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Biofuel production using fast pyrolysis of various plant waste biomasses in fixed bed and twin-screw reactors

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Summary

Fast pyrolysis of six biomasses mustard, camellia, pinewood, sawdust, bamboo, and bagasse was completed at a temperature of 500°C in a fixed bed reactor and a twin-screw reactor. It was found that the yield of bio-oil varied from 48 to 30 wt% in fixed bed reactor and 52 to 39 wt% in a twin-screw reactor, whereas pyrolysis gases yield ranged from 34 to 20 wt% in a fixed bed reactor and 32 to 16 wt% in twin-screw reactor and biochar yield ranged from 36 to 24 wt% in fixed bed reactor and 32 to 16 wt% in a twin-screw reactor. High heating value (HHV) of bio-oil was found to be maximum for bamboo (24.45 MJ/kg) biomass, whereas in the case of biochar, the maximum HHV was obtained for pinewood (27 MJ/kg) and sawdust (28 MJ/kg) biomass. On the characterization of the pyrolysis products, it is found that char obtained comprises mainly carbon while the liquid product, that is, bio-oil, is a mixture of hydrocarbons. The pyrolysis gases consist of a mixture of carbon monoxide, hydrogen, carbon dioxide, and nitrogen.

Novelty Statement

Biofuel production uses various biomasses via two different reactors that is, a fixed bed reactor and a twin-screw reactor. The yield of oil in the range from 48 to 30 wt% in fixed bed reactor and 52 to 39 wt% in a twin-screw reactor and biochar yield ranged from 36 to 24 wt% in fixed bed reactor and 32 to 16 wt% in a twin-screw reactor. The high heating value (HHV) was optimum for bio-oil produced via bamboo biomass (24.45 MJ/kg) whereas HHV for biochar produced via pyrolysis was found to be optimum for pinewood and sawdust biomass (27 MJ/kg and 28 MJ/kg).

Leena Kapoor and Akbar Mohammad cont this study.

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KEYWORDS

biomass, fixed bed reactor, pyrolysis, twin-screw reactor

1 | INTRODUCTION

Biomasses are defined as those materials, exclusive of fossil fuels, which were living organisms that have the potential to be used as a fuel either directly or after converting them. Biomass energy has been in use in India since ancient times, basically in the form of husk, firewood, cow dung cake, and many other natural feedstocks.[1] Unfortunately, the burning of biomass directly produces a high amount of smoke and ash. Consequently, biogas plants were developed as they are pollution-free, that is, they produce no smoke. The Indian government provided various subsidies to establish biogas plants. Newer technologies like biomass gasification were also developed that convert biomass into syngas.[2] A large part of the Indian population resides in rural areas. Based on a survey in 2018, approximately 66% of the Indian population lives in rural areas.[3] Due to the increase in the demand for energy in rural areas, power generation plants based on biomass are on a rising trend. Hence, to plan electrification for around 0.638 million villages in India, biomass can be a vital option. The biomass availability in India is approximately around 500 metric tons per year. Thus, approximately 17 500 MW of power can be created by using biomass as raw material.[4] Apart from agricultural waste, biomass can also be taken from other sources like an industrial waste (eg, bagasse in sugar mills). In India, approximately 550 sugar mills are currently operating and thus, an expected 73 000 MW of energy can be produced by 2030 by using bagasse as biomass.[5] Various other potential sources for biomass include roadside shrubs, road sweepings, agro-based industries, vegetable wastes, plantations, etc.[1] Biofuel has a high potential in the energy sector, since the fuel and thus, oxygen required for their operation can be taken from their immediate environment, and this offers great potential as a power source.[5] Energy through biomass is believed to be the most favorable among the renewable energy sources (RES) as it is widely available worldwide. Biomass pyrolysis has an inimitable advantage of producing solid, liquid, and gaseous fuels, which can be transported, stored, and utilized, far away from their place of production. Due to the negligible amounts of nitrogen and sulfur components present in biomass pyrolysis products, its use does not lead to environmental pollution.[3] Thermochemical conversion is considered one of the most promising ways to achieve high-efficiency conversions of biomasses, converting the biomasses into solid, liquid, and gaseous products at relatively high temperatures.[6] Accordingly, a few technologies have been developed with time: pyrolysis, combustion, liquefaction, gasification, etc. Pyrolysis is considered to be one of the elementary processes for converting the biomass thermochemical; it is also the primary step in combustion or gasification processes.[6] The analyses of the pyrolysis of biomasses can find their uses in controlling and optimizing these processes.[7] Most of the research has been focused on the testing of different reactor configurations and the development of new reactors.[8] High amounts of bio-oil yield and high efficiency are the primary goals for several workers. Recently published reviews classify the reactors as bubbling fluidized bed reactors, ablative pyrolysis, entrained flow reactor, circulating fluidized bed reactors, fixed bed fast pyrolysis reactor, screw reactor, rotating cone, and vacuum pyrolysis reactor.[8]

