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ORIGINAL ARTICLE

Unlocking the potential of biochar derived from coffee husk and khat stem for catalytic tar cracking during biomass pyrolysis: characterization and evaluation

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Abstract

Biochar has the potential to catalyze and accelerate the decomposition process during biomass pyrolysis and tar cracking. However, limited research has been done so far on its suitability as a catalyst. This study aims to characterize the properties of biochar produced from coffee husks (BCH) and khat stems (BKS) at various pyrolysis temperatures (350 °C, 450 °C, 550 °C, and 700 °C) and evaluate their potential application as catalyst for tar cracking in biofuel production. Coffee husk (CH) and khat stem (KS) were selected as feedstocks due to their high potential availability in Ethiopia. The physicochemical characteristics of the biochar materials were analyzed using a range of techniques, including thermogravimetry analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), and Fourier transform infrared (FTIR). The findings revealed that the yield of biochar decreased as the pyrolysis temperature increased for both CH and KS. The biochar exhibited a microstructure with a large specific surface area (SSA) and a porous structure rich in functional groups (O–H, C-H, C = C, C-O, and C–O–C), as well as the presence of inorganic minerals (Na, Cl, Mg, P, Fe, Al, K, and Ca). The XRD and TGA results indicated that the biochar samples were amorphous and thermally stable. The SEM and BET analysis showed changes in surface area and porosity with varying temperatures. In view of this, the present work suggests that biochar with diverse characteristics can be produced by adjusting the pyrolysis environment to suit the intended applications. Hence, CH and KS can be converted into biochar to increase the economic benefits and improve biochar-based catalyst properties for commercial purposes.

Keywords Biochar · Biochar-based catalysts · Catalyst · Pyrolysis · Tar cracking

1 Introduction

Nowadays, energy scarcities and environmental pollution are the most considerable global challenges [1]. The spontaneous exploitation of limited reserves of fossil fuel hydrocarbons has generated a worldwide increase in greenhouse gas releases, primarily of CO_2, CH_4, and other NO_x. This has also prompted a move toward alternative energy sources to reduce the effects of climate change and minimize reliance on finite resources [2]. Reducing dependence on fossil fuels and boosting the share of renewable sources is paramount to realizing net-zero global emissions by 2050 [3]. Lignocellulosic biomass, a renewable resource, is a carbon–neutral complement to fossil fuels and provides a sustainable alternative to conventional fuels and other chemical products [4]. Lignocellulosic biomass can be converted into high-quality biofuel via diverse technologies, including biochemical and thermochemical conversion [5]. Thermochemical conversion approaches represent one of the most favorable and current ways to transpose biomass into more usable and cleaner fuels [4]. Pyrolysis and gasification are the most relevant thermochemical conversion practices

Highlights

- Agricultural residues of CH and KS were used to prepare biochar.
- Biochar catalyzes to upgrade biomass into biofuels.
- The effectiveness of biochar as a catalyst is determined by mineral content/SA/and pore volume.
- Biochar surface functionality impacts catalytic performance.
- At higher temperatures, higher thermal stability biochar is produced.
- Biomass valorization drives sustainability and enables circularity.

Extended author information available on the last page of the article employed to transform biomass to condensable liquid (tar), a solid product (biochar), and gaseous products comprising CO_2, CO, H_2, and CH_4, called syngas [4, 6, 7]. To this end, biofuels derived from biomass have been projected to substitute up to 27% of global transportation fuel by 2050, cutting GHG production by up to 3.7 billion metric tons annually [5]. Moreover, biochar from biomass can generate a significant amount of biodiesel (32.8 to 97.75%) and contribute to catalytic methane decomposition and dry methane transition, with hydrogen decomposition rates ranging from 13.4 to 95.7% [5].

Pyrolysis processes produce pollutants and other precursors like fly ash, NO_x, SO_2 high molecular tars, and alkali metals [8]. Tar formation is a major challenge in pyrolysis and gasification, limiting the commercialization of the technologies [9]. Tars largely hinder the use and applications of bio-oil or syngas as commercial fuels [10]. Tars condense quickly at lower temperatures, leading to operational and environmental issues like pipeline blockages and excessive gas release [8]. The molecular weight of tar is higher than hydrocarbons larger than benzene (C_6H_6), produced during biomass pyrolysis or gasification [11, 12]. Tars, including pyridine, toluene, and naphthalene, are essential components in biofuel production [13]. To minimize their limitations, tar should be cracked or eliminated. Conventional cracking methods are used for cleaning and upgrading biofuels [14]. Heterogeneous in situ and ex situ catalysis is crucial for addressing higher tar concentration challenges [15]. Furthermore, catalytic upgrading can significantly improve biofuels with negative qualities like low heating value, excessive oxygen content, and poor thermal stability [15]. The appropriate catalysts for tar cracking can also highly minimize corrosivity and improve tar conversion efficiency [16]. Materials like Al_2O_3, SiO_2 zeolites, transition metals, dolomite, olivine, and alkali metal-based materials are commonly used due to their high catalytic activity and resistance to deactivation [17, 18]. Nickel-based catalysts are also popular due to their cost and high catalytic activity [18]. However, the quick deactivation of these catalysts due to coke accumulation is a challenge [18]. Biochar, derived from biomass, has unique advantages such as high surface area, oxygen-containing functional groups, and higher mineral contents [19]. Switchgrass biochar activated with KOH showed the best performance in removing toluene [20]. Biochar catalysts also boost syngas production during biomass pyrolysis from 15 to 46 wt.% at 480 °C [21]. Moreover, the exploitation of biochar as a catalyst has the advantage of being sustainable and providing renewable chemicals, thus offering an environmentally sustainable strategy [22].

Biochar is a pyrogenic carbon-enriched material derived from the pyrolysis/gasification of lignocellulosic biomass [23], such as from agricultural product residues, wood biomass, municipal solid waste (MSW), and forestry residues [24], in the presence of an inert atmosphere or with an inadequate amount of oxygen/air. The conventional method for producing biochar is pyrolysis [25]. The relative proportions of products produced from these processes vary widely depending on the precursor feedstock and the pyrolysis conditions [25]. A low temperature and low heating rate process are preferable for producing a higher amount of biochar from biomass pyrolysis [16]. Biochar possesses many desirable properties that offer multiple functionalities. However, it is not a cure-all solution and requires a much broader and comprehensive characterization approach. The presence of inorganic species, chemical hierarchy, mechanical stability, strong thermal resistance, and stable structure are some of the important characteristics of biochar that contribute to its effectiveness as a catalyst [15]. Biochar-based catalysts also possess unique characteristics such as heterogeneity, bifunctionality, recyclability, porosity, and non-graphitizability [26]. Early research has thoroughly reviewed and explored various properties of biochar that can be modified to make them versatile materials with multiple useful applications. They can be utilized for environmental and climate change mitigation, enhancing agricultural soil quality [27, 28], carbon sequestration, carbon capture and storage [23], renewable fuel [28], wastewater treatment [29], fuel cells and supercapacitors [26], heavy metal adsorption [30], and additive materials [31].

