CHAPTER 4

Process parameter variation of *Melia azedarach* sawdust pyrolysis for fuel properties, physicochemical characterization and in-depth speciation analysis

Abstract

Pyrolysis is a thermochemical process carried out at elevated temperature in absence of oxygen to decompose biomass into bio-oil, bio-char and gases. The principal objective of this work was to study the effect of operating parameters (temperature, nitrogen flow rate, bed height, particle size, heating rate and pyrolysis time) on *Melia azedarach* sawdust pyrolysis products and to carry out in line characterization of these products. Experiments were carried out in the temperature ranging from 450-600 °C with ramp rate of 50 °C, 150 to 250 mL/min nitrogen flow rate, 2.1 to 8.4 cm bed height, 0.18 to 0.83 mm particle size, 10-30 °C/min heating rate and 40-80 min pyrolysis time.

Under optimal conditions of pyrolysis at 550 °C, 150 mL/min nitrogen flow rate, 8.4 cm bed height, 0.18-0.29 mm particles, 20 °C/min heating rate and 60 min pyrolysis time, highest bio-oil yield was obtained. Bio-oil was analysed for density, viscosity, pH, higher heating value, carbon residue, Fourier Transform Infrared Spectroscopy, gas chromatography–mass spectrometry and ^{1}H Nuclear Magnetic Resonance. Bio-char was characterized via proximate analysis, ultimate analysis, higher heating value, energy yield, Fourier Transform Infrared Spectroscopy, X-ray diffraction, Scanning Electron Microscope and Brunauer–Emmett–Teller surface area. Characterization of bio-oil confirmed its potential for generating biofuel-bioenergy and chemical feedstocks. High porosity and surface-area of biochar affirmed its usage as substrate for activated carbon and other applications.

4.1 Introduction

Increasing population and industrialization are culminating into an energy and emission intensive scenario (Mishra et al., 2022). Petroleum products are non-renewable and release NO_x, SO_x and CO_2 into the environment which leads to rise in Earth's temperature (Gautam and Mondal, 2023a; Gautam and Mondal, 2023b). So, exploration of renewable, sustainable and environment-friendly energy is needed. We cannot afford to ignore the urgent attention that is needed to be paid towards exploration of renewable, resilient, sustainable and environment friendly energy pathways.

Utilization of waste biomass for energy generation could help in addressing energy crisis, reducing waste, accelerating economic development, and increasing socio-economic resource security by providing added monetary value and sustainability credentials. Various biomass feedstocks include pine nuts, peanut shells, wheat straw, soya hulls, corn stover, spent coffee ground, chicken feather, coffee chaff, miscanthus (Mishra et al., 2022), pigeon pea (Kirti et al., 2022), agro-industrial waste (Dahal et al., 2018), de-oiled seed cakes (Paramasivam et al., 2021), date pits and olive stones (Fadhil and Kareem, 2021) and Crofton weed (Cheng et al., 2019). Sawdust of wood is a lignocellulosic waste biomass comprising of hemicellulose, cellulose and lignin (Ahmed et al., 2020) which makes it highly energy potent (Paparia et al., 2019). Annually around 24.25 million m^3 of sawdust is generated across the world (Chikri et al., 2020). In literature, pyrolysis of sawdust of various woods has been reported (Agnihotri et al., 2022). *Mangifera indica* wood sawdust (Sharma et al., 2023), Deodar sawdust (Rasool et al., 2018), teak sawdust (Kristanto et al., 2022), Pine sawdust (Mishra and Mohanty, 2018), Poplar sawdust (Xu et al., 2021), Red Meranti Sawdust (Azura et al., 2017), spruce-pin-fir sawdust (Zhang et al., 2021), bamboo sawdust (Kwikima et al., 2022), Mahogany (Chukwuneke et al., 2019) and Oak sawdust (Ulusal et al., 2021) have been explored besides many other wood sawdust for bioenergy, biofuel and bio-based chemical production via pyrolysis.

Various thermochemical routes like pyrolysis, gasification and liquefaction are practised (Sabat et al., 2022). Pyrolysis is considered best as it is conducted at atmospheric pressure and requires low temperature as compared to gasification and produces liquid bio-oil, solid bio-char and pyrolytic gases (Sharma et al., 2022). It is generally carried out in 400-600 °C temperature range under inert atmospheric conditions (Diao et al., 2021). During pyrolysis biomass decomposes thermally and release condensable and non-condensable vapours along with solid-phase biochar. Upon condensation, condensable vapours produce bio-oil but it contains oxygenated compounds which reduce higher heating value (HHV), high water content, high acidity and corrosivity pose hindrance in its high-value applications (Diao et al., 2021). Thus, upgradation of bio-oil is required (Agnihotri and Mondal, 2022). Liquid, solid and gaseous pyrolytic products can be utilized as biofuel (Meng et al., 2022).

For realizing biomass potential towards high value-added products study of optimum operating parameters is indispensable. The key parameters impacting pyrolysis product distribution are temperature, rate of heating, sweeping gas flow rate, particle size of feedstock, pyrolysis time and height of bed. It is important to find optimum values of various pyrolysis process parameters so as to get maximum bio-oil yield as it is the prime desired product of pyrolysis (Chen et al., 2022). Bio-oil yield is maximum in the temperature range of 400-550 °C and beyond 600 °C gas yield dominates due to secondary cracking reactions (Xu et al., 2020). High nitrogen flow rate decreases yield of bio-oil because it shortens vapour residence time in reaction zone (Cheng et al., 2029). Particle size of feedstock directly influences heat and mass transfer interactions and small particle size favours formation of more bio-oil and gas while large particle size leads to high yield of bio-char (Fadhil, 2020). Yield of bio-oil increases with increase in bed height of feedstock due to large residence time which facilitates production of more volatiles (Li et al., 2023). Rate of heating during pyrolysis is instrumental in depolymerization of feedstock biomass into volatiles (Al-Layla et al., 2021). Pyrolysis time determines adequate time for complete thermal degradation of feedstock biomass (Fadhil and Kareem, 2021).

The main purpose of this study was to carry out pyrolysis of *Melia azedarach* sawdust (MAS) and to evaluate impact of operating parameters like temperature, sweeping gas flow rate, particle size, packed bed height, pyrolysis time and heating rate variation on products' yield distribution. *Melia azedarach* is a deciduous tree species which belongs to mahogany family, Meliaceae. It is known by common names such as pride of India, Cape lilac, syringa berry tree, Persian lilac, bead-tree, chinaberry tree, Indian lilac or white cedar. Due to its fungal-resistant properties it is used for furniture. It is also used in paper pulp and logistic packaging as it grows rapidly. Huge quantities of MAS are produced globally which makes it a promising feedstock for pyrolysis. Effect of operating parameters on pyrolysis product yield of various biomass has been reported but it is being reported for MAS for the very first time here in this study. This paper includes a novel approach of exploring MAS bioenergy generation potential as no attempt has been made in the past to do so. This work explains optimized operating conditions for pyrolysis process of MAS to yield bio-oil and bio-char under inert atmospheric conditions. Since, the main objective of the work was to maximize liquid fuel yield, so, the focus was only on the pyrolysis bio-oil yield. Characterizations of MAS including proximate, ultimate and HHV analysis were conducted. Bio-oil was characterized for its functional groups and chemical constituents via Gas chromatography–mass spectrometry (GC-MS), Fourier transforms infrared spectra (FTIR) and ^{1}H Nuclear Magnetic Resonance (^{1}H NMR). Bio-char properties were determined by X-ray diffraction (XRD), Brunauer−Emmett−Teller (BET) surface area, FTIR and scanning electron microscope (SEM).

4.2 Material and methods

4.2.1 Collection and preparation of sample material

For this study, MAS was used as the raw material and it was obtained from a sawmill situated in the vicinity of IIT-BHU in Varanasi district of Uttar Pradesh, India. It was rinsed twice with double distilled water to remove dirt from its external surface and then kept in Sunlight for 3 days followed by oven drying at 100 ℃ so as to remove excess moisture from the sample. Post drying, sample was ground and sieved to obtain desired particle size. Prepared samples were stored in air tight glassware and kept inside a desiccator to prevent any contamination or moisture.