Bridgwater[9] has discussed all the reactor configurations in several studies and has discussed the technical aspects, that is, liquid collection methods, heating rate, and char removal methods, with their advantages and disadvantages. Tsai et al[10] have done a detailed analysis of the fast pyrolysis technology focusing on the feedstock characterization that is available in plenty, reactor design, products obtained through pyrolysis, and their upgrading. The commercial processes must necessarily have the stages: proper reception of the feed, its storage, pre-treatment and preparing the feed, conversion of solid biomass into bio-oil through the fast pyrolysis process, and, finally, upgrading the bio-oil to a desirable marketable end-product such as biofuels. Although each one of these reactors is being studied on a lab scale, none of the reactors is superior to the other; however, some reactors have been found more viable for commercial applications than others have. The five technologies are most suitable and feasible for the commercialization process. These are: (a) bubbling fluidized-bed reactors; (b) circulating fluidized-bed reactors; (c) screw reactors; (d) vacuum reactors; and (e) ablative reactors, which can generate adequate amounts of liquid fuel that is, bio-oil. The results obtained from these technologies justify their market attractiveness. Among all these reactors, the fluidized-bed technology is considered to be well-understood while screw reactors are better used for heterogeneous feedstocks. Screw reactors can easily handle feed and smooth operations. A considerable amount of work has been done on biomass pyrolysis. Many different biomass feedstocks have been chosen for pyrolysis, for example, bark, wood, nuts, seeds, algae, grass, forestry

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and agricultural residues, lignin, and cellulose. All these feedstocks have been tested under various pyrolysis conditions and in different pyrolysis reactors. A major portion of research has been done using olive bagasse, wheat straw (agro-biomass), pinewood (woody biomass) biomasses as feedstocks.[11] The intermediate pyrolysis of rapeseed as reported in the literature[12] was studied in fixed bed reactors at a temperature of 550°C with a heating rate of 300°C/min using 0.6- to 0.85-mm particle size solids under nitrogen flow rates of 100 cm^3/min. It resulted in about 65 wt% of bio-oil yield. Neem seed pyrolysis was studied in semi-batch reactors. It resulted in 38 wt% yield of bio-oil operated at 400°C to 500°C at the rate of 20°C/min.[13] The intermediate pyrolysis of groundnut as a feedstock was investigated in the fluidized bed reactor at 400°C to 475°C. It resulted in 63.48 wt % of bio-oil.[14] From all of these studies, the five basic parameters of the resulting oil were identified, namely, viscosity, pH, density, and low heating value (LHV) (24.56 cSt, 4.20, 1.2 kg/m^3, and 31.07 MJ/kg).[15] It is found from the literature survey that only very few studies have been done on fixed bed and twin-screw reactors using the fast pyrolysis method. Biomass pyrolysis incorporates several extremely complex reactions with quite a large number of intermediates and end products.[16] Since devising precise reaction, mechanisms for biomass pyrolysis are difficult, pyrolysis models are devised in a manner that is more macroscopic and empirical. This research is aimed at studying the effects of various process conditions on the fixed bed and screw reactor using a few sample biomasses.This study seeks to understand the potential for producing bio-oil by pyrolysis of certain biomass that is widely available in Uttarakhand, India. The motivation for the study is the need to produce renewable liquid fuels. For experimentation, six different types of biomasses were collected from the local agriculture field in the Dehradun region India. The collected biomass was washed and dried properly to make it ready for experimentation. Two types of reactors were used for the pyrolysis, namely fixed bed reactors and twin screw/moving bed reactors. The experimental results obtained from both the reactors were compared based on yields obtained.