However, biochar derived from agricultural biomass has the potential to be used as a multipurpose catalyst for catalytic functionalities [23, 26]. Biochar with improved pore structure, rich surface area, and oxygen-containing functional groups has a positive impact on biomass tar cracking/removal [11]. Compared to conventional solid-based catalysts, biochar-based catalysts have the potential to be less expensive, easy to produce, more environmentally friendly, recyclable, and biodegradable [15, 26]. Moreover, the most suitable biochar-based catalysts are determined by the reaction and process conditions of the pyrolysis process. The most commonly used lignocellulosic biochar catalysts are noble metals, zeolites, iron, and cobalt [32]. The content of inorganic minerals such as Ca, K, Si, Mg, Mn, and Fe also contributes to biochar catalytic activity for tar cracking [15]. The physicochemical attributes of biochar, such as pH, specific surface area, pore volume, pore size distribution, volatile matter, ash composition, and surface functional groups [6, 33], can be affected by pyrolysis conditions and biomass sample composition [34]. Previous research has shown encouraging progress on the catalytic properties of biochar derived from various biomass sources in tar cracking [9, 20, 35]. Guo et al. [36] produced three different types of activated biochar catalysts from rice husk that were utilized in tar catalytic cracking with different activators (KOH, H_3PO_4, and $ZnCl_2$). The result provides a considerable increase in the amount of CO_2, CO, H_2, and CH_4 gas. Guo et al. [37] also demonstrated high syngas output by converting bigger polycyclic aromatic hydrocarbons with conversion efficiencies of up to 92.6% at 800 °C into lighter tar using char-supported catalysts. Similarly, Zhang et al. [38] also used Ni/PWC (pine wood pyrolysis char) and Ni/PWA (pine wood activated char) as catalysts, with a tar removal rate of 92.6 wt.%, and phenolic and PAH compounds in tar were removed.

High pyrolysis temperatures contribute to the production of biochar with a substantially enhanced surface area, high porosity, and high pH, as well as higher ash content and fixed carbon, but with a low volatile matter content [26]. Due to a substantial amount of organic matter decomposition in the process [33], biochar has the potential to be a highly robust catalyst and/or catalyst support in a broad spectrum of chemical processes owing to its unique chemical structure, which makes it easy to produce by activation and/or functionalization. Biochar also has a large surface area and surface functional groups [4]. Typically, it has a surface area of 8 to 132 m^2/g and a total pore volume of 0.016 to 0.083 cm^3/g. With the appropriate precursor and pyrolysis conditions, biochar can reach pore volumes and surface areas of up to 0.25 cm^3/g and 490.8 m^2/g, respectively [32]. However, other investigations suggested that the catalytic efficiency is influenced by initial concentration, dose rate, pH, pyrolysis temperature, and composition of parent biomass [32]. To meet the tar cracking requirements, the physiochemical properties of the biochar derived from different feedstocks (coffee husk (CH) and khat stem (KS)) and pyrolysis temperatures need to be fully characterized and evaluated.

Although various studies are reported on the potential utilization of biochar for various functionalities, to the author's knowledge no attempt was made to investigate the characterization and potential suitability of the biochar produced from agricultural biomass sources such as CH and KS for tar cracking during the pyrolysis process. Furthermore, a comprehensive understanding of the synthesis, advancement, and cutting-edge uses of catalysts based on biochar is still lacking. Thus, this work intends to analyze and characterize the biochar properties formed at four different temperatures from CH and KS (350, 450, 550, and 700 °C). Various analytical techniques such as proximate analysis values, scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, and the thermal stability of the biochar were also done using thermogravimetric analysis (TGA). Similarly, novel evidence is presented for the potential use of the biochar produced from both materials as catalysts during the pyrolysis of the feedstocks at an industrial scale.

2 Materials and methods

2.1 Sample collection and preparation

Due to its heterogeneity, biomass samples are required to be prepared using conventional techniques and pre-treated [39]. In Ethiopia, samples of coffee husk and khat stem are collected from two distinct sources. The deliberate choice of the samples as biomass sources was based on their abundance and accessibility, particularly in Ethiopia [40]. The khat stem was collected from Jimma City, which is in the southwest of Oromia at a latitude and longitude of 7°40′N, 36°50′E. Coffee husk was collected from Bonga City, which is located at 7°16′N, 36°14′E, southwest of Jimma. For 5–7 days, the samples are dried to lower the moisture content on the surface of the raw biomass as shown in Fig. 1 and to enhance the pyrolysis efficiency [41].

The elemental composition and proximate analysis results of the raw biomass samples are presented in Table S1 of the supplement material. Before the experiments, the raw biomass sample was dried in an oven at a temperature of 105 °C to reduce the moisture content to a negligible level. Subsequently, the raw sample underwent sieving, and only particles smaller than 500 μm were utilized for the experiments. The results are also reported in our previous paper [40]. These results provide valuable insights into the characteristics of the raw materials before any further processing or applications.

2.2 Experimental setup and biochar production

This work produced biochar from CH and KS using a batch-type fixed-bed reactor. The reactor was equipped with a digital microcontroller and a residence time paddle for slow stirring. Bricks were used as insulation to reduce heat exchange with the atmosphere. The slow pyrolysis process was carried

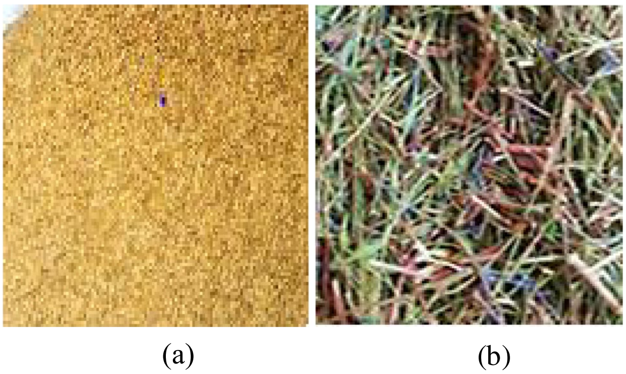

Fig. 1 Original raw biomasses. Coffee husk (**a**) and khat stem (**b**) sample preparation and drying stage

out at different temperatures (350, 450, 550, and 700 °C) and at 4 h residence time. After the pyrolysis, the biochar sample was allowed to cool to ambient temperature for 3 h to ensure stability and diffuse any remaining volatile gases. The weight of the samples and the biochar was determined using an electronic balance, and the weight percentage of the biochar (Eq. 1) was used to determine the ratio of biochar mass (kg) to initial feedstock mass (kg). Fig. S1 in the supplementary material provides a schematic illustration of the experimental setup.

$$\text{Yield }(\%) = \frac{\text{mass of biochar (kg)}}{\text{the initial mass of the feedsctock (kg)}} \times 100 \tag{1}$$

The biochar samples obtained were labeled as BCH350, BCH450, BCH550, and BCH700 for the biochar produced from CH and BKS350, BKS450, BKS550, and BKS700 for biochar produced from KS, respectively. The biochar samples were named after their feedstock and respective temperatures. For example, the biochar prepared from the coffee husk is named BCH, and that pyrolyzed at 350 °C was named BCH350. All biochar measured were milled and passed through a 0.5 mm sieve (80 meshes) and then stored under controlled conditions of temperature and humidity for further analysis and characterization.

2.3 Biochar characterization methods

Biochar characterization evaluates the characteristics and potential applications of biochar materials. However, maintaining economic feasibility is a major challenge in the widespread implementation of biochar for commercial-scale applications. To evaluate the physicochemical characteristics, different characterization techniques employed in these investigations include SEM, FTIR, XRD, BET, XRF, TGA, proximal and ultimate analysis, and pH measurement. Fig. S2 in the supplementary material exhibits the integral conversion technology, experimental setup, characterization methods, and biochar applications.

2.3.1 Biochar chemical properties

The proximate analysis was used to determine the moisture content, volatile matter, fixed carbon, and ash content of the biochar samples. The ASTM standard techniques D1102, E871, and E872 were employed to measure the contents for ash, moisture content, and volatile matter analysis [40]. The ASTM E711 technique was used to measure the calorific value of the samples in an adiabatic bomb calorimeter [40]. Nhuchhen [42] presented an empirical correlation available in the supplementary material to determine the elemental composition (carbon, hydrogen, and oxygen) of the torrefied biomass samples from the proximate data. The pH value was determined through the mixture of biochar with deionized water with a 1:20 (weight/volume) ratio and agitating the mixture with a magnetic stirrer for 0.5 h at 25 °C. After a 30-min settling period, the samples' pH was measured twice using a German-made pH 3310 set 2 pH measuring apparatus. The components that are present in the ash composition in oxide form and their respective concentrations can be determined using a variety of techniques. X-ray fluorescence (XRF) spectroscopy is among the simplest method used in this work.