4.2.2 Pyrolysis experimental segment

Schematic diagram of pyrolysis experimental set-up is shown in Fig. 4.1. Pyrolysis experiments of the MAS were carried out in a fixed bed tubular reactor made up of stainless steel and it was heated externally by 2.5 kW split tube furnace in which temperature control was facilitated by proportional-integral-derivative (PID) controller. Vertical tubular reactor has internal diameter 42 mm and length 500 mm. A single zone electric Narang Scientific Works (NSW)-104 split tube furnace was deployed for pyrolysis. Nitrogen of 99.99% purity was used as the carrier gas as well as for maintaining inert atmosphere inside the reactor. Besides this, nitrogen was used for sweeping pyrolytic vapours from reaction zone to the condensation traps. N_2 cylinder was used as the source of nitrogen gas. Outlet of the reactor was connected to a conical glass flask which was connected to two more conical flasks in series manner, which served as condensation unit. Kim et al. (2016) also used condensation section which comprised of three condensers in series for bio-oil collection (Kim et al., 2016). Ice-cooled condenser (maintained at 0 °C) was used to condense condensable volatiles and followed by this step; non-condensable fractions were collected in gas sampler bags. Prior to collection

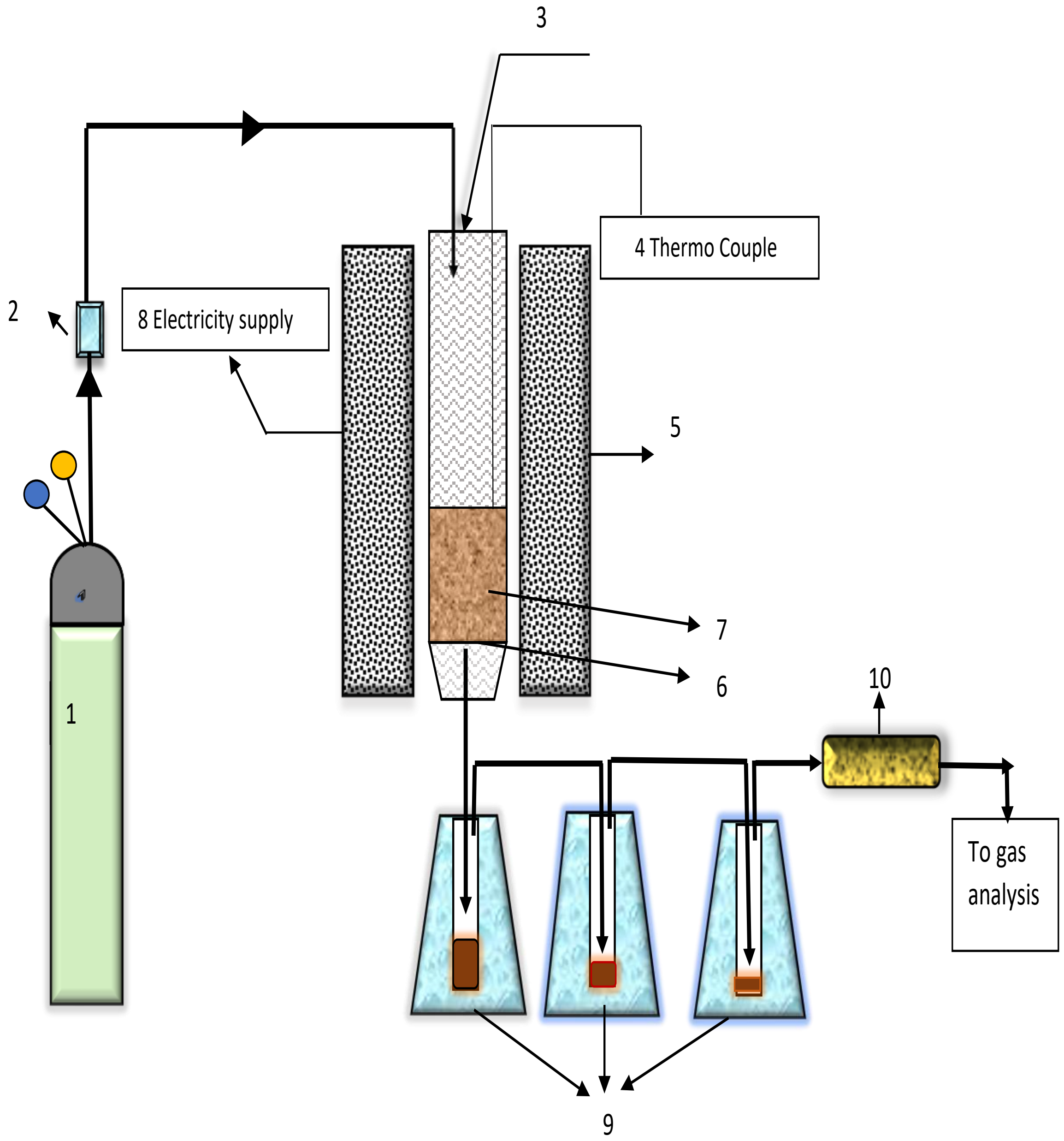

Figure 4.1. Schematic diagram of pyrolysis experimental set-up: 1. Nitrogen cylinder 2. Mass flow controller 3. Stainless steel pyrolysis reactor 4. Thermo-couple 5. PID-controlled electric furnace 6. Sieve support plate 7. Biomass sample 8. Electricity power supply 9. Ice cooled flask condensers 10. Cotton filter, dichloromethane and silica gel column.

pyrolytic gas was passed via columns of dichloromethane and silica gel for impurities and moisture removal. Then, reactor was allowed to cool down to room temperature for collection of bio-char out of it. Nitrogen purging rate was kept at desired value with the help of mass flow controller (Alicat Scientific, New Delhi, India).

For studying effect of operating parameters on pyrolysis products distribution, pyrolysis temperature, flow rate of sweeping gas, packed bed height, heating rate, pyrolysis time and feedstock particle size were varied. For determining the effect of pyrolysis temperature 20 g of MAS sample was fed to the reactor in each run and pyrolysis experiment temperature was hovered between 450 and 600 ℃ with a step-wise increase of 50 ℃ on each run. Sweeping gas flow rate effect was studied using 150, 200 and 250 mL/min N_2 flow rate with 20 g MAS at 550 ℃. Height of packed bed was varied from 2.1 to 8.4 cm and at 550 ℃ reaction temperature with 150 mL/min gas flow rate at 550 ℃. Similarly, for particle size variation effect experiments were carried out at 550 ℃ coupled with 150 mL/min nitrogen purging rate, 20 g MAS was taken in the reactor in particle size having range of 0.18-0.29, 0.29-0.49 and 0.49-0.83 mm. Impact of heating rate on product yield distribution during pyrolysis experiment was assessed using 10, 20 and 30 ℃/min heating rates. 40, 60 and 80 min pyrolysis time was employed to see variation of pyrolysis products yield with time of pyrolysis. For all parametric studies initially sweeping gas was purged for 15 minutes prior to starting the experiment so as to ensure proper inertness and a residence time of 60 minutes was used after reaching final target temperature to make sure reactions take place promptly. Collected bio-oil and bio-char were weighed and their sum was subtracted from initial mass of MAS fed to the reactor for finding gaseous yield. Following expressions were used for calculation of bio-oil, bio-char and gas yield;

$$bio - oil \% \, yield = \frac{mass \; of \; bio - oil}{intial \; mass \; of \; sample} \times 100 \tag{4.1}$$

$$bio - char \% \, yield = \frac{mass \; of \; bio - char}{intial \; mass \; of \; sample} \times 100 \tag{4.2}$$

$$pyrolytic \; gas \% \, yield = 100 - (BO \% \, yield + BC \% \, yield) \tag{4.3}$$

Bio-oil and bio-char have been named as BO and BC, respectively and BO-450 means bio-oil obtained at 450°C temperature condition and so on. All the experiments were performed thrice for validating experimental outputs and here in this paper average values have been reported. The fixed bed reactor, condensation unit and piping system were decontaminated before and after each experimental run for avoiding contamination in sample and resultant products.

4.2.3 Characterization techniques used for MAS, bio-char and bio-oil

4.2.3.1 Characterization of MAS and bio-char

Proximate analysis was performed so as to find out moisture content (MC), ash content (AC) and volatile matter (VM) as per standard protocols of ASTM (ASTM D3173, ASTM D3174 and ASTM D3175). Fixed carbon (FC) content was determined by using eq. 4.4;

$$FC(\%) = [100 - (MC + AC + VM)](\%) \tag{4.4}$$

Ultimate analysis was carried out to find out elemental composition of biomass and its biochar. Carbon, hydrogen, nitrogen was determined by using EURO EA, EURO ECTOR instruments and software, Italy. Oxygen content was found by the difference using eq. 4.5;

$$O\% = [100 - (C + H + N)]\% \tag{4.5}$$

Bomb calorimeter (Rajdhani Scientific, NSTTS Co., New Delhi, India) was employed for determination of HHV of biomass, bio-char and bio-oil.

For calculation of bio-char’s energy yield (EY) following equation was used;

$$EY = \frac{HHV_{BC}}{HHV_{MAS}} \times yield\ of\ biochar \tag{4.6}$$

For gaining knowledge of prevailing functional groups in MAS and its bio-char FTIR was deployed. Nicolet iS5 of THERMO Electron Scientific Instruments LLC was used for this. Hydraulic press was used to palletize samples by blending it with KBr in ratio of 1:10 (Sample: KBr) and samples scanning was done in infrared zone ranging from 4000 to 400 cm^{-1}. Pallet of pure KBr was used as reference sample. For analysing crystallographic structure XRD was carried out using Rigaku SmartLab 9kW Powder type (without χcradle) (RIGAKU Corporation) with wavelength 1.54056 Å. BET surface area was characterized using ASAP 2020 adsorption apparatus (Micromeritics, USA). Surface morphology was inspected by SEM (model EVO - Scanning Electron Microscope MA15 /18 from CARL ZEISS MICROSCOPY LTD).

