



Investigation of the effect of metal powder and metal-supported MCM-41 catalysts on the pyrolysis of horse chestnut fruits and shells (*Aesculus hippocastanum* L.)

Halil Durak¹ · Salih Genel²

Received: 13 March 2024 / Revised: 4 May 2024 / Accepted: 21 May 2024 / Published online: 3 June 2024
© The Author(s) 2024

Abstract

Horse chestnut fruit and horse chestnut shell are derived from the same biomass but exhibit distinct structural characteristics. Different compounds can be produced through the pyrolysis of these materials. The pyrolysis process was conducted on horse chestnut fruit and shell at temperatures of 300, 400, and 500 °C, both with and without various catalysts (Al, Fe, MCM-41/Al, MCM-41/Fe). The synthesis of MCM-41 catalysts utilized a hydrothermal method, and their properties were assessed through XRD, SEM–EDX, and SEM–EDS analyses. The resulting products from the pyrolysis were analyzed using GC–MS and elemental analysis techniques. Optimal efficiency was achieved at 400 °C, with the highest HHV value recorded at 34.38 MJ/kg when Al powder catalyst was present.

Keywords Horse chestnut · Catalytic pyrolysis · Metal powder catalyst · MCM-41

1 Introduction

Renewable energy sources have become essential in tackling the growing global energy needs and reducing the adverse environmental impacts linked with traditional fossil fuel–derived energy generation. Within the realm of renewable sources, biomass energy plays a unique and significant role in the transition towards a greener and more eco-friendly energy framework. Biomass energy is obtained from organic materials such as wood, agricultural residues, forest residues, and dedicated energy crops [1]. The distinctive attribute of biomass as an energy source lies in its inherent potential for sustainability. Provided that it is underpinned by responsible forestry and agricultural practices, biomass can be considered to have a minimal impact on carbon levels, thereby contributing to a sustainable energy landscape. This perspective underscores the necessity of implementing environmentally sound management practices to ensure that

biomass utilization aligns with ecological balance and carbon neutrality objectives [2]. This is due to the fact that the carbon dioxide released during its combustion is approximately equal to the carbon dioxide absorbed by the plants during their growth. Essentially, it signifies a closed carbon cycle, thereby minimizing the emission of greenhouse gases and aiding in the fight against climate change. The significance of biomass energy lies not only in its environmental advantages but also in its versatility. Biomass can be converted into various forms of energy, encompassing electricity, heat, and biofuels, thus presenting a multifaceted solution to our energy demands. Biofuels, such as biodiesel and bioethanol, can propel vehicles, consequently reducing our dependence on fossil fuels and diminishing air pollution. Additionally, biomass can be utilized to generate heat, contributing to heating systems in residential and industrial settings, thereby further reducing the carbon footprint [3, 4].

Biomass can be transformed into new products by thermochemical processes. Thermochemical processes represent innovative and promising approaches for the transformation of waste materials into valuable resources and chemicals. These processes harness high temperatures and chemical reactions to convert various forms of waste into valuable products, thus reducing waste volumes, mitigating environmental impacts, and promoting resource recovery. Pyrolysis, in particular, stands out as a significant thermochemical

✉ Halil Durak
halildurak@yyu.edu.tr

¹ Vocational School of Health Services, Van Yuzuncu Yil University, 65080 Van, Turkey

² Ozalp Vocational High School, Van Yuzuncu Yil University, 65080 Van, Turkey

process with immense potential. It effectively converts organic materials, including biomass and waste, into biochar, bio-oil, and syngas in the absence of oxygen. This process relies on the fundamental principle of thermal decomposition, subjecting the organic material to elevated temperatures within a controlled environment. The result is the breakdown of complex organic compounds into simpler molecules [1, 5].

The selection of raw materials in the pyrolysis process is a crucial factor that directly affects the constitution and output of the resulting liquid and solid outputs. A variety of raw materials are used for pyrolysis, such as wood and forest remains, herbaceous plants, household waste, and lignocellulosic resources. The determination of which raw material to use depends on the particular objectives of the pyrolysis process, with a focus on achieving the desired composition of the final products [6]. Furthermore, the application of catalysts in pyrolysis has gained significant importance in recent years, primarily due to their substantial influence on the content and yield of the products. Catalysts play a vital role in promoting the desired chemical transformations within the pyrolysis reactor. These catalysts encompass a wide range of acidic, basic, and supportive materials, each specifically designed to facilitate the formation of distinct groups of compounds characterized by their high-energy value [7].

In recent years, there has been an increasing interest in the utilization of porous catalysts within the pyrolysis process. Notably, microporous zeolite catalysts such as HZSM-5, HY, and HBeta have garnered significant attention [8–10]. It has been postulated through various studies that catalysts possessing larger pore structures may yield advantageous effects in enhancing the quality of bio-oil. Further research has demonstrated that materials exhibiting mesoporous structures can provide a greater abundance of active catalytic surfaces, with the MCM-41 variant showing particular promise in terms of catalytic enhancement [11]. The efficacy of these catalyst types has been thoroughly investigated across numerous pyrolysis studies. Although pure silicate MCM-41 inherently lacks acidic regions, the introduction of transition metals such as aluminum (Al), copper (Cu), iron (Fe), and zinc (Zn) into its structure has been found to augment its catalytic activity. This enhancement is attributed to the creation of new catalytic sites within the MCM-41 framework, facilitated by the incorporation of these metals [6, 12]. MCM-41 is characterized by a distinct pore distribution, a substantial BET surface area ($> 700 \text{ m}^2/\text{g}$), a notable pore volume, and a pore diameter ranging from 1.5 to 10 nm. This material exhibits a one-dimensional and hexagonal mesoporous structure [7, 13]. The pore structure of MCM-41 possesses a notable characteristic whereby it is modifiable and customizable for further research endeavors. MCM-41 has gained prominence due to its exceptional hydrothermal and chemical stability, rendering it a favored catalyst support material in recent times. In investigations

utilizing MCM-41 and MCM-41/metal catalysts as catalysts in the pyrolysis of ligno-cellulosic biomass, it has been determined that these catalysts exhibit significant activity in the acquisition of certain compound groups [14–16].