2.3.2 Biochar physical properties

The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface areas, pore volume, and pore size distribution of the biochar samples in duplicates. To optimize specific applications, 0.05 g of each sample was put to the test for nitrogen gas adsorption at 77.35 K and then degassed at 300 °C for 8.0 h to eliminate impurities and residual gas [43]. The surface morphology of the biochar samples at various temperatures was examined using a scanning electron microscope (SEM). SEM photomicrographs of biochar particles were obtained by placing them on an aluminum sample piece with equal dispersion on conductive carbon tape. Helium was utilized to prevent the samples from becoming charged, allowing for relatively high magnifications.

The phases and structural characteristics of the biochar can be assessed using the widely used X-ray diffraction (XRD) technique [44]. An X-ray source of Cu-Kα (3 kW) with a scanning rate capacity of 0.0012–70° per minute was used to conduct XRD testing with a Drawell XRD 7000. With Cu-Kα radiation ($\lambda = 1.5405$ Å) operating at 30 kV and 25 mA, the X-ray diffraction spectroscopy was used to capture the XRD pattern with a resolution of 0.01 over an angle range of $5° \leq 2\theta \leq 80°$. The Fourier transform infrared (FTIR) spectral peak positions indicate the available functional groups present on the biochar surface. It also quantifies the intensity of chemical bonding within the materials as a function of temperature [45]. The samples were measured in the 4000–400 cm^{-1} range, with 32 accumulations, at a resolution of 4 cm^{-1}. Adding powdered biochar samples with potassium bromide and pressing them into pellets is a common procedure to prepare the sample for test. Thermogravimetric analysis (TGA) was used to evaluate the thermal stability and decomposition behavior of biochar samples. The study used a NETZSCH STA 409 PC/PG simultaneous DSC-TGA thermogravimetric analyzer to analyze biochar samples under both air and argon atmospheres. About 15 mg of homogeneous samples was used to ensure uniform heating and minimize challenges during thermal decomposition. The experiments were conducted within a temperature range of 30–850 °C and in an alumina container at a heating rate of

20 °C/min. To reduce experimental uncertainties, all measurements were taken twice.

3 Results and discussion

3.1 Effect of temperature on biochar yield

The pyrolysis conditions, such as temperature and residence time, have a substantial effect on biochar production yield [28]. Biochar yield obtained at different pyrolysis temperatures (350, 450, 550, and 700 °C) for BCH and BKS is presented in Fig. 2. The results revealed that an increase in temperature triggered changes in the yield of biochar [46]. The results also showed that the yield for both BCH and BKS decreased when the pyrolysis temperature increased, with a minimum yield of 25.67% for BCH and 26.15% recorded at 700 °C and a maximum yield of 48.73% for BCH and 41.54% for BKS at 350 °C, respectively. This was perhaps due to the initial decomposition of the biomass samples [47] or through the secondary decomposition of the biochar itself [48], since more volatile contents were being released from the biomass sample at higher temperatures reducing yield [46]. Consequently, a lower pyrolysis temperature is more beneficial for obtaining higher biochar yield; however, the temperature must be high enough to promote the complete pyrolysis of biomass into biochar [47]. However, if the temperature is excessively high, carbon and other functional group components on the surface of the biochar are lost in large amounts [28]. The pyrolysis temperature also influences the chemical composition, pH, thermal stability, and heavy metal fate of the biochar [49]. Agricultural residues consistently produced higher biochar compared to wood, which can be attributed to higher lignin content or the presence of substantial amounts of inorganic matter that promote charring reactions. These results also align with previous literature [46].

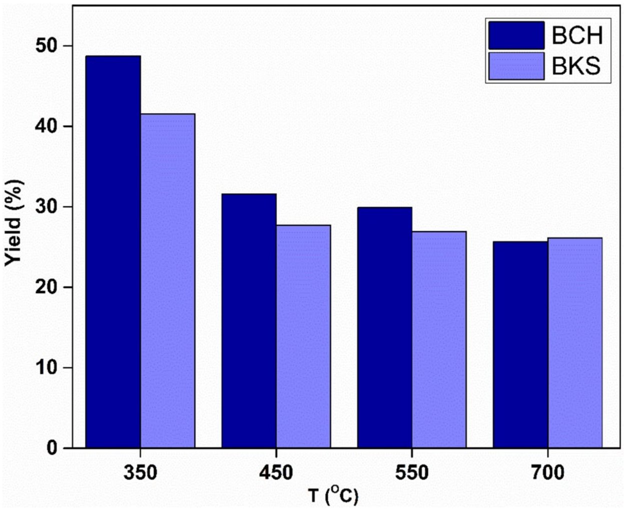

Fig. 2 Biochar yield (%) produced at different temperatures (350, 450, 550, and 700 °C)

3.2 Effect of temperature on chemical characteristics of biochar

The chemical properties of the biochar obtained at various pyrolysis temperatures of 350, 450, 550, and 700 °C are exhibited in Table 1 and Fig. S3 in the supplementary file. Proximate analysis of the biochar indicates that coffee husk has a higher fixed carbon (66.19 wt.%), lower volatile (17.52 wt.%), and lower ash (11.23 wt.%) content compared to biochar produced from khat stem (fixed carbon 48.47 wt.%, volatile 33.01 wt.%, higher ash 12.66 wt.%) at the lower temperature of 350 °C. Previously, comparable proximate results have been reported for coffee husk [46]. Based on the proximate analysis results in Table 1, BCH and BKS produced at temperatures ranging from 350 to 700 °C have low MC and ash content. MC was < 5 wt.% for both BCH and BKS, whereas the ash content was < 15 wt.% for BCH and < 23 wt.% for BKS. Conversely, BKS has a higher VM content (33.01–15.45 wt.%) compared to BCH (17.52–15.30 wt.%). The HHV of biochar yielded at 350, 450, 550, and 700 °C can confirm the characteristics of biochar with the highest affinity of slagging, revealing that biochar could also be used as a source of energy [41]. The HHV [MJ/kg] differences of the biochar samples were very minimal, and the

Table 1 Proximate analysis (%) of biochar produced at different pyrolysis temperatures, including pH levels, and HHV

Biomass samples	Biochar	MC [%]	VM [%]	FC [%]	ASH [%]	HHV [MJ/kg]	pH
Coffee husk (CH)	BCH350	5.06	17.52	66.19	11.23	25.25	7.98
	BCH450	3.05	18.85	64.59	13.51	25.24	9.95
	BCH550	2.84	16.56	68.48	12.07	26.31	10.01
	BCH700	2.01	15.3	69.94	15.03	25.58	10.47
Khat stem (KS)	BKS350	5.86	33.01	48.47	12.66	22.15	8.57
	BKS450	5.00	23.56	51.34	19.61	19.81	9.82
	BKS550	4.62	18.23	55.14	22.01	19.91	10.48
	BKS700	3.89	15.45	57.13	23.52	22.30	10.83

HHV values showed similarities with other investigations [41, 50].

