours to remove any moisture. Then, 7% concentrated sulfuric acid was added to the oil, and the mixture was stirred continuously for two hours at 70 ℃. The oil was separated into two layers, and the sludge was removed, resulting in a 75.8% recovery of oil as shown in Fig. 5.

Next, the oil underwent basic treatment to remove any remaining sludge and neutralize it. A mixture of 7.28g Bentonite and 3.64g CaO was added to the oil, and the solution was stirred continuously for two hours at 70 ℃. The sludge was removed again, resulting in a cleaner and more refined final product.

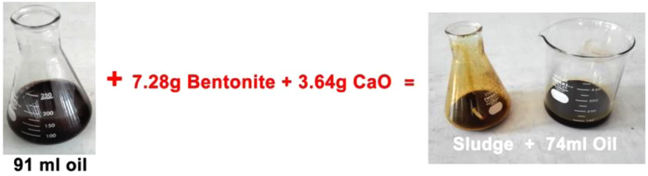

Fig. 5. Condensate Processing.

3. Results and Discussion

3-1. Effect of Temperature

However, the current research revealed that the optimal temperature range for pyrolysis was between 450 ℃ and 500 ℃. As the temperature increased, the yield of oil also increased, reaching a maximum output temperature of 450 ℃. Further temperature increases resulted in a decrease in oil yield, which can be attributed to the fact that higher temperatures favor the production of short-chain hydrocarbons. Consequently, thermal decomposition at higher temperatures leads to an increase in the production of non-condensable gases and a decrease in the amount of oil. The research findings are presented in Figs. 6 and 7.

In Fig. 6 the pyrolysis range is above 350 ℃ and the % yield of all three products the biochar, bio-oil, and gases is affected by the temperature. The maximum yield of oil is at 450 ℃, similarly biochar is at 350 ℃ and gases are at a maximum of 500 ℃.

3-2. Effect of Heating Rate

The research findings indicate that the heating rate has a minimal impact on oil yield during pyrolysis. An increase in the heating rate resulted in a shift of the optimal temperature range towards higher values, which is consistent with the study by Unapumnuk in 2012. The maximum oil yield was observed at a heating rate of 15 ℃ per minute, and at higher heating rates the oil yield decreased slightly. By studying Fig. 8, the effect of heating rate on oil yield can be observed. It can be seen that, in general, the oil yield increases as the heating rate is increased. This is because the optimal temperature range in the present study is 450 ℃, and an increase in the heating rate tends to increase the optimal temperature, thereby resulting in higher oil yield for higher heating rates.

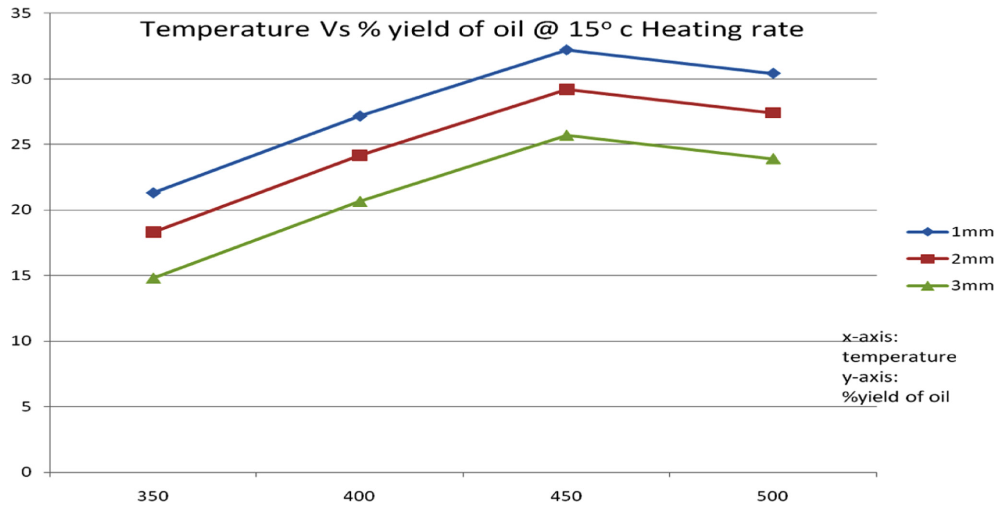

Fig. 6. Effect of temperature at 15 ℃/min heating rate for 1, 2, and 3 mm average sizes.