Aesculus hippocastanum, which is commonly referred to as horse chestnut, is a species of deciduous tree that belongs to the family Sapindaceae. In the realm of scientific classification, horse chestnut is formally designated as *A. hippocastanum* and holds a prominent position as a tree species with a notable historical utilization by mankind. Characteristically, horse chestnut trees tend to attain moderate to sizable stature, achieving heights of 20–30 m. The compound composition of its leaves encompasses 5–7 leaflets that radiate from a focal point, thereby imparting a discernible semblance to a human hand [17]. The most widely recognized attribute of horse chestnut lies in its fruit, colloquially referred to as “conkers.” Enclosed within a spiky pod, these spherical seeds are unveiled during the autumn season, presenting a glossy brown appearance. It is crucial to bear in mind that these seeds are toxic when consumed in their raw state, necessitating processing prior to their employment for medicinal purposes. Horse chestnut boasts an extensive historical employment within traditional medicinal practices, particularly in Europe and Asia. The seeds of horse chestnut harbor a multitude of phytochemicals, with aescin (also known as escin) serving as the most prominent constituent. Aescin, a combination of triterpene saponins, is renowned for its anti-inflammatory and venotonic attributes. Furthermore, horse chestnut seeds contain flavonoids and tannins, which are believed to contribute to the plant’s therapeutic effects [18, 19].

There exist various research studies in the literature that employ horse chestnut as a source of biomass. These studies involve the extraction of liquid and solid products from horse chestnut through diverse processes. One such study investigated the pyrolysis of *Aesculus chinensis* bunge seed (ACBS) in the presence of nano Fe_2O_3 and NiO catalysts, resulting in the production of bio-oil. The bio-oil was found to contain valuable chemical components, namely 1-hydroxy-2-propanone, acetic acid, and furfural [19]. Another study focused on the thermal degradation of Himalayan horse chestnut (HHCN) for the purpose of bioenergy conversion via pyrolysis. This study demonstrated that horse chestnut possesses potential applications as an adsorbent and active electrode material in energy storage devices [20, 21]. A separate investigation explored the utilization of biochar derived from the seed coat of *Aesculus turbinata* (SAT-BC) for triclosan removal. The results of this study indicated that biochar obtained from the seed coat of *A. turbinata* exhibits promise as an effective adsorbent for eliminating triclosan from water [22]. Furthermore, an additional study examined the potential of horse chestnut, a forest biomass, as an environmentally friendly alternative energy source. The findings of this study revealed a significant increase in the

fixed carbon content of horse chestnut, rising from 18.1 to 44.7%, accompanied by a decrease in the volatile substance content from 82.9 to 59.8% [23].

Although horse chestnut fruit (HCF) and horse chestnut shells (HCS) come from the same plant, they have different structural properties. Specifically, HCF contains a variety of chemical compounds, which gives it the potential to form new chemical structures. This ability to generate diverse compounds makes horse chestnut a valuable biomass resource. During pyrolysis, a process that breaks down organic material at high temperatures in the absence of oxygen, these differences could lead to the creation of distinct types of compounds from each substance. Furthermore, the pyrolysis process in this study used metal powders (Al, Fe) and catalysts such as MCM-41/Al and MCM-41/Fe. Mesoporous materials like MCM-41 are known to influence the composition of products formed during pyrolysis. By comparing the effects of direct metal powder catalysts to those combined with MCM-41, this study aims to provide a clearer understanding of how these catalysts affect the outcomes of pyrolysis.

2 Materials and methods

2.1 Materials

Horse chestnut, used as biomass raw material in the trials, was collected in the Sakarya-Geyve region of Turkey. The harvested horse chestnuts were meticulously sorted according to their shells and fruits. Subsequently, they were left to dry in a shaded area with natural airflow for a month. After drying, they were ground into a fine powder and stored in jars. Analytical grade chemicals were used in the synthesis of MCM-41, MCM-41/Al, and MCM-41. For the synthesis processes, a sodium silicate solution was employed, which consisted of 27% SiO₂, 8% Na₂O, and 65% H₂O, and was obtained from Sigma-Aldrich Germany. The cetyltrimethylammonium bromide (CTMABr) with a purity of 99% and Fe(NO₃)₃·9H₂O were sourced from Carlo Erba-France. The Al(NO₃)₃·9H₂O was sourced from Carl Roth-Germany. The aluminum (Al) powder with a particle size of 60 µm and iron (Fe) powder, also with a particle size of 60 µm, both were sourced from Sigma-Aldrich Germany.

2.2 Catalyst preparation and characterization

The synthesis of MCM-41 catalysts can be achieved through various methods, including the hydrothermal, sonochemical, and ultrasound methods. In our literature review, we explored these techniques and characterized the resulting catalysts. Among these methods, the hydrothermal synthesis yielded the highest surface area, making it the method of choice for our study [6, 7]. Therefore, in our research, we opted for the hydrothermal method to synthesize the

MCM-41 group catalysts, utilizing a sodium silicate solution. To prepare approximately 100 g of the synthesis solution using the hydrothermal method, we followed a series of steps. Firstly, we mixed 13.2 g of the surfactant cetyltrimethylammonium bromide (CTMABr) with 70 mL of deionized water using a mechanical mixer (Heidolph RZR-2051) for 2 h to create the surfactant solution. Subsequently, we added 11.3 mL of the sodium silicate solution to the surfactant solution slowly, stirring for an additional 2 h. This mixing resulted in the formation of a gel-like mixture. The gel was then placed in a stainless steel hydrothermal reactor (Uniterm-Lab) with a Teflon container and kept in an oven at 120 °C for 4 days. After this period, the mixture was filtered using a vacuum filtration system (Rocker-Taiwan). The solid obtained was thoroughly washed with deionized water using the same filtration system. The resulting solid product was then placed in a watch glass and allowed to dry at room temperature for 1 day. Subsequently, the dried solid was calcined in a muffle furnace (Thermo Scientific) at 550 °C for 6 h.

In the synthesis of the Al-MCM-41 catalyst, during the preparation of the MCM-41 catalyst, sodium silicate was initially added and mixed for 2 h. Then, 5.3 g of aluminum nitrate (in a molar ratio of Al/Si: 0.2) was dissolved in deionized water and added to the mixture. The solution was stirred for another 2 h with a mechanical mixer (Heidolph-Germany). The same steps were followed for the synthesis of Fe-MCM-41, using 5.706 g of iron (III) nitrate nonahydrate (in a molar ratio of Fe/Si: 0.2). These mixtures were also kept at 120 °C for 4 days, filtered, and subsequently calcined at 550 °C. Additionally, metal powder catalysts (60 µm) were used as received. The metal-to-silicon mole ratios were calculated as per the guidelines provided in our previous work [6, 7].