Biochar produced from CH and KS have FC ranging from 66.19 to 69.94 wt.% for BCH and 48.47 to 57.13 wt.% for BKS, respectively. The rise in pyrolysis temperature shows a slight reduction in VM, revealing a comparable tendency with the biochar yield, while a reverse trend was practiced for the FC [51]. Perhaps instead of producing biochar, higher temperatures allowed the volatile components to further decompose into low molecular weight liquids and gases [47, 48]. Meanwhile, the dehydration of hydroxyl groups and thermal conversion of cellulose and lignin might also occur with increased temperature [41]. These results have proven that the increase in temperature increased the stability of biochar for the loss of volatile fractions [52] and the loss of hydroxyl groups [41]. Additionally, the results of this investigation indicate that feedstock composition has a greater effect on the mineral element content of biochar than temperatures during decomposition. Overall, the results are also consistent with the TGA results shown in the subsequent section.

Furthermore, the biochar pH values varied from 7.98 to an extremely alkaline 10.83 value. The findings also demonstrate that the pH values of the biochar samples in Table 1 increased with increasing pyrolysis temperature [53]. The pH of the biochar increased with temperature, presumably because of non-pyrolyzed inorganic components in the initial raw materials [54]. The pH of biochar is probably related to the occurrence of oxygen-containing functional groups and the quantity of cellulose, hemicelluloses, or lignin it contains. Moreover, at higher pyrolysis temperatures, the biochar's ash content and relative increase also contribute to the pH increases [55].

The ultimate analysis of the biochar revealed that slow pyrolysis increases the carbon content in the biochar while reducing hydrogen and oxygen contents. This result also reasonably matches with the previous literature since pyrolysis releases most of the non-carbon elements particularly H and O in the form of gases and tars [54]. The concentration of carbon (wt.%) produced from CH at different temperatures exceeded 65 wt.%, while that of KS exceeded 54 wt.% and reached the highest value at 700 °C. Furthermore, with increase in pyrolysis temperature, the H/C and O/C ratios in Table 2 are reduced because of the evaporation of moisture content (dehydration) and decarboxylation reactions, indicating increasing aromaticity and a lower hydrophilic tendency [56], where the higher ratio of O/C at the lower temperature is also an indication of the existence of carboxyl, hydroxyl, and carbonyl on the surface of the biochar [57].

The effectiveness of cracking tar using biochar as a catalyst is due to the richness of inorganic elements like Ca, K, Na, Mg, and Fe, which act as catalysts for the decomposition of tar compounds [26]. These elements are vital for many catalytic products, including tar cracking, methane decomposition, and bio-oil upgrading [19]. However, the nature of the feedstock material significantly impacts the quantity and composition of inorganic constituents found in biochar [26]. Techniques like X-ray fluorescence (XRF) spectroscopy can determine the availability and relative quantities of these elements. The analysis reveals that the concentration of inorganic components in biomass materials enhances ash content, with some minerals being highly active in catalytically cracking tars, reducing tar content during the process. Calcium oxide (CaO) has been proven to be an effective and economical in situ catalyst in biomass pyrolysis or gasification, improving the quality of hydrogen products from biofuel. Ultimately, tar cracking could result in increased yield and quality. Based on the XRF analysis, some of the most important elements in their oxide forms are SiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O, and P_2O_5 for both biochar materials. The results exhibited valuable mineralogical components of biochar. A corresponding deviation in concentration (%) was witnessed during the changes in the pyrolysis temperature [41]. Table S2 in the supplementary material provides the ash composition results for both materials.

3.3 Effect of temperature on physical characteristics of biochar

Figures 3 and 4 show the secondary electron scanning microscopy (SEM) images of the biochar obtained from CH and KS at different pyrolysis temperatures. The SEM images

Table 2 Elemental composition (%) of biochar derived from CH and KS at diverse pyrolysis temperatures

Biomass samples	Biochar	C [%]	H_2 [%]	O_2 [%]	H/C	O/C
Coffee husk (CH)	BCH350	67.966	4.410	20.737	0.064	0.305
	BCH450	68.608	2.511	16.890	0.036	0.246
	BCH550	71.539	1.886	15.399	0.026	0.215
	BCH700	76.468	0.070	7.666	0.001	0.100
Khat stem (KS)	BKS350	54.843	5.553	30.339	0.101	0.553
	BKS450	56.635	5.699	24.609	0.100	0.434
	BKS550	58.354	4.908	19.929	0.084	0.341
	BKS700	59.346	4.347	16.890	0.073	0.284

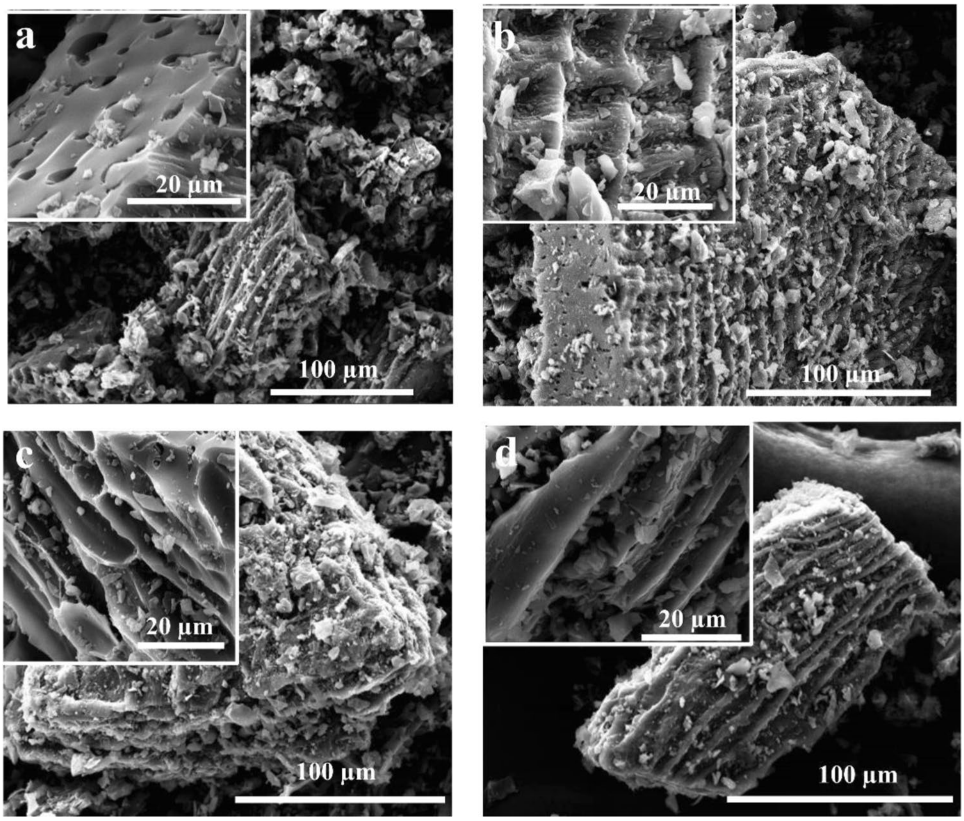

Fig. 3 Secondary electron scanning electron microscopy (SEM) images of the biochar obtained from coffee husk (BCH) at various pyrolysis temperatures **a** 350 °C, **b** 450 °C, **c** 550 °C, and **d** 700 °C