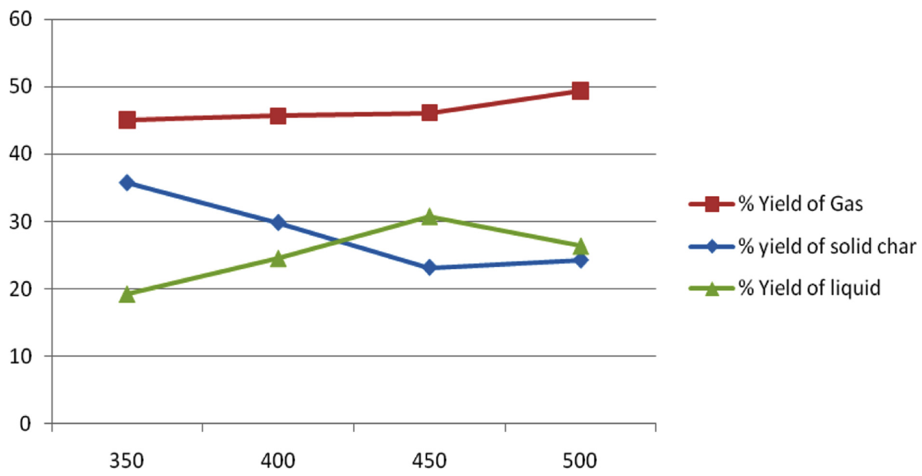

Fig. 7. % Yield of Gas, char, and oil at different temperatures.

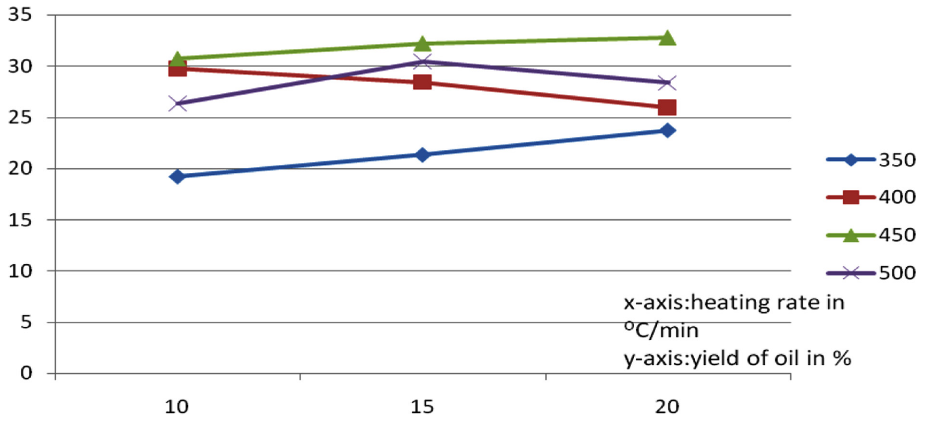

Fig. 8. Effect of heating rate in ℃/min on yield of oil at different temperatures.

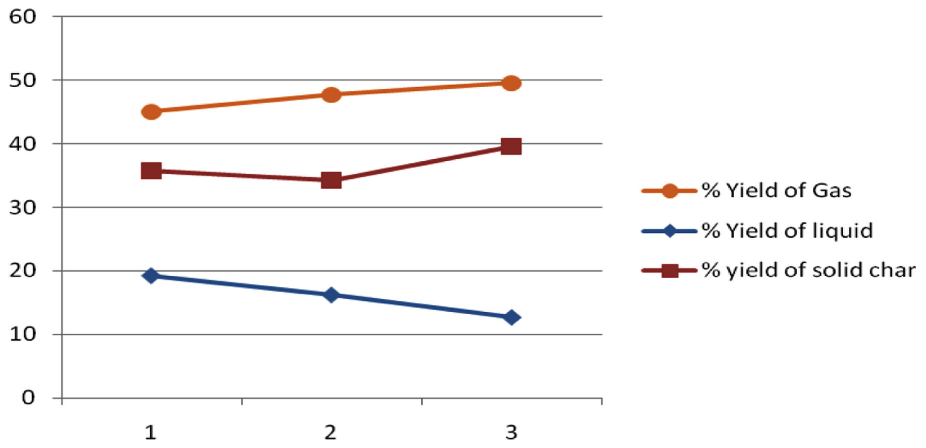

Fig. 9. Effect of particle size on% yield of products at fixed temperature.