Furthermore, it is worth noting that the sodium silicate used in our experiments has a composition of 27% SiO₂, 8% Na₂O, and 65% H₂O, with an average molar mass of 32.88 g/mol. Its density is determined to be 1.391 g/mL, and its volume was measured at 11.3 mL. As a result, the mass of the sodium silicate used was calculated as follows:

$$\begin{aligned} m_{\text{Sodium silicate}} &= d_{\text{Sodium silicate}} \times V_{\text{Sodium silicate}} \\ &= 1.391 \text{ g/mL} \times 11.3 \text{ mL} = 15.7183 \text{ g} \end{aligned}$$

Since the sodium silicate contains 27% SiO₂, the mass of SiO₂ in the sample is as follows:

$$m_{\text{SiO}_2} = 15.7183 \text{ g} \times 0.27 = 4.2439 \text{ g}$$

The molar mass of SiO₂ is 60.086 g/mol, so the amount of SiO₂ in moles is as follows:

$$n_{\text{SiO}_2} = m_{\text{SiO}_2} / M_{\text{SiO}_2} = 4.2439 \text{ g} / 60.086 \text{ g/mol} = 0.07063 \text{ mol}$$

Given the 1:1 molar ratio of SiO₂ to sodium silicate, the amount of Si in the sample is also 0.07063 mol.

In the case of the Al-MCM-41 catalyst, the molar ratio was specified as Al/Si = 0.2. Consequently, nAl, representing the moles of aluminum in the sample, was determined as 0.2×0.07063 , resulting in nAl = 0.014126 mol. The amount of aluminum nitrate (nAl(NO₃)₃·9H₂O) used was adjusted accordingly based on this molar quantity. Similarly, for the Fe-MCM-41 catalyst, the molar ratio was set as Fe/Si = 0.2. As a result, nFe, denoting the moles of iron in the sample, was calculated as 0.2×0.07063 , leading to nFe = 0.014126 mol. The quantity of iron (III) nitrate nonahydrate (nFe(NO₃)₃·9H₂O) employed in the synthesis was adjusted in accordance with this molar value.

The obtained MCM-41, Al-MCM-41, and Fe-MCM-41 catalysts underwent comprehensive characterization using a combination of techniques, including XRD (X-ray diffraction), BET (Brunauer–Emmett–Teller) analysis, SEM (scanning electron microscopy), SEM–EDX (SEM with energy-dispersive X-ray analysis), and SEM–EDS (SEM with energy-dispersive spectroscopy). X-ray diffraction (XRD) analysis was performed using a Rigaku-SmartLab equipped with Cu-K α radiation (wavelength of 1.5408 Å). The diffraction patterns were collected over an angular range from 10 to 70°, with a step size of 0.02° per increment and a dwell time of 3 min per step, at a temperature of 25 °C. The specific surface areas of both the catalysts and their respective supports were determined using BET analysis, which was conducted using the Oantachrome Autosorb Iq2. Prior to N₂ physisorption, each sample was degassed at 110 °C for 18 h. SEM and EDX analyses of the prepared materials were conducted using a Zeiss Sigma 300 device. For non-conductive samples, Au/Pd coating was applied using an SC720-coating machine.

The XRD analysis results, as illustrated in Fig. 1, reveal important insights. The XRD pattern of MCM-41 aligns with characteristic MCM-41 peaks reported in previous studies. In the XRD plot of Al-MCM-41, the primary MCM-41 structure peak is evident, while there is an absence of peaks associated with the aluminum structure (2θ = 38.100, 780, 44.370) or the Al₂O₃ structure (2θ = 43.360, 35.140, 57.520). These results suggest that the introduction of aluminum into the MCM-41 structure does not disrupt the characteristic MCM-41 framework. It can be concluded that aluminum is uniformly incorporated within the MCM-41 crystal lattice.

In contrast, as the Fe/Si ratio in the Fe-MCM-41 structure increases, the added iron does not integrate into the crystal lattice but instead forms a Fe₂O₃ phase on the external surface of the catalyst. The XRD graph of Fe-MCM-41 exhibits characteristic peaks of Fe₂O₃ [6, 7].

Moreover, BET analysis results indicated that MCM-41 possessed a surface area of 750 m²/g, Al-MCM-41 had a surface area of 345 m²/g, and Fe-MCM-41 had a surface area of 380 m²/g.

Figure 2 presents the SEM–EDX and SEM–EDS results, showing that the metals added to the MCM-41 structure

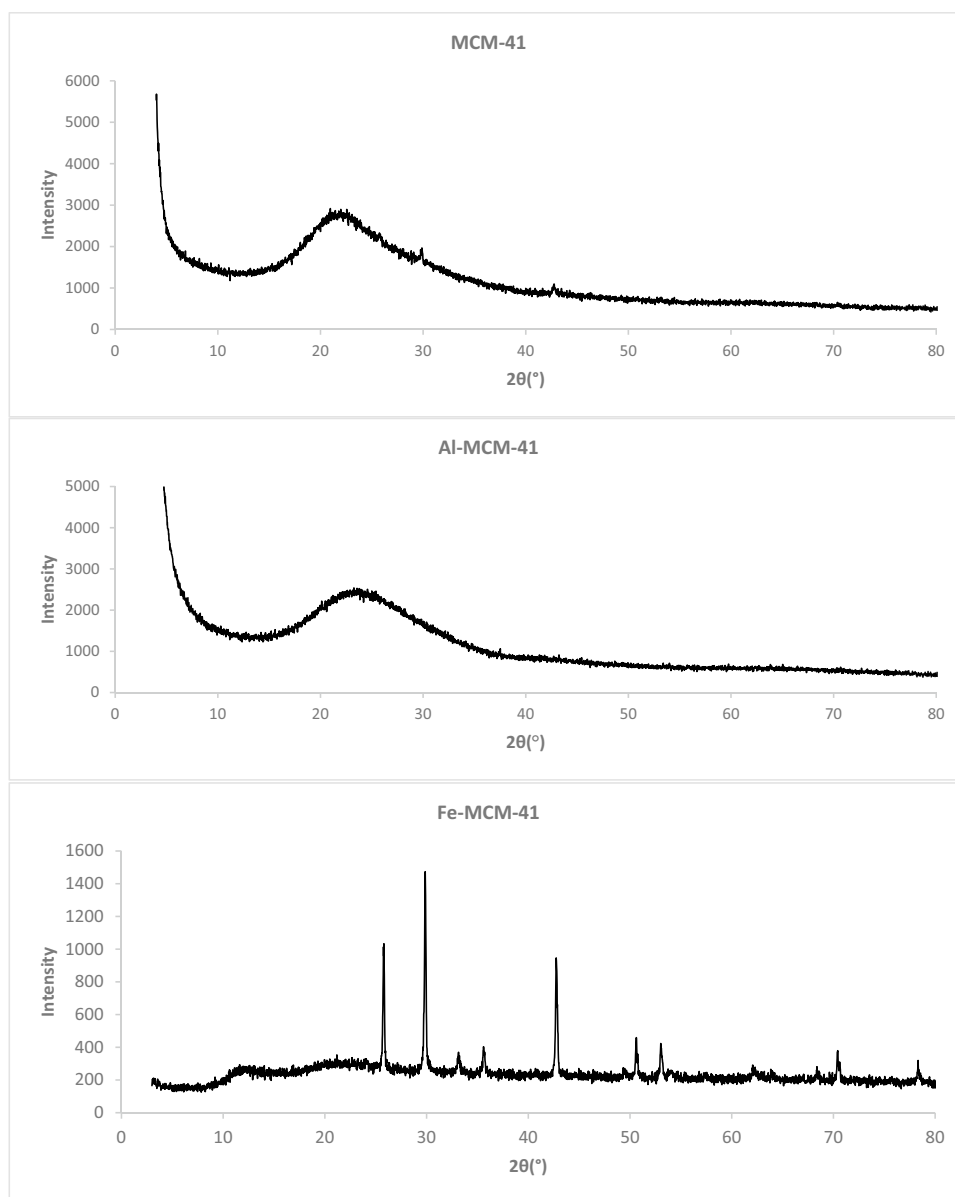
were effectively integrated into the structure, demonstrating a homogeneous distribution throughout the material.