2 | MATERIALS AND METHODS

2.1 | Biomass feedstock

Biomass such as sawdust, bagasse, bamboo, mustard, camellia, and pinewood which is otherwise waste was collected from the nearby region. The pretreatment of biomass was done to remove dirt, foreign materials, dust, etc. Biomass feedstock was then crushed and sieved to size ranges 2 mm. Biomass feedstock was then dried to remove the moisture content. The pyrolysis experiments using these biomasses were then performed at a temperature of 500°C.

2.2 | Experimental setup

The pyrolysis experiments were performed in two different biomass pyrolysis reactors, that is, twin-screw reactor and fixed bed reactor. The twin-screw reactor is made up of a horizontal pipe (AISI 316 steel). Inside the reactor pipe, two screws each of length 565 mm are assembled along the length of the reactor. The rotation of the screws moves the biomass along the reactor, that is, from the inlet toward the hot zone and then toward the outlet of the reactor. The reactor's outer surface is covered with an electrical resistance wire to provide the heat for the pyrolysis reaction. The temperature of the reactor is monitored with the help of two K-type thermocouples, one placed inside and the other one outside of the reactor. After completion of the reaction, hot vapors are made to pass through the condenser unit to get the liquid product, that is, bio-oil, while the solid product, that is, bio-char, is collected in a cylindrical enclosed flask attached to the reactor. The non-condensable gases move to an exhaust system.

The second rector used for this study is a fixed bed reactor. This is a vertical reactor system, which consists of a vertical tube made of INCONEL 800. The length of the vertical tube is around 3 ft. and the inner diameter of the vertical tube is around 25 mm. The vertical tube is covered with the electrical furnace, which provides the heat for the pyrolysis reaction. In this reactor, setup three thermocouples are installed along with digital temperature indicators. The hot vapors produced via pyrolysis reaction are made to pass through two glass condensers where cold water is circulated for quenching the vapors that are obtained via pyrolysis to get the desired bio-oil. The solid obtained within the reactor is cooled and is then weighed. The gas formed is measured by making a difference.

2.3 | Experimental

Before starting the experiments, the operating conditions like the temperature of the reactor, biomass feed rate, screw velocity in the case of the twin-screw reactor, and the nitrogen flow rate were pre-defined. The first step

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TABLE 1 Proximate, ultimate, and high heating value of biomass feedstock

Properties	Bamboo	Mustard (Khari)	Camellia	Pinewood	Sawdust	Bagasse
	Proximate analysis wt%					
Volatile matter	76.72	70.78	80.20	58.23	70.31	71.7
Ash content	2.57	14.98	4.78	2.3	6.98	6.8
Moisture	10.25	6.86	0.49	12.95	9.37	6.8
Fixed carbon	10.84	7.38	14.53	21.84	17.75	19.2
	Ultimate analysis wt%					
Carbon	44.90	46.31	38.90	48.96	43.17	44.61
Nitrogen	0.72	4.45	0.71	0.32	0.09	0.86
Hydrogen	6.038	7.055	5.875	4.761	5.081	5.671
Sulfur	0.018	0.036	0.165	0.05	0.04	0.02
Oxygen	48.342	42.149	54.35	34.51	36.87	43.52
	Calorific value (MJ/kg)					
Theoretical	16.2	19.06	13.02	17.86	16.02	16.31
Experimental	16.8	20.24	16.12	18.1	15.15	17.2

followed to perform the experiments was the preparation of biomass samples, that is, the biomasses used were first crushed, sieved, and dried completely. The temperature of the reactor was then set in the control panel attached to the reactor which ultimately raises the reactor temperature to the required set limit. The temperature in the reactor is monitored with the help of thermocouples arranged along the reactor length. Three thermocouples were being used in the case of the fixed bed reactor and two thermocouples were used in the case of the twin-screw reactor. The temperature of the reactor was maintained constant throughout all the experimental runs with the help of the temperature control panel. The coolant used was pumped along with the condensers. The continuous nitrogen supply was maintained to create an inert atmosphere inside the reactor. The motor in the case of the twin-screw reactor was then switched on to rotate the twin screws in the reactor. In the case of the fixed bed reactor, the pre-weighed biomass sample was kept inside the reactor for various time intervals while in the case of the twin-screw reactor the biomass sample is fed into the feeding hopper from where it moves inside the reactor with the help of the screw arrangement. As the twin screw rotates the biomass samples move inside the reactor where the pyrolysis reaction takes place. The experimental run was considered complete when no biomass sample is observed in the feeding hopper and no gaseous product is visible at the exhaust of the reactor. At this stage, the heater and rotational motor (in the case of the twin-screw reactor) are switched off. The nitrogen supply is then stopped. The coolant pump is then switched off. The bio-oil and char thus obtained are then collected and weighed. After the collection of bio-oil and char, the whole reactor assembly was cleaned properly with acetone.