3-3. Effect of Particle Size

In addition to temperature and heating rate, particle size was also investigated as an operating parameter in the present study, and its effect on the yield of products was plotted in Fig. 9. The figure illustrates the effect of particle size for a specific heating rate. The results indicate that particle size has a negligible effect on the yield of liquid, as shown in Fig. 9. There is not a large difference in the yield of oil at 1 mm and 3 mm, but as the particle size increases the oil yield decreases minutely. Similarly, the other products in pyrolysis, i.e., char and gases show an increase in trend but minutely as particle size increases. However, the maximum yield of oil is shown at 1mm average size of feedstock.

3-4. Effect of Catalyst

In this experiment ZnO catalyst is used in a quantity of 5:1.which is only 5% of feedstock. A catalyst is added to enhance the rate of

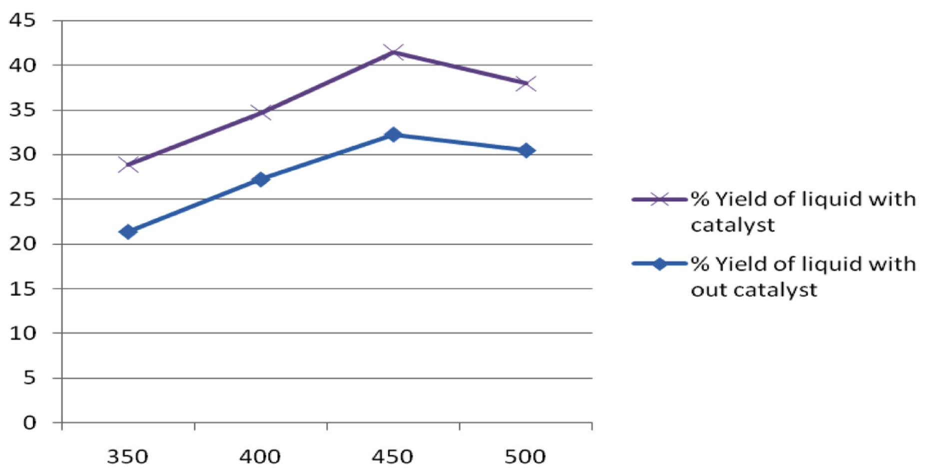

Fig. 10. Effect of catalyst ZnO on oil yield in pyrolysis.

pyrolysis. Fig. 10 illustrates that the yield of oil increases from 32.21% to 41.45% due to the addition of a catalyst. In catalytic pyrolysis, the catalyst is used to promote the decomposition of complex organic molecules into simpler molecules such as gases, liquids, and char. The catalyst used in the process can be in the form of a solid or a liquid. Catalytic pyrolysis has potential applications in the production of renewable energy.

4. Conclusion

First, the thermal degradation of feedstock was investigated by TGA and DTG analysis at 10C/min of different particle sizes of 1, 2, and 3mm from a temperature range of 0 to 1000 ℃. The optimum temperature was found to be 450 ℃ for maximum degradation and oil yield was indicated around 37%. It was found from the experiment that the maximum yield of bio-oil was 32.21% at 450 ℃, particle size of 1 mm, and heating rate of 15 ℃/min. While using the catalyst ZnO at the same operating condition the bio-oil production increased to 41.05%, which was the objective to reduce the waste and convert waste to energy in present research. The heating value of produced oil was 22 MJ/kg in comparison with low-quality biodiesel oil that could be used as a fuel.

Properties of bi-oil produced	Bio-Oil	Bio-Diesel
Density	1.18 g/cm^3	0.90 g/cm^3
Viscosity at 40 ℃	0.80 centistokes	1.9 centistokes
Boiling point	487 ℃	350 ℃
Moisture Content	15%	0.5%
Calorific Value	22 MJ/kg	41 MJ/kg

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Competing Interests

The authors declare that they have no competing interests.

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