2.3 Pyrolysis experiments

HCF and HCS were ground separately and used in experiments. TGA analyzes of HCS and HCF can be seen in Fig. 3. Due to the structures of HCS and HCF, minor differences are observed in the TGA graphs. Mass loss in HCF increased after 200 °C, and the most severe decrease was observed at 300 °C. In HCS, mass loss increased after 250 °C and became most severe after 300 °C. Considering all these behaviors against temperature, the pyrolysis temperature was determined as 300, 400, 500 °C. Brems et al. [24] and Van de Velden et al. [25] described both heat transfer and intra-particle diffusion limitations can be ignored if experiments are carried out at a low-to-moderate heating ramp for biomass particles of size below about 300 μ m. Therefore, considering the particle size of the samples used in this study and the thermal ramps applied during the experiments, it can be stated that both internal and external heat and mass transfer limitations can be disregarded. This ensures the accuracy and reliability of the measurements, leading to more robust results. Pyrolysis of horse chestnut was carried out in a fixed bed reactor (Uniterm lab) shown in Fig. 4. Throughout the pyrolysis experiments, a continuous supply of nitrogen gas at a flow rate of 100 ml/min was provided to the reactor. In accordance with the each experiment, 10 g of horse chestnut powder (HCF or HCS) were introduced into the reactor, along with 20% catalyst (2 g) for catalytic pyrolysis experiments. Subsequently, connections were established to the reactor and liquid product collection bottles.

Before commencing the heating process, the interior of the reactor was purged with nitrogen gas for a duration of 5 min to eliminate any residual air. The heating of the reactor was achieved using an external electric furnace. The reactor system was maintained at a constant temperature for a period of 30 min during the pyrolysis experiments. Following this interval, the heating of the furnace was ceased, and the gas flow was sustained until the temperature returned to room temperature, thereby preventing any combustion of solid materials within the reactor. To collect the bio-oil, the collection bottles were cooled to – 8 °C through the utilization of a mixture involving salt, ethanol, and water. Gaseous products were not collected; instead, they were discharged into a chimney through a hose and fan. Nitrogen gas was continuously circulated throughout the entire pyrolysis process to establish an inert atmosphere within the reactor. The HCF and HCS underwent pyrolysis under various conditions, including with MCM-41, Al-MCM-41, Fe-MCM-41, Al powder, and Fe powder catalysts, as well as without any catalyst. The pyrolysis was conducted at temperatures of 300, 400, and 500 °C, with a constant heating rate of 100 °C/min.

Fig. 1 X-ray powder diffraction patterns of MCM-41, Al-MCM-41, Fe-MCM-41



The liquid products obtained during the pyrolysis process, which comprised of aqueous (pyrrolignic acid) and oil (pyrolytic oil) phases, were extracted and separated from each other by means of washing with dichloromethane. Decantation using a separating funnel was utilized for this purpose. The oil phase (pyrolytic oil) was subsequently subjected to drying using anhydrous sodium sulfate. After the completion of the pyrolysis process, the solvent was evaporated from the mixture containing the bio-oil at 313 K and 11 kPa by employing a rotary evaporator. The yield of bio-oil was determined by measuring and recording the amount of bio-oil recovered after evaporation. The remaining solid residue, along with the catalyst, was weighed to determine the biochar yield. The conversion and product yields were calculated using the following equations.

$$\text{Conversion (\%)} = \frac{(W_{\text{Biomass,db}} - W_{\text{Solid,db}})}{W_{\text{biomass,db}}} \times 100 \quad (1)$$

$$\text{Liquid yield (wt \%)} = \frac{(W_{\text{Liquid}})}{W_{\text{Biomass,db}}} \times 100 \quad (2)$$

$$\text{Solid yield (wt \%)} = \frac{(W_{\text{Solid,db}})}{W_{\text{Biomass,db}}} \times 100 \quad (3)$$

$$\text{Gas yield (wt \%)} = 100\% - \text{liquid yield (wt \%)} - \text{solid yield (wt \%)} \quad (4)$$

where $W_{\text{Biomass,db}}$ and $W_{\text{Solid,db}}$ are the weights of initial biomass and remaining solid (bio-char) respectively on dry basis.