TABLE 2 ASTM standards for proximate analysis

Proximate analysis	Standards
Moisture	ASTM E871
Ash	ASTN E830, ASTN D 1102
Volatiles	ASTM E872/E897
Fixed carbon	By difference

2.4 | Biomass characterization

Elemental analysis of all biomass samples has been done using an elemental analyzer (Perkin Elmer, 2400 series II). The results of the proximate analysis, ultimate analysis, and high heating value are shown in Table 1. The proximate analysis for biomass samples was done as per the standard ASTM method, as shown in Table 2. The calorific value of all biomass feedstock is determined through experiments in a bomb calorimeter. The theoretical calorific value has been calculated using a modified Dulong equation:

$$CV\left(\frac{MJ}{kg}\right) = \frac{33.5\times wt\%carbon}{100} + \frac{14.2\times wt\%hydrogen}{100} - \frac{15.4\times wt\%oxygen}{100}. \quad (1)$$

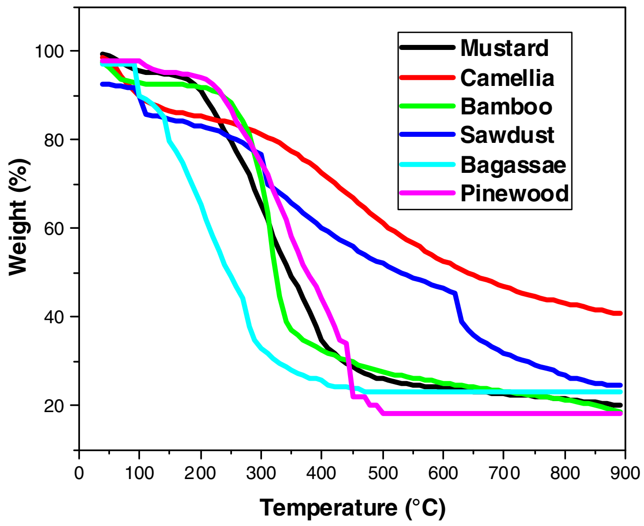

FIGURE 1 TGA analysis for different biomasses

The TGA analysis for selected biomass samples in this study is done in a TGA instrument (TGA-Q600) with the N_2 flow rate maintained at 40 mL/min and a heating rate of 10°C/min. The sample taken for TGA analysis was 10 mg. All the selected samples for this study were heated to 900°C.

The amount of moisture present in the biomass samples significantly affects the conversion of biomass via pyrolysis, so the moisture has to be removed before carrying out pyrolysis. The ash content in biomass usually helps in catalyzing secondary pyrolysis reactions, which has a major influence on product yield while the volatile matter content and fixed carbon present in the biomass samples shows the ease with which biomass feedstocks can be burnt.

3 | RESULTS AND DISCUSSION

3.1 | Thermogravimetric analysis

Figure 1 shows the results of thermogravimetric analysis for six-biomass feedstock used in this study. It is found that all the six biomasses started to devolatilize between the temperature ranges of 200°C and 300°C. Major weight loss in all the biomass samples occurs at around 300°C to 400°C. At 400°C, the weight loss becomes steady and slower; this indicates the formation of biochar, and continued up to 500°C as a result the pyrolysis temperature was chosen at 500°C. The range of degradation temperature for Hemicellulose, Cellulose, and Lignin are 200°C to 300°C, 250°C to 350°C, and 200°C to 500°C, respectively.[17]

3.2 | Proximate and ultimate analysis of biomass

Figure 2 shows the effect of moisture content on the yield of biochar, bio-oil, and pyrolysis gases. The moisture content present in the biomass affects the heat transfer rate significantly, which, in turn, influences the product yield. In this study, it was found that the high moisture content of the biomass leads to high liquid yields. Consequently, biomasses such as pinewood, sawdust, and bamboo are more favorable in bio-oil production (related to the lignin content). The ratios of moisture content, ash content, volatile matter, and fixed carbon content of various biomasses have an important effect on the product yields. The biomass containing high volatile matter results in high quantities of bio-oil and syngas, whereas the fixed carbon increases the biochar production. The carbon, oxygen, hydrogen, nitrogen, and ash content significantly affect the pyrolysis products. It was found that the biomass feedstocks with low nitrogen and mineral contents result in high bio-oil and syngas production.