4.2.3.2 Characterization of bio-oil

Pyrolytic bio-oil was characterized for its chemical and physical properties including pH, density, HHV, viscosity and carbon residue. FTIR and ^{1}H NMR analyses of bio-oil were also done. Systronics digital pH meter was used to measure pH. Standard protocol of ASTM D1298 was used for density measurement while viscosity was determined by Brookfield digital viscometer (LVDV-II þ Pro). HHV was measured by a bomb calorimeter (Model C-200, IKA, Germany) and carbon residue estimation was done by Ramsbottom Carbon residue (RCR- IP 14/65) method. FTIR peaks of bio-oil samples were obtained by Nicolet iS5 of THERMO Electron Scientific Instruments LLC in the range of 4000–400 cm^{-1}. ^{1}H NMR analysis was conducted by AVH D 500 AVANCE III HD 500 MHz OneBay NMR Spectrometer (BRUKER BioSpin INTERNATIONAL AG). GC-MS is an analytical technique which amalgamates properties of gas-chromatography and mass spectrometry to recognize various substances prevailing in bio-oil sample. Constituting compounds of pyrolytic bio-oil were recognized using VARIAN 240 GC–

MS coupled with VM5MS capillary column (30 m × 250 μm × 0.25 μm). Helium was employed as carrier gas and 1 μL of test sample bio-oil was administered at 250 ℃ temperature of injector inside column maintaining a split ratio of 1:10. Initially oven temperature was kept at 40 ℃ (holding time 10 min) and then heated up to a temperature of 250 ℃ at the rate of 10 ℃/min (holding time 15 min). Ultimately, temperature was lifted to 275 ℃ with ramping rate of 10 ℃/min (holding time 10 min). The chromatographic peaks were identified by data of the National Institute of Standards and Technology library (NIST, USA).

4.3 Results and discussion

4.3.1 Effect of process conditions on pyrolytic products' yield distribution

4.3.1.1 Effect of temperature variation

Temperature plays a substantial role in pyrolysis products distribution (Altamer et al., 2021; Muley et al., 2015). Effect of temperature on distribution of yield of products is shown in the Fig. 4.2a. Experiments were performed at temperature 450, 500, 550 and 600 ℃ with keeping 150 mL/min N_2 flow rate, 8.4 cm bed height, 0.18-0.29 mm particle size, 20 ℃/min heating rate and 60 min pyrolysis time. With increment in temperature of pyrolysis yield of bio-oil increased from 42.64 wt.% at 450 ℃ to 50.67 wt.% at 550 ℃. On further increasing reaction temperature bio-oil yield slightly decreased. Bio-char yield decreased from 35.29 to 23.26 wt.% as temperature was increased from 450 to 600 ℃. High yield of bio-char was obtained at low pyrolysis temperature because of lower primary decomposition of MAS and secondary decomposition of the char residues at low temperature but at high pyrolysis temperature both primary and secondary decompositions increased which resulted in lower bio-char yield at high temperature of pyrolysis. Similar results were announced for paulownias wood (Yorgun and Yildiz, 2015). Lower bio-oil yield at lower reaction temperature could be due to non-availability of temperature required for complete pyrolysis and a reaction temperature of 550 ℃ facilitated complete pyrolysis. On further increasing temperature beyond 550 ℃ bio-oil yield decreased due to dominance of secondary cracking reactions in that temperature zone. The role of the temperature in the process of pyrolysis is to fulfill the heat requirement for the decomposition of feedstock biomass. The bio-oil yield of MAS attained a maximum value, at 550 °C, likely due to strong cracking at this temperature and also inhibiting over breakdown of MAS into gaseous products (Yorgun and Yildiz, 2015; Park et al., 2018). So, 550 ℃ was chosen as pyrolysis temperature for other experiments. Yield of gaseous fraction increased from 22.07 to 27.93 wt.% with increasing reaction temperature from 450 to 600 ℃. On the other hand, decrease in bio-char and increment of pyrolytic gas yield with increase in temperature was recorded due to char and pyrolytic gases getting converted into gaseous phase via secondary cracking (Guedes et al., 2018).

4.3.1.2 Effect of sweeping gas flow rate variation

Fig. 4.2b depicts the impact of variation in flow rate of sweeping gas on yield of pyrolysis products. Rate of flow of sweeping gas was varied from 150 to 250 mL/min for studying its influence on pyrolytic products yield, while using 550 ℃ temperature, 8.4 cm bed height, 0.18-0.29 mm particle size, 20 ℃/min heating rate and 60 min pyrolysis time. From Fig. 4.2b, it is clearly evident that flow rate of sweeping gas significantly influenced product yield distribution and bio-oil yield varied from 46.51 to 50.67 wt.%, bio-char yield varied from 21.42 to 24.42 wt.% while yield of pyrolytic gas hovered between 24.91 to 32.07 wt.%. Maximum bio-oil yield was obtained at minimum flow rate of sweeping gas of 150 mL/min. Gaseous yield increased with increasing flow rate but bio-oil and bio-char yield decreased slightly. The sweeping gas flow rate affects the residence time of volatile matter in the reaction and condensation zones of pyrolysis.

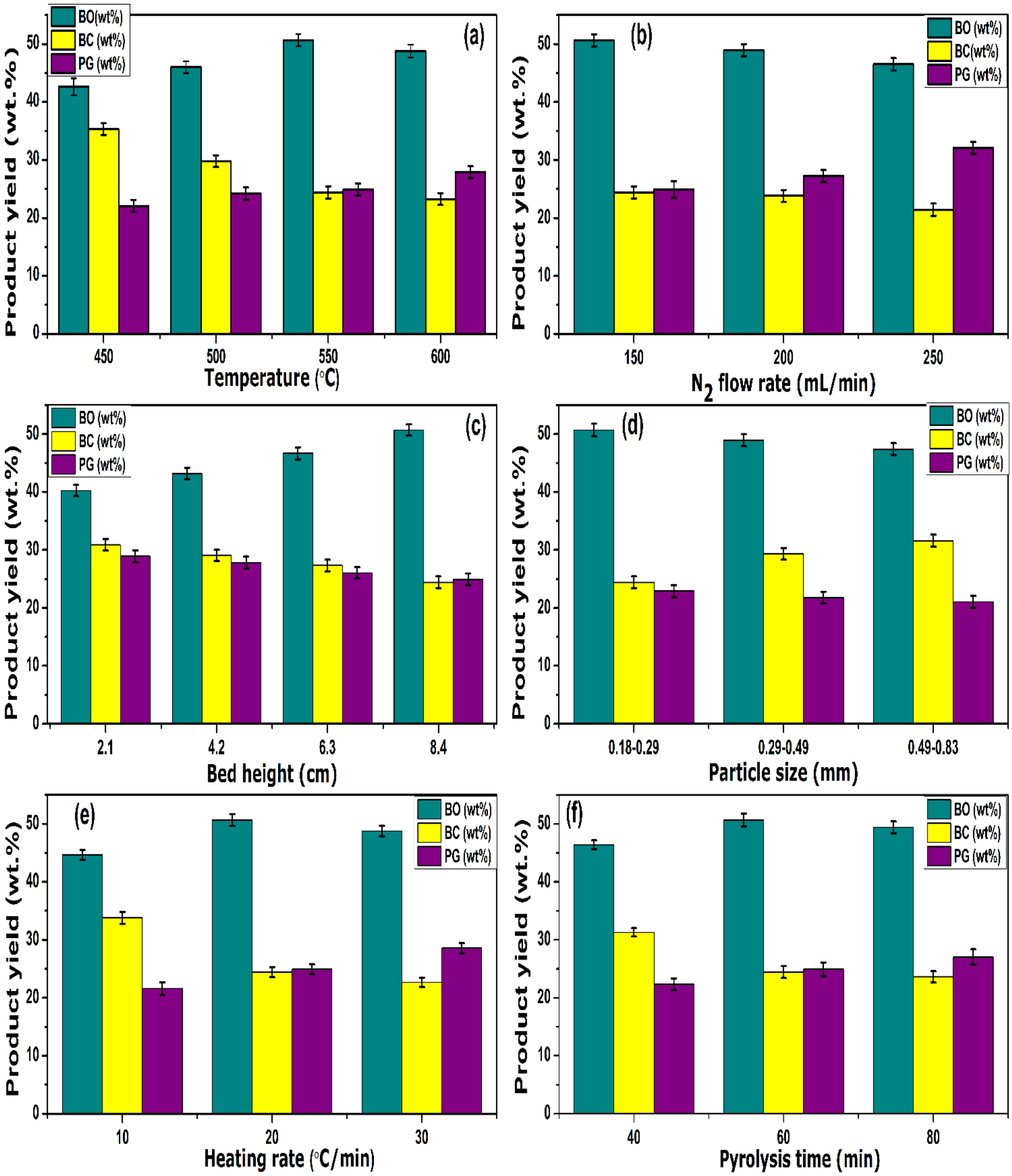

Figure 4.2. Effect of parameter variation (a) temperature (b) sweeping gas flow rate (c) bed height (d) particle size (e) heating rate (f) pyrolysis time (Temperature 550 °C, 150 mL/min N_2 flow rate, 8.4 cm bed height, 0.18-0.29 mm particle size, 20 °C/min heating rate and 60 min pyrolysis time unless stated their variation)

Vapours got pushed out quickly and residence time of vapour within the reaction zone was reduced when sweeping gas flow rate was high which in turn interrupted various secondary reactions such as thermal cracking, secondary cracking, recondensation and repolymerization. The reason for the decreased bio-oil and increased gaseous products' yield could be either limited cooling or uncondensed volatiles leaving the pyrolysis system as gases due to high sweeping gas flow rates. Also, at high gas flow rate there are chances of vapours getting drained out of the condenser quickly which hinders bio-oil formation whereas at low gas flow rate vapours get enough retention time within the reactor as well as in condensation zone which might facilitate enhanced secondary cracking reactions leading to high liquid yield (Yorgun and Yildiz, 2015).