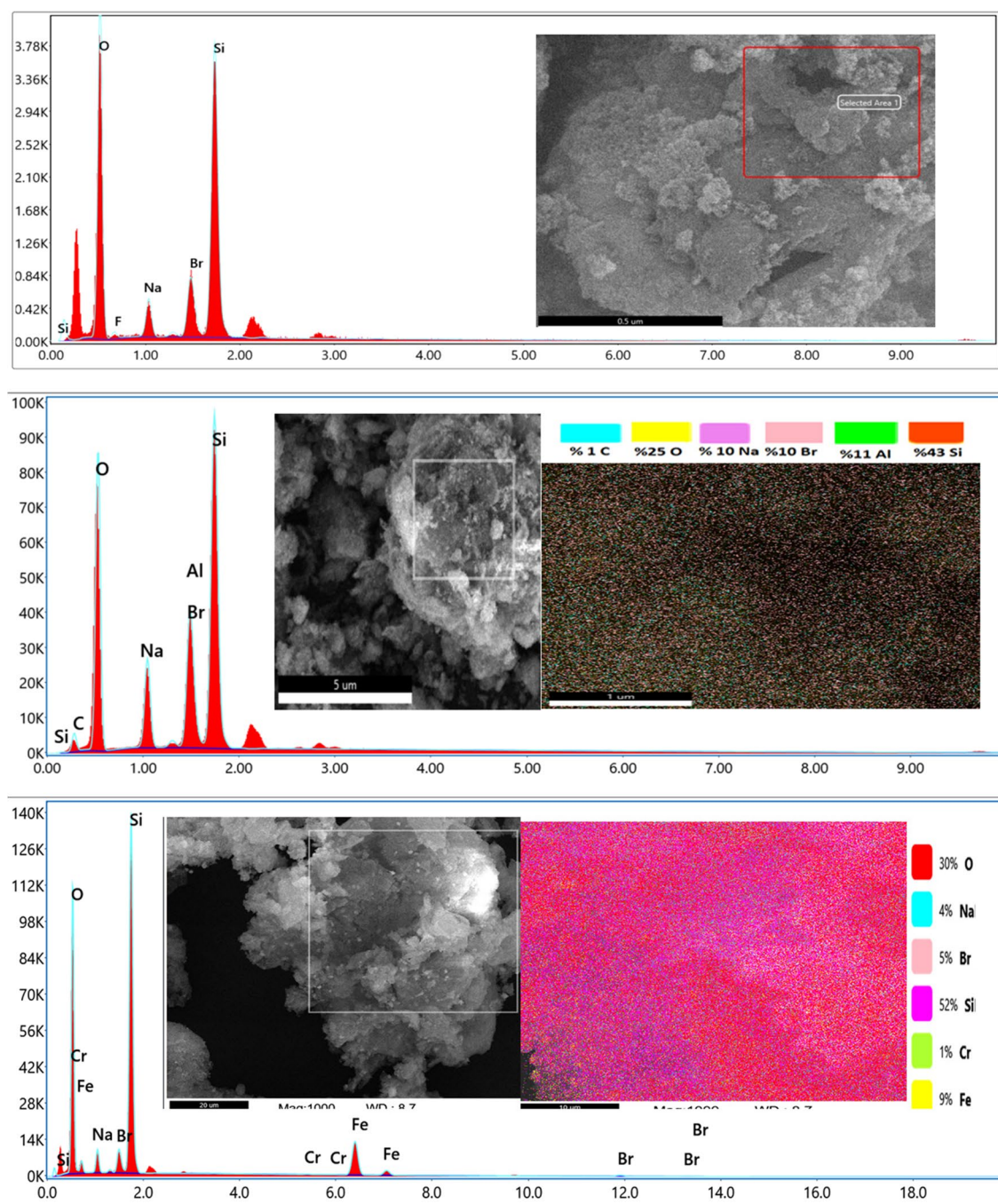


Fig. 2 SEM-EDX and SEM-EDS spectra of MCM-41 (a), Al-MCM-41 (b), Fe-MCM-41 (c)

3 Result and discussion

3.1 Effect of temperature on product yields

HCF and HCS were used in the trials as two different raw material sources. The impact of temperature on the pyrolysis of both HCF and HCS exhibited striking similarities. The results of the HCF pyrolysis experiments are elucidated in Fig. 5. Upon scrutinizing the experimental

outcomes, it becomes evident that akin curves were obtained in trials conducted both with and without the catalyst. Across all experimental conditions, a discernible pattern emerged, characterized by an initial upsurge in product yield up to 400 °C, followed by a subsequent decline. Notably, the zenith of product yield was consistently achieved at 400 °C. As anticipated, the production of biochar displayed a diminishing trend with increasing temperature. Furthermore, the gas product yield and

Fig. 3 TGA analysis of horse chestnut fruit (HCF) and horse chestnut shell (HCS)

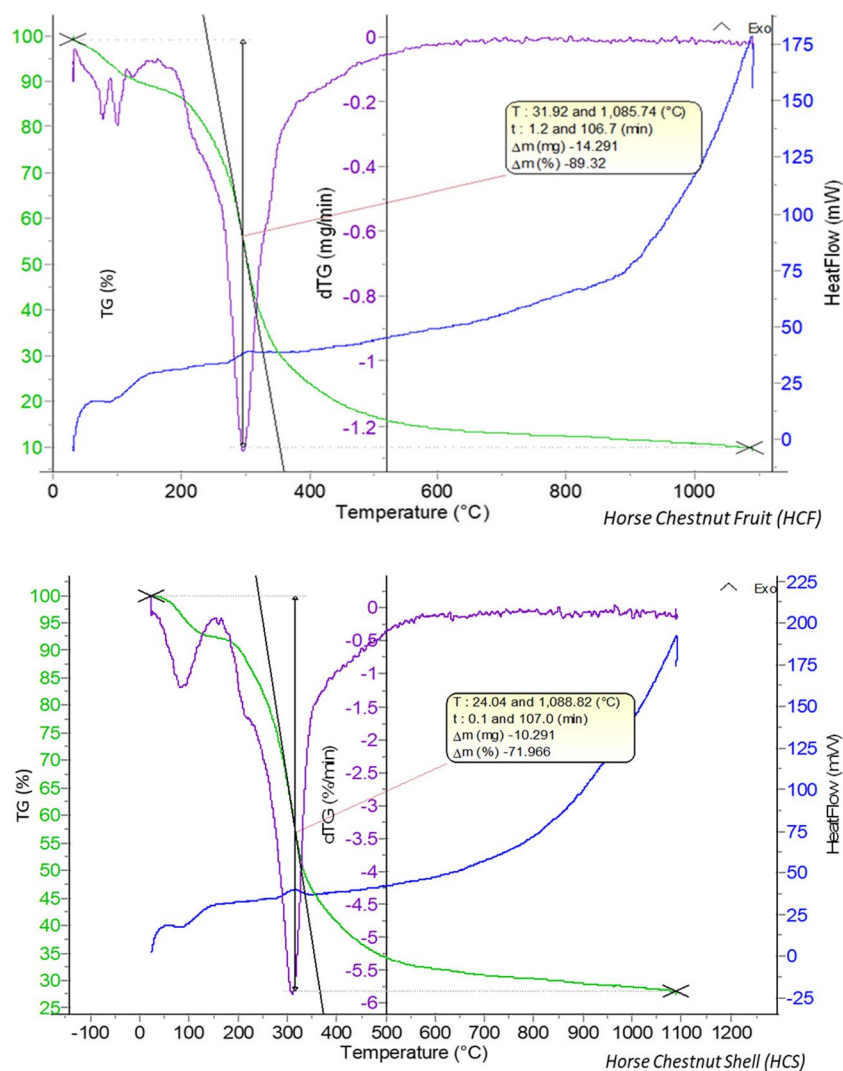
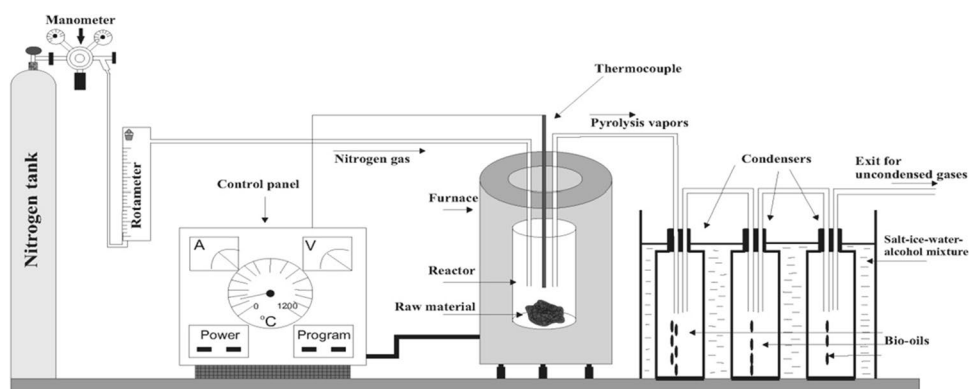