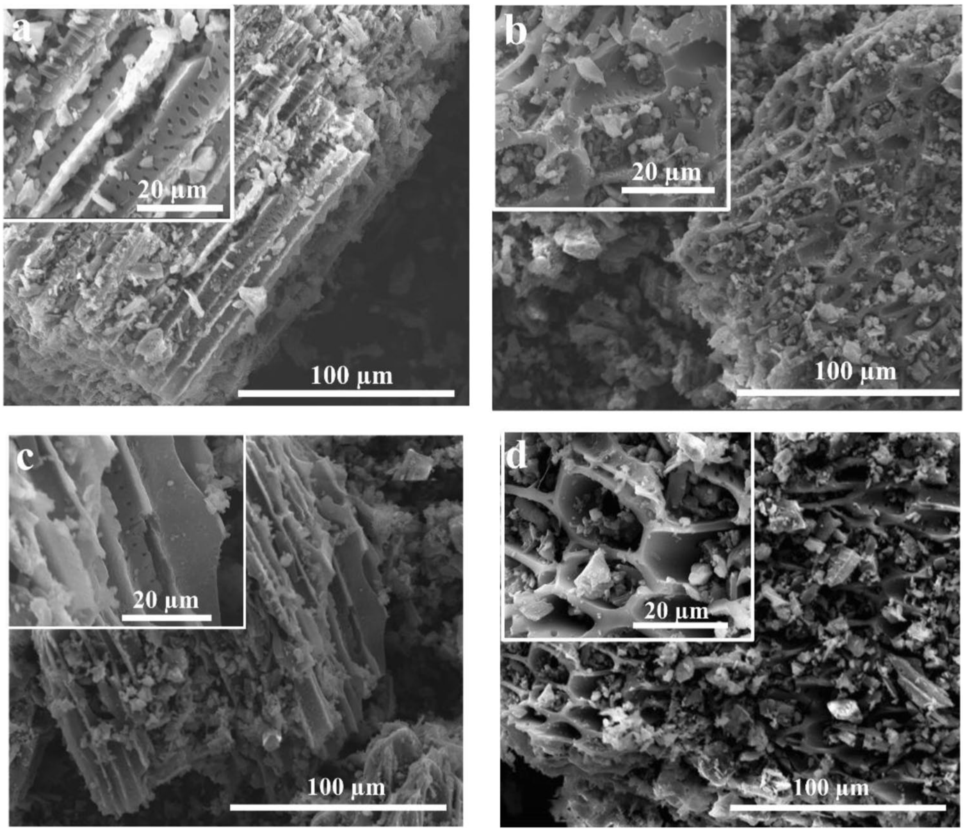

Fig. 4 Secondary electron scanning electron microscopy (SEM) images of the biochar obtained from khat stem (BKS) at various pyrolysis temperatures **a** 350 °C, **b** 450 °C, **c** 550 °C, and **d** 700 °C

were presented to visually display the change in the pore surface structure of biochar obtained at various temperatures. They revealed that the surface structure of the biochar changes with temperature. Figures 3a–d and 4a–d also show the micrographs at higher and lower resolutions for the different pyrolysis temperatures (350, 450, 550, and 700 °C). The microstructure of the biochar is highly affected by the temperatures and process parameters, which leads to variation in the pore surface structure [58]. Previous research also indicates that biochar produced below 450 °C has a limited porous structure due to the presence of organic and volatile chemicals that block the pores and reduce the adsorption potential [59]. On the other hand, Fig. 3c, d for BCH and Fig. 4c, d for BKS show how at higher temperatures a porous structure with large holes and cracks are developed. This is explained by thermal cracking and the breakdown of biomass components [60]. Moreover, low molecular weight volatiles decompose at higher pyrolysis temperatures, forming deeper and bigger pores that increase pore volume and surface area [58]. The pore and surface area increase due to increasing organic material volatilization, resulting in a porous structure. However, prolonged volatilization widens pores and reduces the surface area beyond certain temperatures [61]. In addition, the biomass melts, softens, and combines to form a mass of capsule-like structures, as observed in the images of Fig. 3a for BCH and Fig. 4a for BKS. The production of volatile gases contributes to the formation of vascular bundles or channel structures [33]. As temperatures increase, more volatile gases are released from the biomass, causing cracks to form on the surface of Fig. 3b for BCH and Fig. 4b for BKS, resulting in a morphology with numerous pore structures. As more components decompose, the skeletal structures of Fig. 3c for BCH and Fig. 4c for BKS appear unstable. Lastly, for Fig. 3d for BCH and Fig. 4d for BKS, the final temperatures at which samples were collected, a cracking phenomenon is also observed within the pore structure [34].

The nature of raw biomass and the pyrolysis temperatures at which the biochar is produced greatly affect the amount and composition of inorganic elements present in the biochar samples [19]. The EDSscans provide qualitative and semi-quantitative information on the distinct species found on the surface of the biochar. In addition to the expected elements (C and O), Na, Cl, Mg, P, Fe, Al, K, and Ca were found in both biochar samples, as depicted in the map scans in Fig. 5. Figure 5 also reveals a slight difference in the peak intensities of K, Ca, Cl, Mg, P, Fe, Al, and Na between the biochar samples. In general, biochar samples were relatively rich in nutritional and mineral elements. Previous literature also reported that biochar is catalytically active in cracking tar because of its presence of inorganic elements including Fe and K [26].

The Brunauer–Emmett–Teller (BET) nitrogen gas physisorption method is commonly used to measure surface area at 77 K in the relative pressure range $P/P_O = 0.05–0.30$ [62]. The amount of nitrogen gas absorbed by a sample under vacuum is used to measure its surface area using the non-destructive BET method [62]. Table 3 shows the biochar samples' surface area, pore volume, and pore size. Understanding the surface area of biochar is essential to improve its effectiveness and possible applications. The results revealed that the BET surface area was found to be 139.90, 152.90, 180.80, and 149.80 $m^2\ g^{-1}$ for BKS at pyrolysis temperatures of 350, 450, 550, and 700 °C samples, respectively. The surface area recorded for BCH was 140.90, 148.10, 185.20, and 190.40 $m^2\ g^{-1}$, for the different pyrolysis temperatures of 350, 450, 550, and 700 °C, respectively. Both biochar materials revealed increments in surface area with

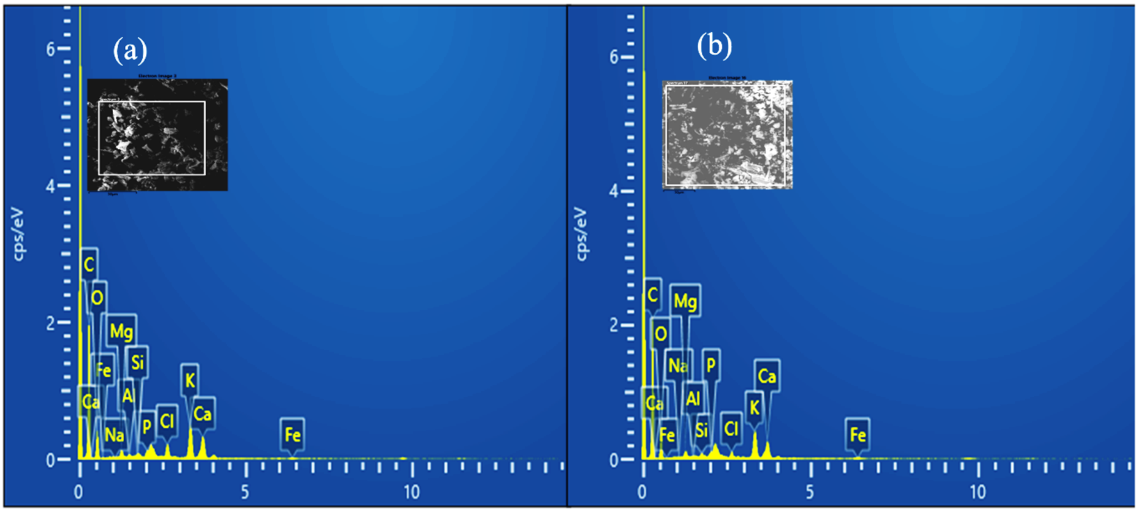

Fig. 5 Representative EDS area scans of **a** BCH and **b** BKS, respectively

Table 3 Morphological properties of the biochar samples

Feedstock	Biochar from coffee husk (bch)			Biochar from khat stem (bks)		
Temp. (°C)	Pore volume (cm^3/g)	Pore size (Å)	SA BET (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)	SA BET (m^2/g)
350	0.221	13.850	140.90	0.219	13.850	139.90
450	0.233	13.850	148.10	0.240	13.240	152.90
550	0.395	13.850	185.20	0.359	13.850	180.80
700	0.403	14.480	190.40	0.232	13.240	149.80