4.3.1.3 Effect of bed height variation

Effect of variation in packed bed height on pyrolysis product distribution is depicted in Fig. 4.2c. With increasing bed height yield of bio-oil showed a directly proportional relation means bio-oil yield increased as height of bed was increased. Meanwhile, solid product that is bio-char yield showed an inversely proportional relation with variation in bed height, similarly with increasing height of bed, pyrolytic gaseous yield also decreased. Bed height was varied from 8.4 to 2.1 cm and temperature, N_2 flow rate, particle size, heating rate and pyrolysis time were kept fixed at 550 °C, 150 mL/min, 0.18-0.29 mm, 20 °C/min and 60 min, respectively. Bio-oil yield was recorded to vary from 50.67 to 40.22 wt.% corresponding to bed height variation from 8.4 to 2.1 cm, respectively. So, 8.4 cm bed height was chosen as it resulted in maximum bio-oil yield. While bio-char yield ranged from 24.42 to 30.87 wt.% and pyrolysis gas yield surged from 24.91 to 28.91 wt.% when bed height was decreased from 8.4 to 2.1 cm. The pyrolytic reactions mostly take place in dense feedstock bed. Enhancement in bio-oil yield could be attributed to the fact that increased bed height prevents early escape of condensable volatile vapours and longer resistance time in reaction zone leads to cracking of primary organic vapours along with accelerated secondary cracking of organic matter. Similar results were reported by Tripathi et al. (2016) (Tripathi et al., 2016) in their study. Low bed height resulted in high bio-char and gas yield because low bed height results in less residence time and less secondary cracking reactions which cause less cracking of primary organic vapours and form more bio-char and less bio-oil.

4.3.1.4 Effect of particle size variation

For influence of particle size, MAS particles of feedstock were used having mesh no. 80, 48, 32 and 20 which have size 0.18-0.29, 0.29-0.49 and 0.49-0.83 mm. Frozen parameters were temperature 550 °C, 150 mL/min N_2 flow rate, 8.4 cm bed height, 20 °C/min heating rate and 60 min pyrolysis time. In Fig. 4.2d impact of particle size is depicted which reveals that as particle size was increased bio-oil and gas yield decreased while that of bio-char increased. Particle size selection is one of the key parameters for pyrolysis experiment as it directly affects rate of heat transfer thus influences product yield distribution. Since, biomass is a bad heat conductor so, particle size of feedstock can play a significant role in deciding best condition for its proper decomposition during pyrolysis (Guedes et al., 2018). Large particle sized biomass requires long time to transfer heat supplied to its outer surface to penetrate through it and reach inside core of the particle whereas in case of small particle sized biomass heat penetrates quickly and uniformly up to the core of the particle (Hanandeh et al., 2021). Particles of small size produce more bio-oil as high heat transfer occurs in them which promotes prompt and efficient devolatilization of biomass. Small particles lead to the formation of more hot volatiles which further condense into liquid providing high bio-oil yield. In large particles more bio-char formation occurs because vapours which are formed due to thermal cracking have to travel longer distance of char layer that accelerates secondary reactions.

4.3.1.5 Effect of heating rate variation

Rate of heating is one of the prominent factors that governs product yield distribution of pyrolysis. So, it becomes essential to study influence of rate of heating for process parameter’s optimization. Three heating rates 10, 20 and 30 °C/min were used for experimental purpose and other parameters were chosen to be at their optimal values (550 °C temperature, 150 mL/min N_2 flow rate, 8.4 cm bed height and particles of size 0.18-0.29 mm with 60 min pyrolysis time). It is clearly evident from Fig. 4.2e that yield of bio-oil increased from 44.63 to 50.67 wt.% as heating rate was increased from 10 to 20 °C/min but at 30 °C/min bio-oil yield diminished and heating rate of 20 °C/min resulted in highest yield of bio-oil. This pattern in bio-oil yield could be attributed to the fact that application of heating rate higher than optimum value gives rise to swift depolymerization of MAS into primary volatiles along with accelerated secondary reactions in pyrolytic vapours. Yield of bio-char declined with increase in the pyrolysis heating rate due to the fast and significant primary decomposition of MAS and secondary decomposition of the char residue. Pyrolytic gaseous products yield increased with increasing heating rate due to fast depolymerization of MAS into preliminary volatiles. At a 20 °C/min heating rate, better mass and heat transfer along with secondary reactions, like tar cracking and repolymerization, occurred properly and resulted in mere condensable volatiles (Al-Layla et al., 2021). Similar trend of pyrolysis product distribution as a result of variation in heating rate has been declared for Alternanthera philoxeroides (Bhattacharjee and Biswas, 2019), Samanea saman seeds (Mishra et al., 2020) and corncob (Demiral et al., 2012).

4.3.1.6 Effect of pyrolysis time variation

Duration of pyrolysis is a pivotal parameter which affects pyrolysis product distribution. The experiments for residence time of 40, 60 and 80 min were accomplished with 550 °C temperature, 150 mL/min carrier gas flow rate, 0.18-0.29 mm particle size, 8.4 cm bed height and 20 °C/min heating rate. Impact of residence time of MAS inside the reactor on product yield is illustrated in Fig. 4.2f. Pyrolysis of MAS was allowed to take place inside the reactor for residence time of 40, 60 and 80 min after attaining temperature of 550 °C. Bio-oil and pyrolytic gas yield improved while bio-char yield lowered when pyrolysis time was increased. The maximum bio-oil yield 50.67 wt.% was noticed for 60 min residence time and it got reduced by 2.28 wt.% when pyrolysis time was further increased to 80 min. Yield of pyrolytic gases enhanced with increasing pyrolysis time owing to the fact that prolonged period of pyrolysis accelerated gasification of primary pyrolysis vapours and bio-char devolatilization because of secondary thermal degradation reactions (Al-Layla et al., 2021). When pyrolysis residence time was increased the prolonged thermal degradation period resulted in decrease in bio-char yield and increase in non-condensable pyrolytic gases yield. Further devolatilization and gasification of the char due to secondary thermal decomposition reactions led to lower bio-char yield upon increasing the pyrolysis residence time. 60 min of pyrolysis time resulted in the production of more volatiles and which up on condensation resulted in high bio-oil yield. Similar findings were announced for Crofton weed (Cheng et al., 2019), pistachio shell (Acıkalın et al., 2012) and sawdust of furniture waste (Uzun and Kanmaz, 2013). So, a pyrolysis time of 60 min duration was adopted as this duration was found to be suitable enough to dispense time for complete thermal decomposition of MAS while preventing further gasification of products.

4.3.2 Characterization of biomass and pyrolytic products

4.3.2.1 Physicochemical characterization of MAS and bio-char

Physicochemical properties of MAS along with its biochar are presented in Table 4.1. Results of proximate analysis of MAS revealed that it is highly rich in volatile matter (78.3 wt.%) while deficient in ash and moisture content (2.04 and 6.64 wt.%, respectively). In MAS fixed carbon content was found to be 13.02 wt.% and it is responsible for biochar production in pyrolysis. High volatile matter leads to high bio-oil yield. Therefore, high content of volatile matter is a desired trait of biomass for pyrolysis because bio-oil is the prime targeted pyrolytic product. Biomass having moisture content less than 10 wt.%, high volatile matter and low ash content is best suited for pyrolysis and yields desirable results. Results of ultimate analysis affirmed that it has high carbon amount (43.84 wt.%) which makes it favourable for energy production. High carbon content results in more heating value of the fuel. Oxygen content was found to be 48.79 wt.% and high oxygen content yields higher volatile matter but it lowers the HHV. Hydrogen was 6.49 wt.% and it is a key factor for determination of energy properties of solid biofuels. MAS consisted nitrogen in negligible quantities and sulphur was not found in it, which makes it safer from environmental point of view as compared to conventional sources of energy. HHV of MAS was found to be quite high (16.34 MJ/kg) affirming its candidature for bio-energy generation. Similar results were found for different physicochemical characterizations for Sal sawdust, pine sawdust and areca nut husk (Mishra and Mohanty, 2018) and soybean stalk (Agnihotri and Mondal, 2023).

Quantitative assessment of biochar was done by carrying out its proximate, ultimate and HHV analysis as shown in Table 4.1. Volatile matter decreased from 37 to 24.4 wt.% as pyrolysis temperature was increased from 450 to 600 °C meanwhile, fixed carbon and ash content increased from 51.94 to 63.39 wt.% and from 5.15 to 8 wt.%, respectively. This pattern was observed because of removal of volatiles from biomass and increase in ash content indicates increase in inorganic mineral contents in biochar at high temperature. High ash content lowers the efficiency of fuel so it is an undesirable trait (Peng et al., 2023). Decrease in volatile matter in biochar as compared to MAS biomass sample shows conversion of volatiles of MAS into bio-oil.