3.3 | Product yield

The amount of bio-oil and biochar produced via fast pyrolysis experiments in both the reactor setup was calculated by weighing the biomass samples before and after each of the experiments. The product yields are then calculated based on the weight of the products formed and the weight of the initial samples taken. The product streams obtained through fast pyrolysis presence of condensate of organic compound, commonly known as biochar, and gaseous products known as non-condensable vapors. It is observed that a higher bio-oil yield was found for pinewood, bamboo, and sawdust due to their high volatile matter content. It is found that pinewood and bamboo biomasses resulted in maximum bio-oil yield (52 wt%) and lowest biochar yield (24 wt%). This is due to the presence of high cellulose and hemicellulose content in the biomass which results in high bio-oil yields in comparison to biomass with high lignin content.[18] The high volatile matter in these biomasses also favors high bio-oil production. A high ash content result in a decreased production of bio-oil while the production of char and gas increases. Thus, a higher bio-oil yield can be obtained in biomasses having higher amounts of volatile matter and a lower amount of ash. The percentage of the lighter components was found to be lower in the case of the twin-screw reactor in comparison to a fixed bed reactor as also being observed by other workers.[19] The pyrolysis experiments were performed at the temperature of 500°C, at a nitrogen flow rate of 526 mL/min, the

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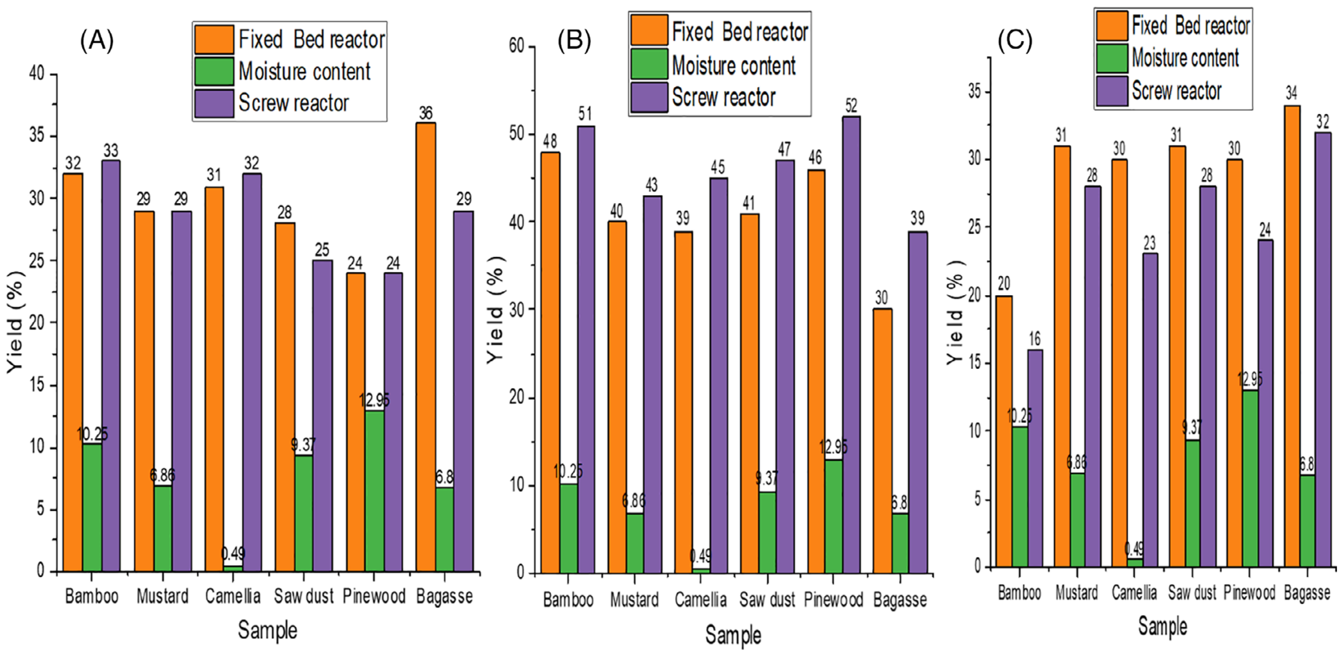