temperature; however, the changes could be marked by an optimum at a certain temperature beyond which a significant decline could be expected [63]. The surface area of the khat stem increased with rising pyrolysis temperature, but then slightly decreased or the changes were minimal at higher temperatures. This was also consistent with findings reported for biochar from corn stover (96, 284, 298, 288 m^2/g) and sugarcane bagasse (83, 221, 236, 240 m^2/g) at 500, 600, 700, and 800 °C, respectively [64]. In contrast, miscanthus and switchgrass exhibited an opposite trend, with a sudden increase in surface area as pyrolysis temperature increased from 500 to 600 °C, resulting in a surface area of 119 to 303 m^2/g for miscanthus and 115 to 290 m^2/g for switchgrass. These findings reported the surface areas for biochar from miscanthus (119, 303, 324, 316 m^2/g) and switchgrass (115, 290, 326, 311 m^2/g) at pyrolysis temperatures of 500, 600, 700, and 800 °C, respectively [64]. The reason is due to the temperature effect, slow pyrolysis of biochar production was not sufficient to bring spontaneous changes in the surface area of the biochar. The removal of volatile materials from the biomass surface forms holes in the subsequent biochar structure, providing the biochar with a larger surface area. The BCH at 700 °C and BKS at 550 °C produced the highest BET surface area for biochar samples. Moreover, it has been reported that micropores play a key role in the specific surface area [65].

As shown in Fig. 6, the FTIR spectra of the feedstocks (CH and KS) and the biochars (BCH and BKS) reveal the presence of various surface functional groups, including O–H, C-H, C = C, C-H, C-O, and C–O–C. These groups indicate the presence of aliphatic chains, aromatic structures, and oxygen-containing compounds [65, 66]. The structure of biochar components is nearly identical to the original biomass, extending from two peak positions (1064 cm^{-1} for KS and 1095 cm^{-1} for CH) [67]. This suggests that the decomposition of biomass during slow pyrolysis contributed to the incomplete conversion of the initial biomass to biochar [26, 60]. Figure 6 also presents the FTIR spectra of all biochar samples showing a broadband signal in the 3500–3300 cm^{-1} area, indicating O–H stretching and possibly hydroxyl groups, phenol, or moisture [65]. Regardless of the pyrolysis temperature, all biochar samples have a comparable OH group [65]. Higher temperatures during biochar production cause an abundance of aromatic compounds such as carboxyl (–COO–) and hydroxyl (–OH), to evaporate due to decarboxylation, demethanation, and dehydrogenation [68]. As also seen in Fig. 6, the intensity of the hydroxyl peak varies slightly due to the loss of hydroxyl groups, declining as temperatures increase from 350 to 700 °C [69]. The FTIR spectra of the biochar products with respective available functional groups and peak points are also presented in the supplementary file (Table S3). The catalytic performance in cracking tar is influenced by the presence of functional groups containing oxygen, which facilitate the cracking of high molecular tar and lead to more effective removal [9]. The slowest phase in catalytic reformation using biochar as a catalyst is the formation of tar radicals over these O-containing functional groups [9].

Furthermore, biochar samples contain various functional groups, including carboxyl (C = O) stretching (1600–1500 cm^{-1}), aromatic C–C stretching (2800–2750 cm^{-1}), C-H alkanes (2750–2700 cm^{-1}), and several aromatic C-H ring forms at 1400–1300 cm^{-1} and 800–700 cm^{-1}, respectively. As the reaction progresses, some peaks disappear, while C-H peaks become more aromatic and less aliphatic, representing aromatic carbon mixes [65, 67]. FTIR spectra (Fig. 6) show the presence of oxygenated hydrocarbon-typical functional groups predominate in biochar, consistent with the carbohydrate structure of cellulose and hemicelluloses. At higher temperatures, graphite-like structures develop, confirming the existence of less intense peaks [67].

Figure 7a, b exhibits the X-ray diffraction (XRD) patterns revealing the crystalline and amorphous structure of biochar derived from coffee husk (BCH) and khat stem (BKS) at different temperatures. All biochar samples had comparable structures, with a primarily amorphous structure. Natural cellulose is responsible for the diffraction peaks at $2\theta = 24.4–26.10°$ for BKS and 23.93–24.98° for BCH [70]. The severe d-spacing in the biochar XRD peaks is due to the presence of unconverted cellulose and -OH, C = C, and C-O groups [71]. The XRD investigation for wood-derived biochar samples also shows comparable patterns, despite the absence of crystalline phases in the sample [59]. This

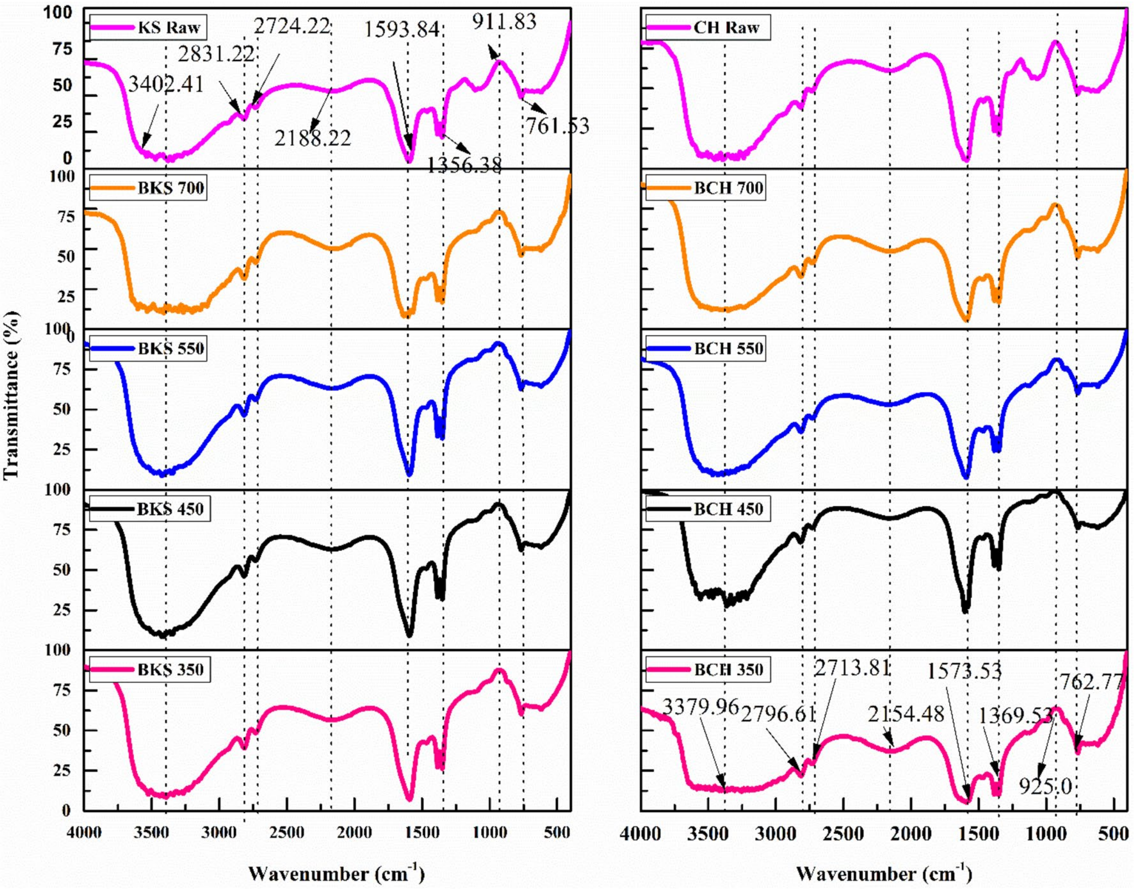

Fig. 6 FTIR spectra of the biochar obtained from khat stem (BKS) and coffee husk (BCH) at various pyrolysis temperatures (350, 450, 550, and 700 °C)

might be explained by a high electron-to-atom ratio in the assessed samples [68, 70]. The biochar from BCH displays narrow peaks at 24° at low temperatures (i.e., 350 °C) and vanishes at 700 °C. The amorphous molecules are mainly caused by the porous nature of biochar, which traps X-rays. In general, biochar samples have nearly amorphous phases and unique properties [71].