Table 4.1. Physicochemical properties of MAS and its biochar

Property	**MAS**	**BC-450**	**BC-500**	**BC-550**	**BC-600**
MC (wt.%)	6.64	5.91	5.4	4.8	4.21
VM (wt.%)	78.30	37	32	25.43	24.4
AC (wt.%)	2.04	5.15	5.92	7.2	8.0
FC (wt.%)	13.02	51.94	56.58	62.57	63.39
C (wt.%)	43.84	72.68	74.93	76.56	78.96
H (wt.%)	6.49	4.11	3.76	3.12	2.67
N (wt.%)	0.88	0.81	0.78	0.74	0.71
O (wt.%)	48.79	22.4	20.53	19.58	17.66
H/C	1.59	0.68	0.60	0.49	0.41
O/C	0.75	0.23	0.21	0.19	0.17
EY	-	0.43	0.42	0.36	0.39
HHV (MJ/kg)	16.34	23.51	24.76	24.95	25.39

The O/C and H/C ratio of MAS (0.75 and 1.59, respectively) was found to be the highest and it decreased for bio-chars as temperature was increased which indicated the decomposition of several functional groups. Higher atomic H/C ratio in MAS indicated more energy that is released during burning of the fuel. Low O/C ratio results in less smoke and soot formation during combustion (Li et al., 2022). HHV is a key factor for determining quantitative energy contents of any fuel. HHV of MAS was estimated to be 16.34 MJ/kg while that of its bio-char was found to be 23.51, 24.76, 24.95 and 25.39 MJ/kg for 450, 500, 550 and 600 °C, respectively. HHV of bio-char was higher than MAS and it increased with increase in pyrolysis temperature. This pattern was observed because of improved carbonization at high temperature condition. Similarly, HHV of timber sawdust was reported to increase from 27.2 to 29.4 MJ/kg on increasing pyrolysis temperature from 450 to 900 °C (Wang et al., 2022). High HHV of bio-char makes it suitable to be utilized as a solid fuel.

Energy yield (EY) was another parameter which was evaluated for bio-char as depicted in Table 4.1. It indicates amount of energy remained in products of pyrolysis and is evaluated with the help of HHV and product yield. As pyrolysis temperature was increased a decreasing trend in EY values were noted which is quite favourable. It happened so because of high conversion of volatiles into gaseous and liquid products. Li et al. (2022) also reported decreasing trend of EY for pyrolytic bio-char of sawdust on increasing temperature from 450 to 900 °C (Li et al., 2022).

4.3.2.2 Morphological study of MAS and bio-char

SEM was deployed so as to monitor the surface morphology of MAS and its bio-char corresponding to various pyrolysis temperature. In Fig. 4.3 SEM photographs of the same have been presented. Both MAS as well as bio-char possessed porous structure but surface area of bio-char got augmented as compared to that of MAS. This happened because volatile fractions of MAS volatilized from biomass interstices due to high temperature resulting in higher number of pores coupled with enhanced internal specific surface area of pores. Spherical craters of MAS surface were transformed into open channel cells of bio-char post carbonization and devolatilization of MAS. Rich porous morphology and enhanced specific surface area of bio-char is favourable as it makes bio-char efficient to be used in various applications such as soil conditioning, catalyst support, solid-liquid adsorption and as a waste water treatment substrate (Shi et al., 2023). Results of BET surface area characterization reinforced this. Because BET of bio-char increased from 2.242 (for BC-450) to 240.163 (for BC-550) m^2/g. These findings of SEM and BET underscored the huge specific surface area, profuse microscopic porous crystallographic structure with lots of open channels existing in bio-char. These results are in good harmony with findings of Shi et al. (2023) (Shi et al., 2023).

4.3.2.3 XRD analysis of MAS and bio-char

XRD is a tool used for finding the crystallographic structure of any material. The XRD spectra of MAS and its biochar obtained at different conditions from its pyrolysis is depicted in the Fig. 4.4. The intensity and sharpness of peak at values of 2ϴ about 17^o and 23^o are a testimony of the cellulose present in the MAS in amorphous as well as in crystalline structure. But pyrolysis completely altered the crystallographic structure of the bio-char as compared to that obtained for the MAS prior to pyrolysis. At elevated temperature these peaks at 17^o and 23^o got flattened because of decomposition of crystalline cellulosic matter present in MAS. These peaks indicate they are aromatic (He et al., 2018). At a value of 2ϴ around 27^0 another peak is observed which corresponds to the crystalline properties of quartz (Singh et al., 2016). So, at higher temperature crystalline portion of cellulose gets transformed into amorphous one and leading to an almost amorphous biochar which means the amorphous nature increased and crystalline nature decreased in biochar.

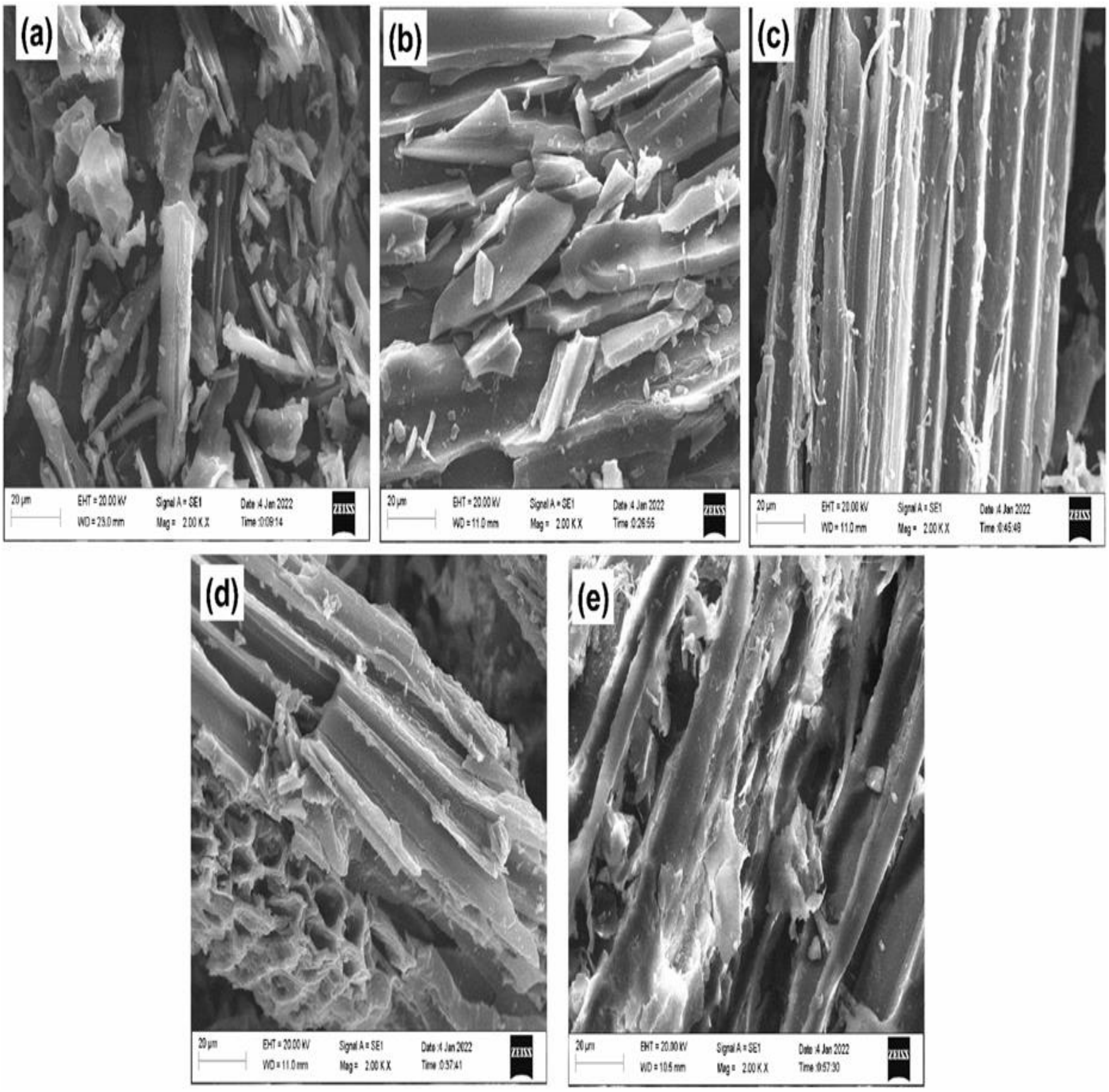

Figure 4.3. SEM (Mag = 2.0 K X) images of (a) MAS (b) BC-450 (c) BC-500 (d) BC-550 (e) BC-600