Fig. 4 Schematic diagram for the fixed-bed tubular reactor system

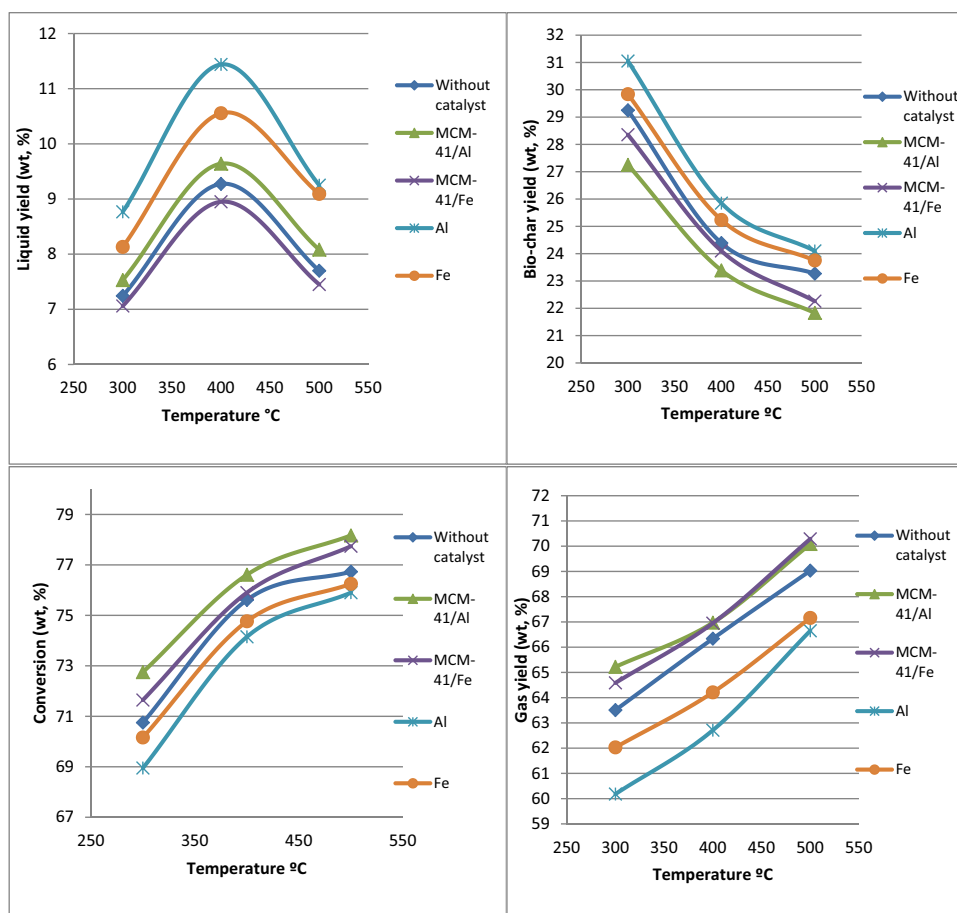


conversion rates demonstrated an augmenting tendency, albeit with a decreasing slope, specifically at the 400 °C temperature point.

The results of the HCS pyrolysis experiments are elucidated in Fig. 6. The influence of temperature on HCS was analogous in nature. The acme of liquid product yield

was achieved at 400 °C. Moreover, the gas product yield and conversion rates exhibited an upward trajectory with escalating temperature. The sole discrepancy from HCF was the divergence in the conversion rate, which showed a steeper incline with rising temperature, while the gas product yield displayed a shallower slope at 400 °C. This

Fig. 5 The effects of temperature and catalysts on product yields of horse chestnut fruits (HCF)



difference can be attributed to the contrasting structural compositions of HCF and HCS. HCF is richer in organic compounds, while HCS contains a higher proportion of fundamental biomass structural components.

3.2 Effect of catalysts on product yields

In our experimental investigations, Al, Fe metal powders, MCM-41/Al, and MCM-41/Fe catalysts were used to evaluate their effects on the pyrolysis of HCF and HCS. Figure 5 shows the trial results for HCF feedstock, both with and without catalyst. Our findings reveal notable differences in product yields when catalysts are added. In general, Al and Fe metal powder catalysts exhibited higher efficiency in increasing liquid product yield compared to the control (no catalyst). Additionally, the MCM-41/Al catalyst exhibited much greater activity than MCM-41/Fe. Broadly speaking, the presence of Al proved to be more effective than the presence of Fe. The highest liquid product yield was observed as 11.44%, 10.55%, and 9.64% in Al, Fe metal powders, and MCM-41/Al catalyst, respectively.