3.3.1 Effect of temperature on the thermal stability of biochars

In Fig. 8a–d, thermogravimetric (TG) curves of the biochar (BCH and BKS) were obtained at 20 °C/min under argon (Fig. 8b, d) and air atmospheres (Fig. 8a, c) from 30 to 850 °C. The reactivity of biochar significantly decreased compared to raw materials [40]. Under an argon atmosphere, the maximum weight loss was around ~ 22% for BCH and ~ 30% for BKS at 850 °C. Under an air atmosphere, 65–70% of the total weight of the biochar sample was decomposed, possibly due to the presence of combustible components. The thermal decomposition characteristics of all biochar samples showed minor differences [41]. In the lower range of temperature below 150 °C, a small ~ 5% weight loss was observed due to dehydration, moisture removal, and light volatile matter. The apparent weight loss related to dehydration was not substantial in all biochar samples, possibly due to the hydrophobic nature of the biochars correlated to feedstock [47]. TGA curves under the Ar atmosphere were consistent with previous results. Biochar samples prepared at high temperatures provided higher thermal stability and thermal resistance.

3.4 Potential application of biochar as a catalyst

Biomass pyrolysis is a favorable approach to transforming biomass material into energy and other value-added products. Catalysts can be employed to execute and enhance the decomposition of biomass during the pyrolysis process. During biomass pyrolysis, catalysts are essential for achieving maximum quantities and accelerating the rate of production of bio-oil and other valuable byproducts [72]. Researchers can further enhance the pyrolysis mechanisms by meticulously determining and developing biobased catalysts [3, 4]. Among the most exploited and commercially competitive

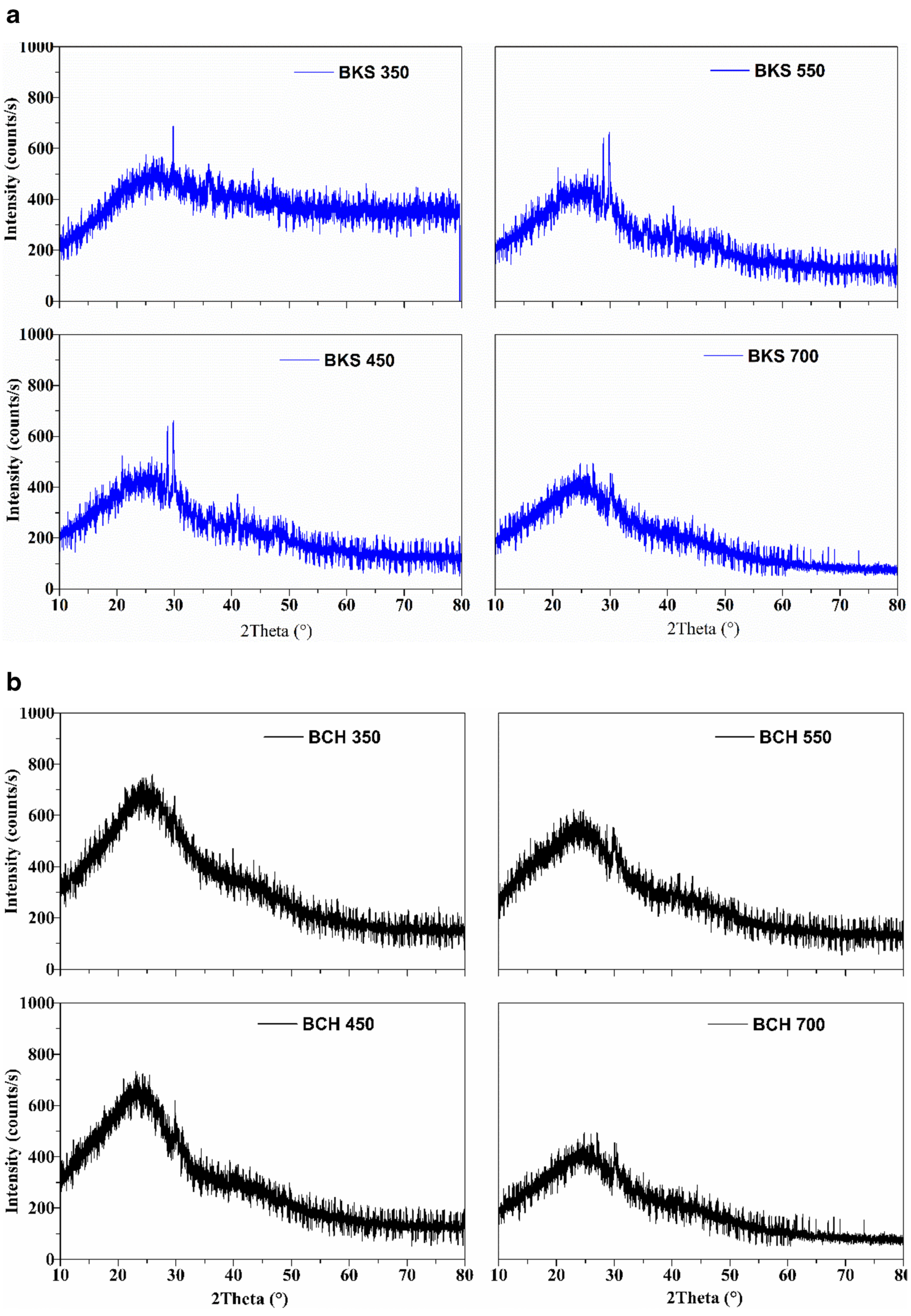

Fig. 7 **a** XRD analysis of the biochar samples produced from the khat stem (BKS) at different temperatures of 350, 450, 550, and 700 °C. **b** XRD analysis of the biochar samples produced from the coffee husk (BCH) at different temperatures of 350, 450, 550, and 700 °C