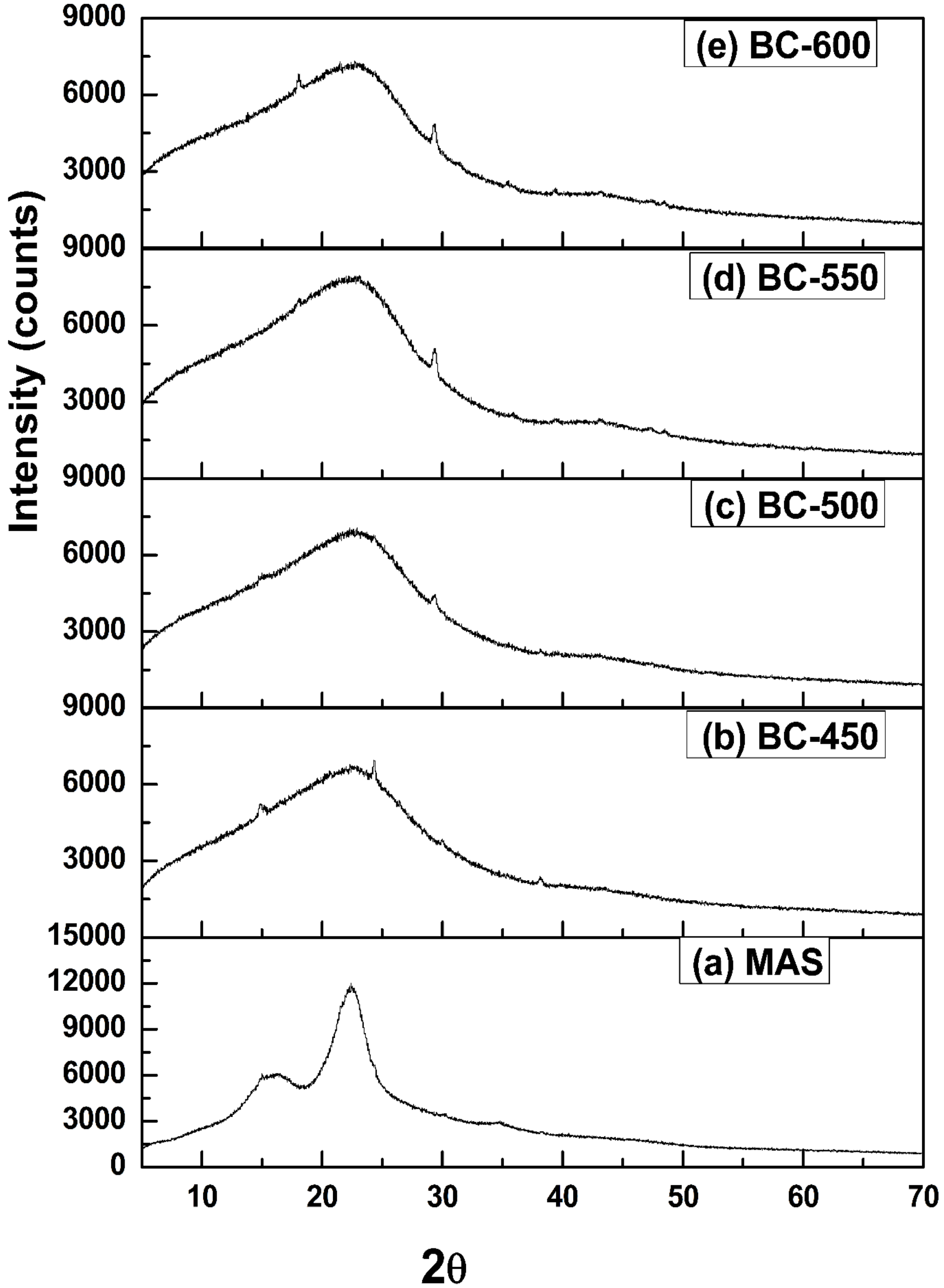

Figure 4.4. XRD analysis of (a) MAS (b) BC-450 (c) BC-500 (d) BC-550 (e) BC-600

4.3.2.4 FTIR analysis of MAS and biochar

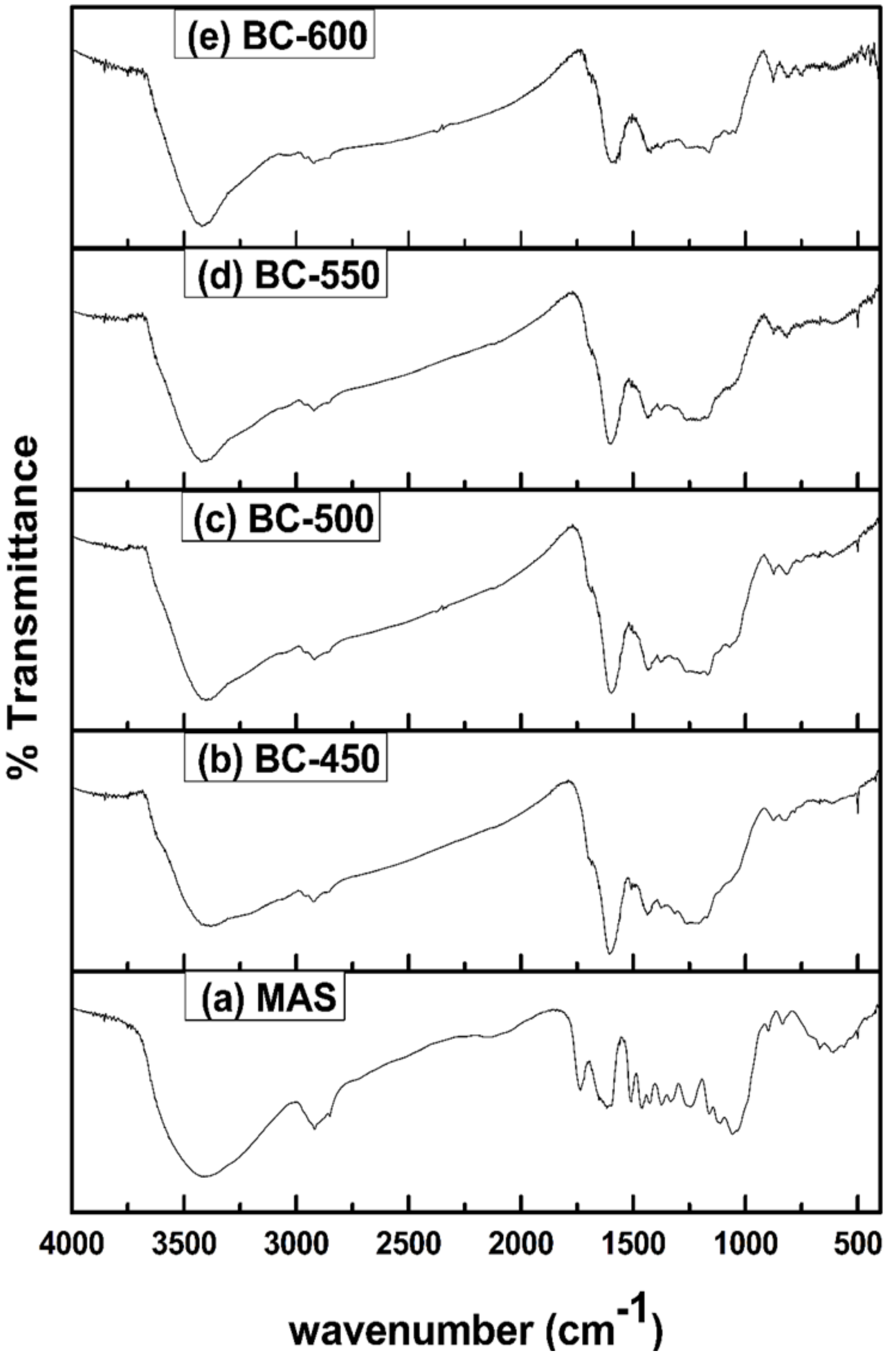

Figure 4.5. FTIR spectra of (a) MAS (b) BC-450 (c) BC-500 (d) BC-550 (e) BC-600

The FTIR analysis is an efficient technique which enables us to identify different functional groups prevailing in any material. The FTIR analysis of MAS and its biochar obtained by pyrolysis process was performed and their corresponding spectra are shown in Fig. 4.5. FTIR spectra of biochar exhibited significantly different nature from that of MAS and this difference could be attributed to thermal treatment. For MAS, the peak at 3400 cm^{-1} corresponds to hydrogen bonded vibration stretch of O-H containing groups like phenol, alcohol such as methanol and water. The peaks of wavenumber ranging between 2800 to 2900 cm^{-1} for biochar and MAS is designated to the stretching and deformation vibrations of aliphatic C-H groups. This peak is steeper in MAS sample as compared to that obtained for its biochar. This could be attributed to demethylation, demethoxylation and dehydration of lignin which leads to the decrement in aliphatic compounds with increase in temperature. This reveals that with increasing temperature biochar has acquired more of aromatic traits and aliphatic containing groups reduced (Soni and Karmee, 2020). The peaks at 1400.2 and 1600 cm^{-1} indicate presence of lignin within MAS sample. In the spectra between 1750-750 cm^{-1} various bands are present which correspond to a variety of functional groups existing in hemicellulose, cellulose and lignin with intensities depending upon the fraction of the constituent components. Peaks at 1369–1374 cm^{-1} associated with aliphatic C–H stretching confirmed the presence of cellulose and hemicellulose. Peak at wavenumber 600-750 cm^{-1} points out C-H bond bending vibrations. Different inorganic compounds in the ash are responsible for the peaks detected below 600 cm^{-1} in the FTIR spectra.