FIGURE 2 Effect of moisture content on (A) bio char yield, (B) bio-oil yield, and (C) pyrolysis gases

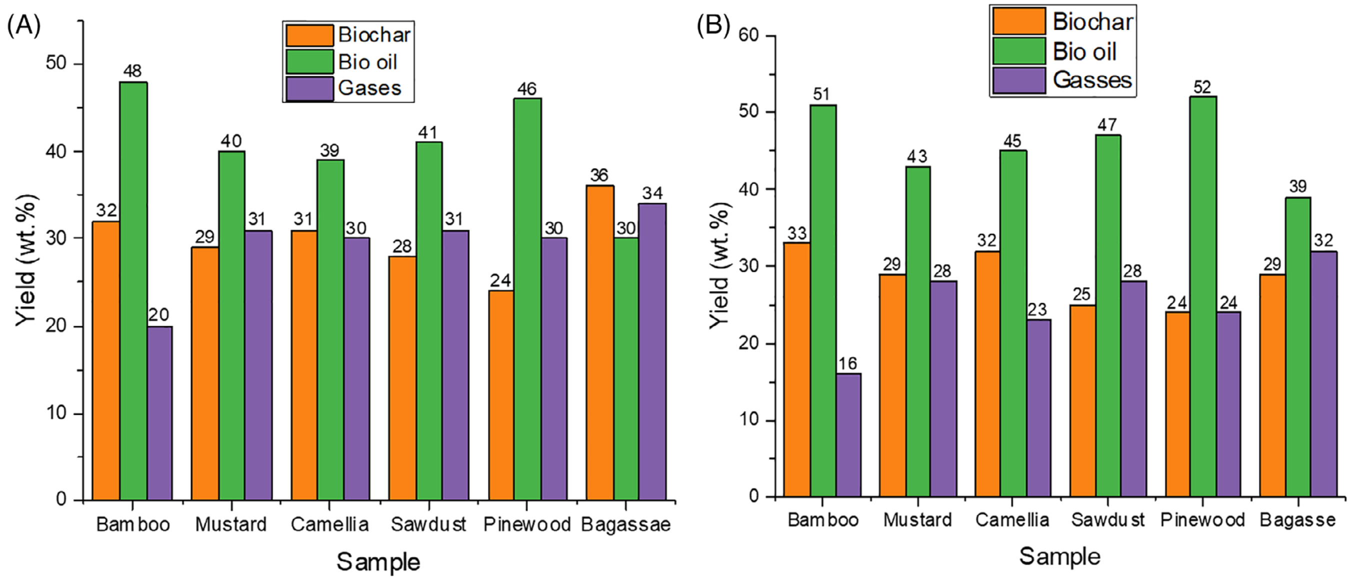

FIGURE 3 Experimental result of product yield from (A) fixed bed reactor and (B) screw reactor

residence time of 2 min. In the twin-screw reactor, the screw rpm was kept at 55 rpm. The mass flow rate of biomass in a screw reactor is 0.5 kg/h. The product yield from both the reactor system is shown in Figure 3. A considerable amount of liquid is obtained in both the reactors, that is, auger and fixed bed reactor. From Figure 3 it can be observed that the product yields, that is, liquid and gas are found to be different based on the reactor type. The liquid yield decreases (from 2 to 10 wt%) while the gas yield increases (from 2 to 10 wt%) in the fixed bed reactor when compared to the screw reactor. This result is due to the high heating rate in the twin-screw reactor.

3.4 | Bio-oil and biochar analysis

The product streams obtained through fast pyrolysis presence of condensate of organic compound better known as oil, the solid formed commonly known as biochar, and gaseous products known as non-condensable gases. It has been

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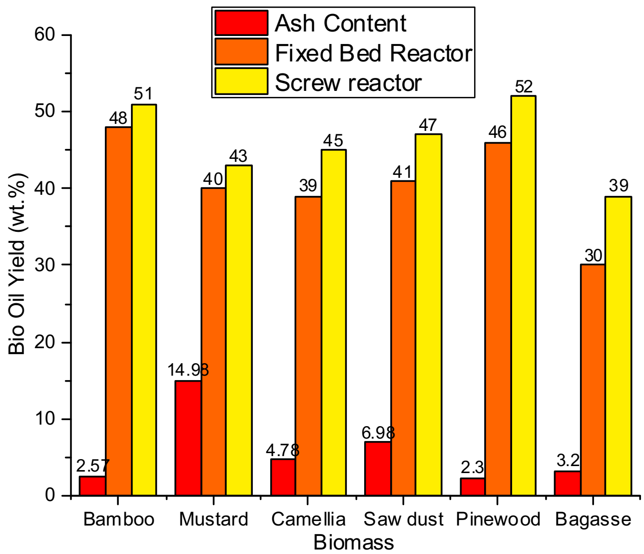