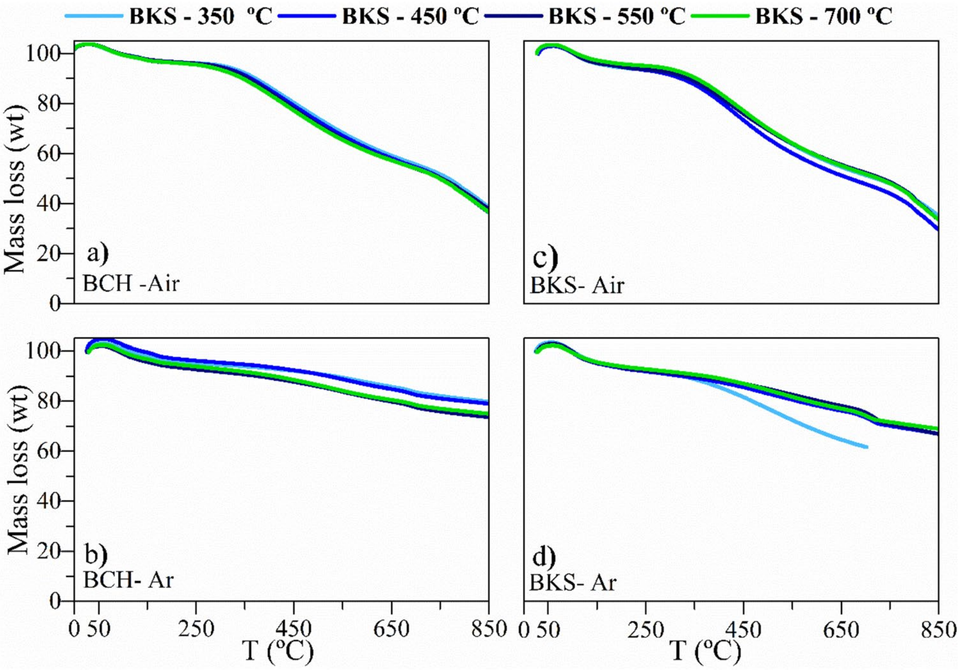

Fig. 8 TGA of biochars (BKS and BCH) produced at different temperatures

catalysts are microporous zeolites which are recognized as the most promising in terms of effectiveness and ability to provide the necessary attributes. Particularly, the top advantages of zeolites are the effectiveness of deoxygenation and decomposition of large tar molecules, though the foremost drawbacks include reductions in tar organic phase and deactivation of catalyst due to ash accumulation [73]. In addition to zeolite-based catalysts are catalysts such as mesoporous aluminosilicates, extensively utilized catalysts for bio-oil deoxygenation, and alkaline compounds [73]. A few studies also utilized different kinds of catalysts, including fly ash [74].

Additionally, biochar can be employed as an adsorbent material in the post-treatment process to improve the quality of pyrolysis liquid oil for multiple applications, or it can be used as a catalyst to accelerate the thermal decomposition of biomass and other wastes [75]. Pertaining to this, even at high temperatures (850 °C), the biochar produced at different temperatures (350, 450, 550, and 700 °C) shows great thermal stability. Consequently, it can be employed as a catalyst during the pyrolysis process to crack high molecular weight tars and enhance the quality of liquid fuel for use in boilers, transportation, and other possibilities [41]. One effective technique to maintain this stability is to add support materials like silica (SiO_2) or alumina (Al_2O_3), the XRF analysis also revealed that the amount of these materials is significant as reported in the supplementary material (Table S2). Support materials enhance the structural integrity, active site dispersion, surface area, and thermal stability of biochar-based catalysts. These substances sustained catalytic activity by preventing the catalytic aggregation of active sites. Support materials can also increase the selectivity of biochar-based catalysts for tar cracking. Additionally, they shield the catalyst from deactivation at elevated temperatures, preventing sintering and maintaining its lifetime and effectiveness [41]. However, biochar has various inherent characteristics that contribute to its effectiveness as a catalyst such as biomass compositions, technological technique selection (pyrolysis, gasification), temperature, and reaction time and can influence the characteristics of biochar [26]. The effectiveness of biochar as a catalytic is the same as conventional catalysts like dolomites ($MgCO_3$.$CaCO_3$), olivine (Mg^{2+}, Fe^{2+}) $2SiO_4$), and Ni- and alkali metal-based catalysts, which could prove excellent for tar reformation. Its properties can be modified by so-called modifications, such as adding more pores on the surface to increase the surface area, altering the functional groups represented on the surface, or adding metal or metal oxide nanoparticles to the structure of the biochar [76].

Some of the common treatments for biochar are chemical modifications/treatments, physical or mechanical modifications, biological and impregnation with mineral oxides [77]. The different mechanisms and selection of treatment methods are also highly dependent on specific applications of the biochar. In general, chemical methods are the common and most effective treatment mechanism to enhance the properties of biochar and can involve one or two steps. In the primary method, the pyrolysis and activation are conducted simultaneously in a single phase when the activating chemical agent is present. In contrast, a second method involves pyrolysis of the biomass feedstock and then activating it with the right chemical agent or feedstock pre-treatment before the pyrolysis process [77]. Some of the methods during the chemical treatment of biochar materials include acid modification, alkalinity modification, oxidizing agent modification, metal salts, or oxidizing agent modification which are the most common [78]. The physical treatment method has gained attention as a cost-effective and greener method [79]. Biochar modified with physical activation increases adsorption for heavy metals, organic pollutants, and nutrients because of the increased specific surface area (SSA) and porosity. Furthermore, the physical activation method is safer and cleaner and provides impurity-free biochar than chemical activation does [79]. Biochar modification with physical activation methods such as steam/gas activation and ball milling activation are relatively low-cost and have lower environmental risks [80]. Recently, microwave and magnetic biochar modification methods were also reported to improve the physicochemical properties of biochar for specific applications. Furthermore, impregnation with clay minerals and mineral oxides is also reported as a novel idea to treat biochar by doping with minerals such as vermiculite and montmorillonite, which can enhance biochar performance. They possess excellent ion exchange capabilities and large pore structures, which are beneficial for removing various contaminants in aquatic ecosystems [80].

As coffee husk and khat stem biochar have better physical properties, particularly for the catalysis capability, the BCH and BKS biochar were selected to study their application as a catalyst. The pyrolysis temperature significantly impacts the pore size and surface area of biochar. The surface area of biochar produced at a higher temperature within a particular temperature range increases. Increased temperature enables volatile compounds to come out of the biochar, making the holes bigger and the surface area larger. Due to its high porosity and surface area, biochar may hold significant of moisture. Conversely, elevated temperatures during pyrolysis result in a decrease in the overall amount of polar functional groups present in biochar, hence improving its hydrophobicity [26]. XRF analysis of the achieved biochar revealed the presence of silica (SiO_2), alumina hydroxide Al_2O_3, and other compounds as indicated in Table S2 of the supplementary material. They also have a high adsorption capacity, which can be employed to eliminate various contaminants from the produced liquid oil. However, there has been little investigation into the utilization of biochar and activated carbon as catalysts in the pyrolysis of biomass waste to crack high molecular tars [41].

4 Conclusions and recommendations

Biofuel production requires careful selection of catalysts, which have evolved from acidic to basic, homogeneous to heterogeneous, and chemical to enzymatic. Biochar as a catalyst must be extensively investigated to make it effective for various functionalities. Biochar applications provide numerous environmental benefits, but economic elements must be calculated based on production cost and conversion technology investment. This study produced two agricultural biomass-derived biochars (BKS and BCH) at different pyrolysis temperatures. The physical and chemical properties of the biochars were influenced by the type of parental materials and pyrolysis temperature. Higher pyrolysis temperature reduced the percentage yield of biochar, increased fixed carbon content, and decreased volatile matter compared to the original material. However, biochar produced from both feedstocks has a promising microstructure with a large specific surface area (SSA), and pour structure, and is rich in functional groups and inorganic minerals. Both biochar materials revealed increments in surface area with temperature; however, the changes could be marked by an optimum at a certain temperature beyond which a significant decline could be expected. Furthermore, the quality of the material used to develop the biochar affects its functionality. Future research should focus on improving the properties of biochar produced from BKS and BCH, with further functionalization of biochar materials. This study suggests that catalytic tar cracking using biochar is a promising technology due to its porous structure, good catalytic activity, and low cost.

We certify that the submission work is not under review at any other journal.

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Data availability The data analyzed during this study which supports its findings are available only upon official request to the corresponding authors.

Declarations

Competing interests The authors declare no competing interests.

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