4.3.2.5 NMR study of bio-oil

To identify type of carbon and functional groups prevailing in bio-oil NMR analysis was done. Fig. 4.6 shows ^{1}H NMR spectra of bio-oil obtained as a result of pyrolysis of MAS (at 550 °C) versus chemical shift in parts per million (ppm) on horizontal axis. Different types of protons present in the molecule exhibit distinct nature based on the neighbouring chemical environment, facilitating their structural elucidation. Entire NMR spectrum was categorised into several zones. ^{1}H NMR characterization of BO revealed presence of alcohol, ketone, alkyl and aryl compounds in it. Aliphatic, olefinic and aromatics were recognized as major portions prevailing in it. Chemical shift hovering between 0.5 -3.0 ppm indicated aliphatic portions, in 3.0-5.0 ppm range chemical shift was due to olefinic fractions and chemical shift from 6.0 to 9.0 ppm was ascribed to aromatic compounds. These findings are in line with the findings of other researchers such as Altamer et. al. (2021); Soni and Karmee (2020) (Altamer et. al., 2021; Soni and Karmee, 2020).

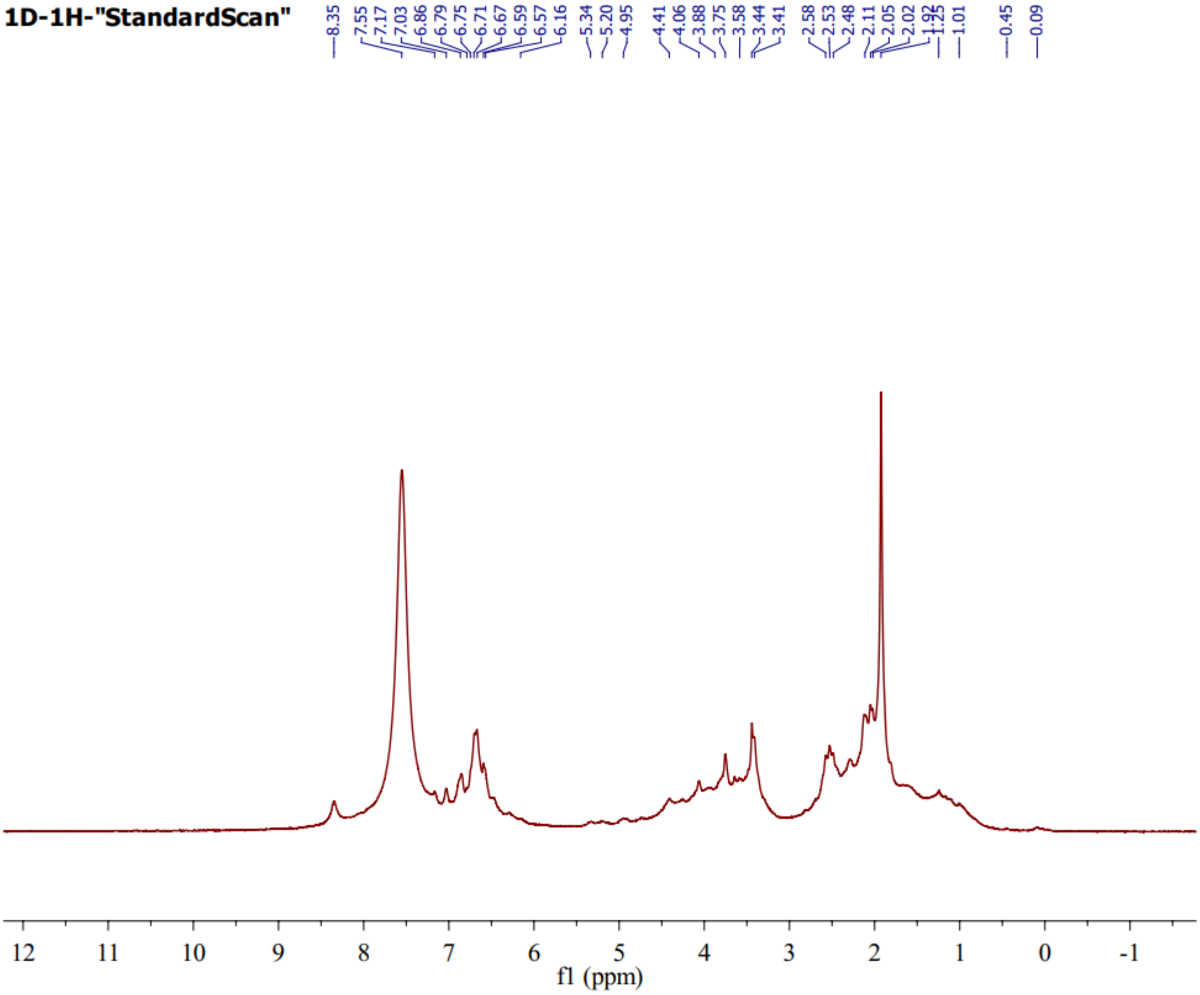

Figure 4.6. ^{1}H NMR spectra of bio-oil obtained at 550 °C

4.3.2.6 FTIR analysis of bio-oil

FTIR is a spectroscopic technique that figures out chemical bonds of a molecule by generating an infrared absorption spectrum. The spectra generate a profile of the sample, a distinctive molecular fingerprint which is used for screening and scanning of samples for various components. Fig. 4.7 displays the FTIR spectra obtained for bio-oil at different pyrolysis temperatures. It is clearly evident from the diagram that a huge number of atomic groups like O-H, C-H, C=C, C=O and C-O are constituents of bio-oil. A wide peak from 3600 to 3400 cm^{-1} signifies hydrogen bonded O-H stretch of alcohols and phenols. This peak is much broader as compared to other peaks in the IR spectra and this peak was more intense for BO-450 than that obtained for BO-600. The peaks arising at 2918 and 2845 cm^{-1} indicated C-H stretching of alkenes and alkanes in pyrolytic bio-oil and these peaks became more intense as temperature was increased from 450 to 600 ℃. Peaks at 1731.28 and 1617.57 cm^{-1} represent C=O stretches corresponding to carbonyl group of the bio-oil. These stretching vibrations indicate that ketones, aldehydes and carboxylic acids are present in the bio-oil. The wavenumber 1527.8, 1511.3, 1516.24 and 1523.7 cm^{-1} are ascribed to secondary amine vibrations. The peaks originating at wavenumbers 1454.5, 1462.7 and 1444.9 cm^{-1} are C=C aromatic vibrations of benzene ring. A large number of peaks occurring in the range of 1250 to 1040 cm^{-1} are designated to C-O stretching and vibrations of esters and ethers of bio-oil (Gaurh and Pramanik, 2018). Presence of peaks around 925 and 616 cm^{-1} are attributed to alkenes and alkynes of bio-oil. FTIR spectra obtained at 450, 500, 550 and 600 ℃ were more or less similar only their intensities varied slightly. From all these findings, it can be concluded that bio-oil obtained from MAS pyrolysis is a blend containing enormous organic compounds consisting of aromatics and paraffins etc. which could serve as a source of transportation fuel after upgradation or as high-value chemical source.