FIGURE 4 Effect of ash content on bio-oil yield

observed that various types of feedstocks produce different amounts of char, bio-oil, and varying gas compositions. The samples taken from all the biomasses have shown similar compositions, which indicate good process stability. The percentage of the lighter components was found to be lower in the case of the twin-screw reactor in comparison to the fixed bed reactor as has also been observed by other workers. The screw reactor is associated with a fast-heating rate and long residence times of the vapors, which results in the formation of a severe product. Slow heating rate results in the gradual degradation of biomasses. The highest bio-oil yield found using the screw reactor was with pinewood (52 wt%) and the lowest with bagasse (39 wt%). This may be due to the presence of low ash content (2.3 wt%) and high cellulose content in the pinewood which got converted into bio-oil. Because of high ash content, agro biomasses such as camellia, mustard, and bagasse presented lower yields of bio-oil, as shown in Figure 4. On the other hand, by using the fixed bed reactor configuration the maximum amount of bio-oil was produced with bamboo. The yields of biomasses obtained in this study are comparable to those obtained in other studies[20] involving screw reactors and fixed bed reactors. Available information collected from various sources[21] establishes that the maximum bio-oil yield from various biomasses was found to be 50.12 wt% at pyrolysis temperatures of 500°C under the sweeping gas of N_2 with a flow rate of 100 mL/min. This is similar to our present work.

3.5 | GC analysis of bio-oil

The components present in bio-oil produced from biomass pyrolysis were found through a gas chromatography-mass spectrometry (GC-MS) study using the NIST library. Components such as aldehydes, carboxylic acids, ketones, phenols, esters, and amides were found to be the main chemical groups present in bio-oils. It was observed that pinewood biomass contains significant amounts of phenolic components, which is due to the lignin content found in pinewood in comparison to other biomasses used in this study. Similar results were observed when compared to other studies.[22] GC-MS analysis, thus, reveals that bio-oil from various biomasses consists of mainly ketones, alkane, alkynes, amines, alkene, imine, alcohols, and heterocyclic compounds.

Through GC-MS analysis, it is observed that bio-oils obtained from various biomass samples have similar components with a little amount of variation in the percentage of saturates and aromatics. It is found that the aromatics and saturates percentage were less in bio-oil produced from the fixed bed reactor in comparison to bio-oil obtained from the moving bed reactor due to early removal of pyrolysis products from the fixed bed reactor. Through this study, it is also observed that hydrocarbons are the most abundant product found in bio-oils. Other workers had found naphthalene, fluorine, and other polycyclic aromatic compounds in bio-oil but in this study, none of these hydrocarbons was detected. This may be due to the different biomass types, short gas residence times, and low reaction temperatures.

The calorific value of bio-oils obtained via pyrolysis in both the systems is found to be high, that is, comparable to light fuel oil and, thus, can be used as a synthetic liquid fuel. The biochar thus produced consists of initial mineral matter formed due to process severity. The ash content in biochar is found to be high and has similar values as those reported by other workers.[23] The ash percentage was found to be 9 to 15 wt% based on the characteristic of the biomass feed. GC-MS was performed on an Agilent 6890 N unit with a GC column 25-μm thickness, DB- 1701, 60 × 0.25 mm.