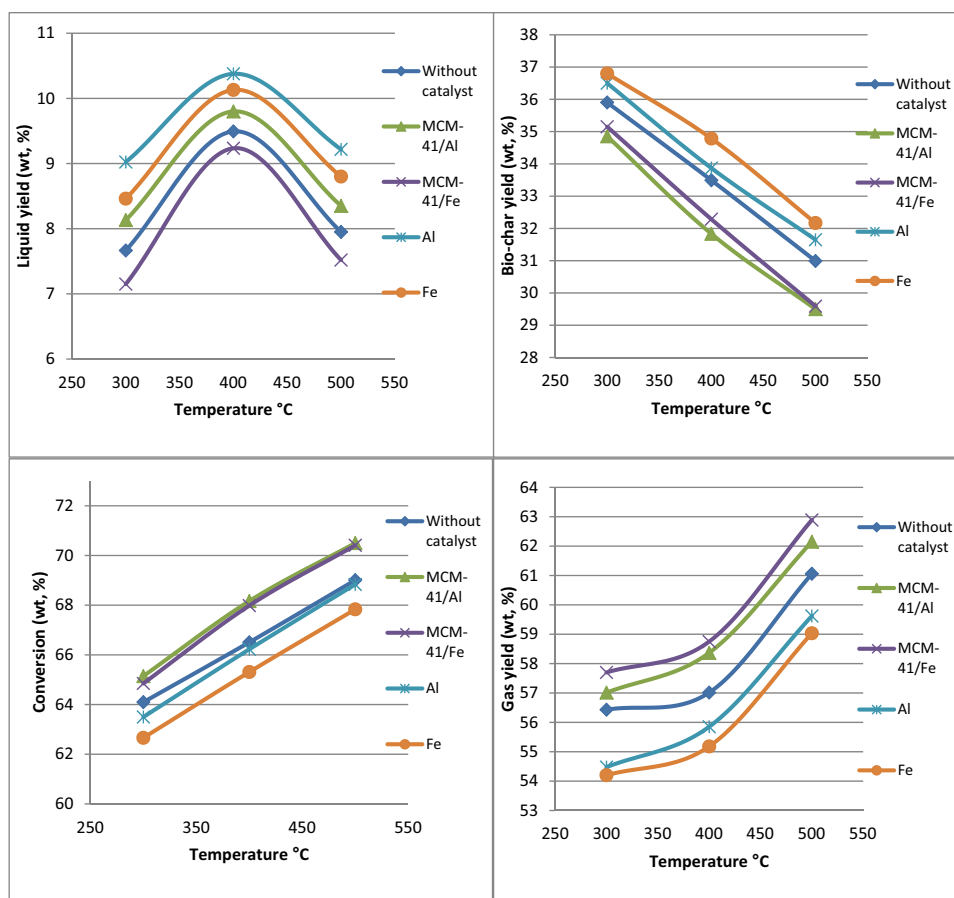
It is important to note that while Al and Fe metal powder catalysts were found to be effective in biochar production,

MCM-41/Al and MCM-41/Fe catalysts showed remarkable effectiveness in the production of gas products. This result is probably attributed to the porous structure of MCM-41, which provides an optimal environment for secondary reactions. When evaluating conversion rates according to liquid and gas product yields, MCM-41 group catalysts exhibited the highest conversion rates.

As seen in Fig. 6, similar results were obtained in the trials conducted with HCS raw material. In these trials, the highest liquid product yield was recorded as 10.37%, 10.13%, and 9.80% for Al, Fe, and MCM-41/Al, respectively. The patterns observed for biochar, gas product, and conversion rate data were consistent with those observed in the HCF experiments.

In summary, our experiments have shown that Al and Fe catalysts are effective in promoting liquid product formation, while MCM-41 group catalysts are superior in increasing gas product yield. The remarkable efficiency of MCM-41 group catalysts in gas product production has a significant impact on their ability to improve conversion rates. This result underlines the critical role of catalyst selection in optimizing pyrolysis processes for the conversion of HCF and HCS feedstocks into valuable products.

Fig. 6 The effects of temperature and catalysts on product yields of horse chestnut shells (HCS)



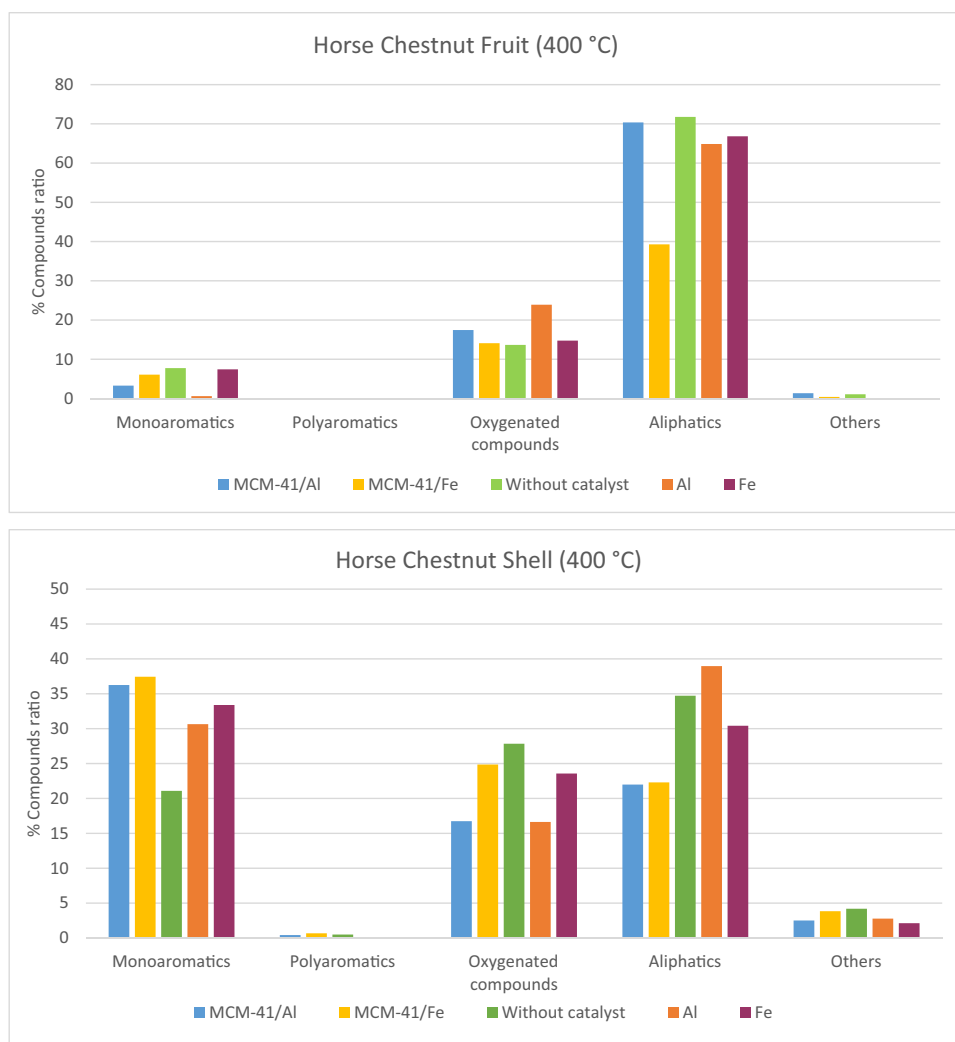
3.3 Characterization of pyrolysis products by GC–MS and elemental analysis