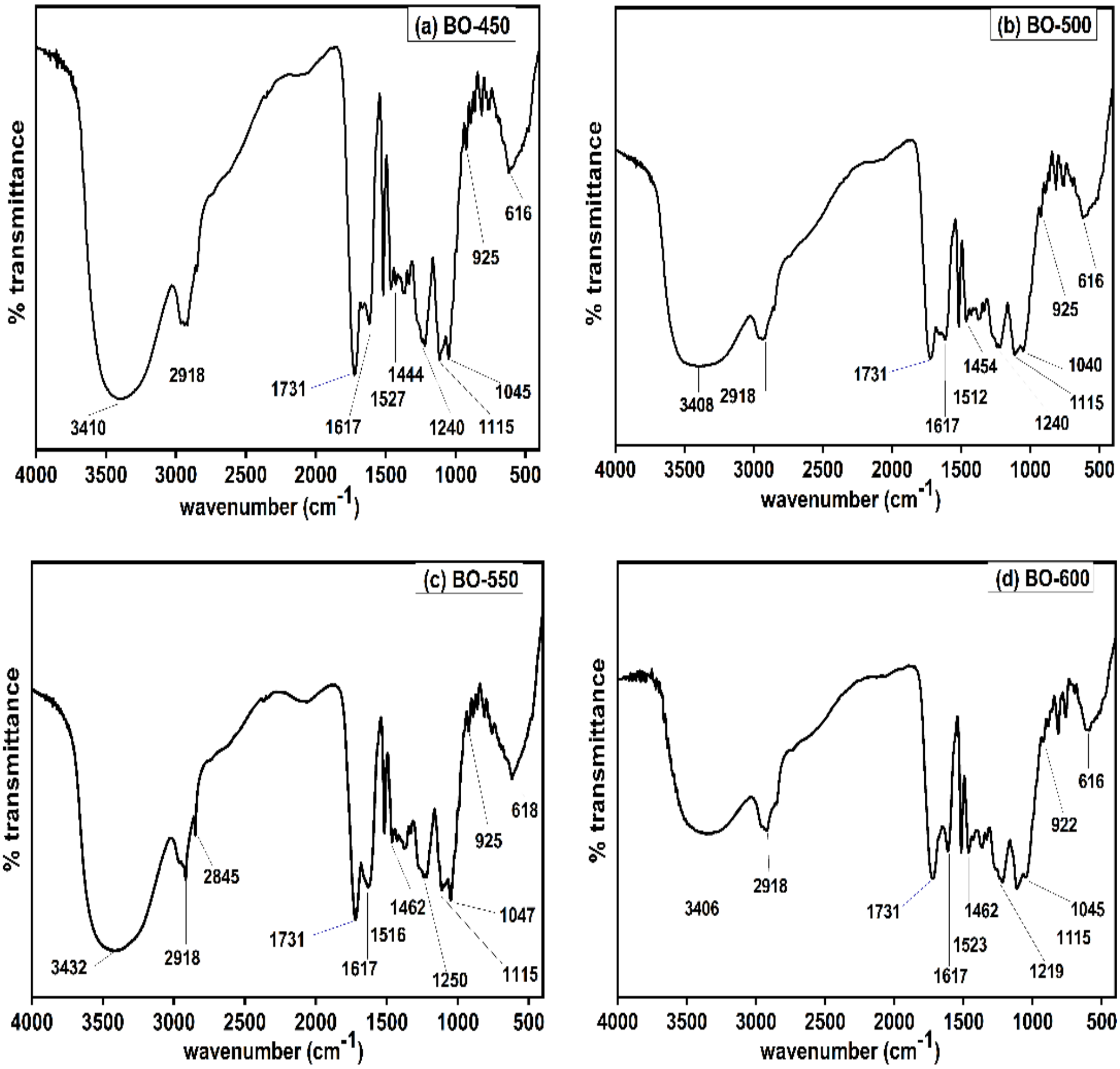

Figure 4.7. FTIR spectra of bio-oil obtained at (a) 450 °C (b) 500 °C (c) 550 °C (d) 600 °C

4.3.2.7 GC-MS analysis of bio-oil

The quantitative evaluation of chemical contents of pyrolytic bio-oil is essential for proposing its application in the field of bioenergy generation. GC-MS analysis was implied for quantification of chemical compounds of bio-oil. GC-MS quantification of bio-oil obtained at optimum condition of 550 °C is depicted in Table 4.2 which summarizes peaks of chromatographs along with area% and retention time for particular compound. Results of GC-MS analysis revealed that bio-oil is a complex mixture consisting of numerous chemical compounds. The prominent class of chemicals prevailing in bio-oil include aldehydes, aliphatics, ketones, alcohols and phenols. These chemical compounds were formed due to decomposition of lignocellulosic content of MAS. Phenolic compounds like 2-Methoxy-4-methylphenol and phenol were formed due to lignin content of MAS (Yorgun and Yildiz, 2015). Hemicellulose and cellulose part of MAS was accountable for oxygenated chemical compounds. Presence of high phenol and other phenolic chemical species result in high value of HHV. Although, enhancement in bio-oil quality and its heating value could be accomplished by upgradation of bio-oil by catalytic route. Pyrolytic bio-oil with high portion of phenols can be utilized for various chemical extractions. The aliphatic and aromatic hydrocarbons present in bio-oil are favourable for its application towards transport fuels. Bio-oil can also serve as a source of various bio-based chemical compounds owing to the fact that it contains a large number of valuable chemical compounds. Upgraded bio-oil can be blended with conventional fuels besides the recovery of valuable chemicals from it.

Table 4.2. GC–MS analysis of bio-oil obtained at 550 °C

Peak no.	**Retention time (min)**	**Compound Name**	**Molecular formula**	**Area (%)**
1	8.463	Bicyclo[2.2.1]heptan-1-ol	$C_7H_{12}O$	1.638
2	14.474	12-heptadecyn-1-ol	$C_{17}H_{32}O$	0.653
3	15.210	Phenol	C_6H_6O	1.267
4	17.224	Alpha-hydroxy-p-cresol	$C_7H_8O_2$	0.550
5	17.382	2,4,4-Trimethylecyclopente-3-one	$C_8H_{12}O$	9.103
6	17.996	3-(3’butenyl)cyclohexanone	$C_{10}H_{16}O$	1.034
7	19.216	2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	8.864

8	20.521	3-Hexadecylfuran	$C_{20}H_{36}O$	5.314
9	22.087	Hexylresorcinol	$C_{12}H_{18}O_2$	0.638
10	22.858	Methyl 13-octadecenoate	$C_{19}H_{36}O_2$	5.957
11	23.452	3-tert-Butylcatechol	$C_{10}H_{14}O_2$	3.023
12	24.191	Homovanilly alcohol	$C_9H_{12}O_3$	0.469
13	24.622	Furelic acid	$C_{10}H_{10}O_4$	1.585
14	25.327	2-Ally-4,6-dimethoxyphenol	$C_{11}H_{14}O_3$	0.453
15	25.499	2-Methoxy-4-propyl	$C_{10}H_{14}O_2$	1.472
16	25.926	4-tert-Butylcatechol	$C_{12}H_{18}O_2$	1.108
17	26.702	2-methoxy-4-propyl-phenol		6.073
18	30.751	7-Methyl-9,10-anthraquinone 1-carboxylic acid	$C_{16}H_{10}O_4$	1.650
19	36.721	10,11-(3',6'-Dimethylbenzo) [3.2] paracyclophane	$C_{23}H_{22}$	0.359
20	38.635	2-methoxy-4-(methoxymethyl)-phenol	$C_9H_{12}O_3$	2.170

4.3.2.8 Physicochemical characteristics of bio-oil

Table 4.3 summarises the physicochemical properties of bio-oil obtained at various pyrolysis parameters. Bio-oil exhibited a pungent odour accompanied by a cocoa-tinged appearance. Water content of bio-oil ranged from 49.7 to 57.13 wt.%. Water content of bio-oil decreased with increase in temperature. Similar trend was noticed by Muley et al., (2015) for pine sawdust bio-oil (Muley et al., 2015). The density of bio-oil increased from 1069.8 to 1095.8 kg/m^3 as temperature increased from 450 to 600 °C. Carbon residue decreased from 6.4 to 4 wt.% as temperature was raised from 450 to 600 °C. Low viscosity provides better flowing properties. As pyrolysis temperature was increased from 450 to 600 °C, viscosity increased from 2.15 to 2.73 cP due to occurrence of high polymerization reactions at high temperature. Zheng and Kong (2010) also reported increase of viscosity of pyrolytic bio-oil obtained from rice husk on increasing temperature (Zheng and Kong, 2010). pH of bio-oil ranged between 2.41 and 2.66 because it comprised of organic acids such as carboxylic acid and acetic acid in it. pH increased on increasing temperature because of decrease in the amount of organic acids in the bio-oil with increasing temperature. It is likely that acid compounds reacted by reactions like esterification and transesterification which produced water and long ester chains and that was in accordance with the higher water content in bio-oil. Similar observations were made for pH of *Acacia* sawdust bio-oil (increased from 2.9 to 3.4) on increasing temperature from 400 to 600 °C (Ahmed et al., 2020).

Table 4.3. Physicochemical properties of bio-oil

Property	**BO-450**	**BO-500**	**BO-550**	**BO-600**
Density (kg/m^3)	1069.8	1077.2	1084.3	1095.8
Viscosity (cP) at 25 °C	2.15	2.31	2.66	2.73
Water content (wt.%)	57.13	55.86	52.31	49.7
pH	2.41	2.63	2.59	2.66
Carbon residue (wt.%)	6.7	5.8	4.3	4
HHV (MJ/kg)	14.9	18.13	23.4	25.6

HHV of bio-oil increased to 25.6 from 14.9 MJ/kg when temperature was increased from 450 to 600 °C. A similar trend of increasing HHV with rising temperature was reported for bio-oil of *Acacia* sawdust (Ahmed et al., 2020). This could be due to decrease of oxygenated compounds in bio-oil with increase in temperature. HHV could be further increased by upgrading of bio-oil. Upgraded bio-oil exhibits enhanced characteristics which make it suitable to be blended with conventional transportation fuels and other high-value added applications.

4.4 Conclusions

Pyrolysis of MAS was holistically and comprehensively examined to evaluate effect of operating parameters on pyrolysis products' yield. As per the findings of this study on the effect of operating parameters (pyrolysis temperature, flow rate of sweeping gas, packed bed height, particle size of biomass, heating rate and pyrolysis time), pyrolysis of MAS is best suited to be carried out at 550 °C, 150 mL/min nitrogen flow rate, 8.4 cm bed height and particle size in the range of 0.18-0.29 mm at a heating rate of 20 °C/min coupled with 60 min pyrolysis time. Highest quantity of bio-oil was produced corresponding to these values of operating parameters. These values of operating parameters provided adequate heat and mass transfer for breakdown of MAS into condensable volatile hydrocarbon compounds inhibiting over breakdown of MAS into gaseous products. In bio-oil aliphatic, olefinic and aromatic compounds like alcohol, ketone, alkyl and aryl were confirmed by FTIR, GC-MS and ^{1}H NMR analysis, indicating its potential as chemical feedstock. Bio-char was analysed by proximate, ultimate, HHV, energy yield, XRD, BET, FTIR and SEM. Bio-char exhibited huge specific surface area, profuse microscopic porous crystallographic structure with lots of open channels in it, therefore it can be used as an adsorbent for wastewater treatment, precursor for developing activated carbon, for preparation of porous carbon materials etc. From this work it can be inferred that pyrolysis of MAS is a pragmatic approach for generation of energy and waste management. These features of MAS pyrolysis make it suitable for strengthening energy self-sufficiency.