3.6 | Calorific value for biomass

The calorific values were determined experimentally and theoretically (HHV) for all the biomass feedstock is used in this study. The calorific value thus determined from both sources has an error of ±5%. It is found from this study that pinewood and bamboo bio-oil resulted in high calorific values in comparison to respective biochars and biomasses. The biochar has a high calorific value in comparison to biomass samples due to the presence of a lower percentage of hydrogen and oxygen than carbon, which significantly increases the energy value of the fuel as more energy is contained in C–C bonds than in C–O and C–H bonds.[24] Figure 5 shows the calorific values of

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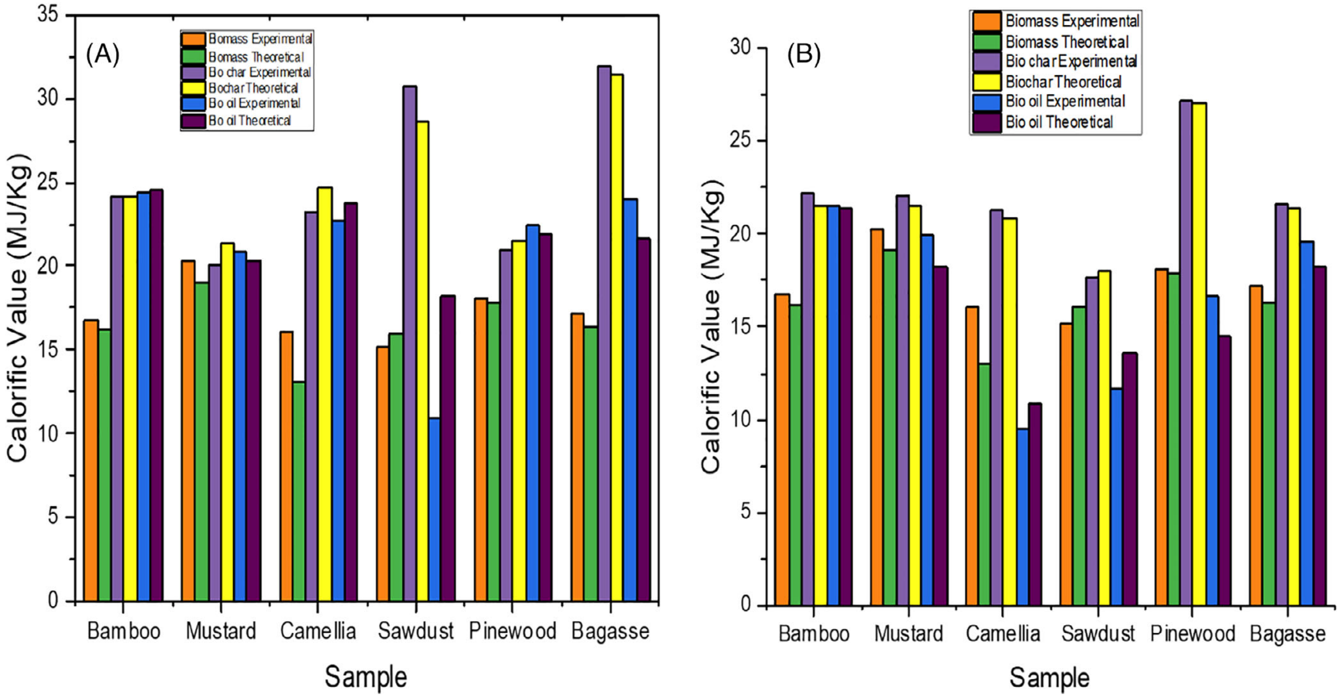

FIGURE 5 Experimental and theoretical calorific value of biomass samples and products: (A) fixed bed reactor; (B) screw reactor

bio-oils obtained from the pyrolysis of bamboo, mustard, camellia, pinewood, bagasse, and sawdust. Bridgwater[25] stated that a higher heating value of bio-oil is produced from higher temperatures and shorter times.

4 | CONCLUSIONS

Biomass pyrolysis experiments were performed in two different types of reactors, that is, fixed bed and twin-screw reactors operating under similar temperature conditions 500°C and in an inert atmosphere of nitrogen. Biomass pyrolysis of biomasses at fast pyrolysis in a twin-screw reactor produced a maximum bio-oil yield of 52 wt% with pinewood, biochar of 33 wt% from bamboo and gas of 32 wt% from bagasse. In a fixed bed reactor, the optimum oil of 48 wt% with bamboo, biochar of 36 wt% and pyrolysis gases 34% from bagasse. Bamboo has produced bio-oil with a higher calorific value (24.45 MJ/kg) comparable with bagasse (24 MJ/kg). Pinewood and sawdust have produced biochar with higher calorific values (27 and 28 MJ/kg). The pyrolysis products obtained from this study can be used as a possible energy source or chemical feedstock. Bio-oil can be used as a liquid fuel by improving its properties.

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CONFLICT OF INTERESTS

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no datasets were generated or analyzed during this study.

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