The liquid products resulting from the pyrolysis experiments of HCF and HCS at 400 °C underwent comprehensive analysis via gas chromatography–mass spectrometry (GC–MS). The detailed composition of these compounds is provided in Table S1-2, with graphical representations available in Fig. 7. Notably, the composition and quantities of these compounds exhibited variability contingent upon the raw material source. Moreover, discernible differences were observed in the presence of catalysts, indicating their pivotal role in directing specific compound formations compared to non-catalyzed experiments. Upon scrutiny of the compound groups derived from HCF, it became evident that the overall proportions of catalysts, particularly in the context of monoaromatic formation, were relatively diminished compared to experiments conducted without catalysts. Table S1 illustrates that the types of compounds were more abundant in catalyzed experiments, indicating a supportive role of catalysts in facilitating the generation of novel products through secondary reactions during the pyrolysis of HCF. Conversely, the types and quantities of products obtained from HCS demonstrated distinctions attributable

to the structural disparities between HCF and HCS. Across the spectrum of catalysts employed, consistent effectiveness was noted in the formation of monoaromatic compounds, with MCM-41/Al and MCM-41/Fe emerging as the most potent catalysts. The porous structure of the MCM-41 group, in particular, was identified as a contributing factor to its efficacy. This unique structural attribute enhanced the likelihood of secondary fragmentation reactions within the compounds, thereby promoting their formation. Notably, polyaromatic compound yields were found to be minimal. In terms of aliphatic compound formation, Al metal powder emerged as the most effective catalyst. This observation underscores the divergent compound formation activities exhibited by various catalysts in these experimental setups. It is noteworthy that the catalysts demonstrated nuanced mechanisms, influencing distinct compound groups in a manner reflective of their specific structural and chemical attributes. The porous nature of certain catalysts, such as MCM-41, appears to play a crucial role in promoting secondary reactions and, consequently, influencing the types and quantities of compounds generated.

Elemental analysis findings of the liquid products obtained from the experiments carried out for HCS and HCF at a temperature of 400 °C are displayed in Table 1. The liquid

Fig. 7 Compound groups of liquid products obtained HCF and HCS at 400 °C and 500 °C



products acquired from catalyst-free trials of HCS demonstrate lower carbon ratios and energy values. The structure of HCS bears a closer resemblance to lignocellulosic biomass resources. Consequently, the GC–MS results reveal that the catalysts facilitated the formation of polymerization reactions rather than deoxygenated reactions. Conversely, different formations from HCS were observed in the transformation mechanism of HCF. One factor contributing to this distinction is the dissimilarity in composition between HCS and the lignocellulosic biomass structure, with the HCF containing more specific organic compounds such as aescin [17, 18]. These structures are prone to breaking down more readily in high temperature and pressure environments. The catalysts displayed a greater efficacy in transforming these fragmented small monomeric structures. With the assistance of the catalysts, deoxygenation and polymerization reactions became dominant within these structures. Consequently, compound groups with elevated carbon content and diminished oxygen content were obtained. In comparison to experiments without a catalyst, the utilization of the catalyst resulted in products

with heightened carbon content and energy value. Notably, the Al powder catalyst exhibited remarkable efficiency, yielding a determined carbon content of 70.03 and a high heating value (HHV) of 34.38 MJ/kg.

The comparative analysis of thermal and catalytic pyrolysis of biomass materials such as HCF and HCS reveals distinct advantages and disadvantages, suggesting the suitability of specific conditions and processes for optimizing product yield and quality. In thermal pyrolysis without catalysts, the process benefits from simplicity and potentially lower operational costs, as it does not require additional materials or complex setups. This method is particularly advantageous for producing a straightforward yield of bio-char and other primary pyrolysis products. However, the primary disadvantage of thermal pyrolysis is its relatively inefficient conversion rates and lower quality of liquid and gas products, as evidenced by the lower carbon ratios and energy values in catalyst-free trials.

Conversely, catalytic pyrolysis involves the use of catalysts such as Al and Fe metal powders, and MCM-41/

Table 1 Elemental analysis of liquid products obtained by 400 °C pyrolysis of HCF and HCS

	HCS	Without catalyst	MCM-41/Al	MCM-41/Fe	Al	Fe
C		59.12	52.90	53.74	56.07	54.77
H		7.76	6.58	6.31	6.72	6.94
N		0.653	0.65	0.73	0.62	0.62
O		32.47	39.87	39.22	36.59	37.67
H/C molar ratio		1.56	1.48	1.40	1.43	1.51
O/C molar ratio		0.41	0.56	0.55	0.49	0.52
HHV Mj/kg		25.35	20.20	20.21	22.07	21.75
HCF		Without catalyst	MCM-41/Al	MCM-41/Fe	Al	Fe
C		64.23	65.74	66.47	70.03	66.22
H		8.54	8.65	8.24	8.98	8.38
N		0.945	0.95	1.34	8.38	1.02
O		26.29	24.67	23.95	12.61	24.38
H/C molar ratio		1.58	1.57	1.48	1.53	1.51
O/C molar ratio		0.31	0.28	0.27	0.14	0.28
HHV Mj/kg		29.32	30.27	30.07	34.38	30.11

Al and MCM-41/Fe, which enhance the breakdown of complex organic materials into more desirable and higher value products such as monoaromatic and aliphatic compounds. This method significantly improves the yield and quality of liquid products and facilitates higher conversion rates into gas products due to the catalytic activity and the structured environment provided by catalysts like MCM-41.

However, the use of catalysts in pyrolysis introduces additional costs for catalyst preparation and potential challenges in catalyst recovery and recycling, which can complicate the process and increase operational expenses. Moreover, the effectiveness of the catalyst can be highly dependent on the specific biomass structure, as different materials interact variably with catalysts. This necessitates a tailored approach where the choice of catalyst and process conditions must be optimized based on the specific characteristics of the biomass used. In summary, while catalytic pyrolysis offers enhanced control over product quality and efficiency, leading to potentially higher economic returns from value-added products, it also demands more sophisticated technological inputs and greater initial and ongoing investment compared to thermal pyrolysis. The choice between these two methods should therefore consider the specific requirements of the end products, the available resources, and the economic constraints of the operation.

4 Conclusion

In conclusion, our experimental analysis of HCF and HCS in the pyrolysis process at 400 °C demonstrated that the structural differences in the raw materials

significantly influenced their reactivity and the quality of the resulting products. Metal powder catalysts such as Al proved to enhance the yield and energy values of the liquid products, achieving an impressive HHV of 34.38 Mj/kg for HCF, which indicates a superior performance in removing oxygen from the compounds and facilitating the formation of higher energy products. Conversely, the MCM-41 group catalysts promoted the formation of more structurally varied compounds, thereby diversifying the product spectrum. The findings also emphasize the advantages of catalytic over thermal pyrolysis. While thermal pyrolysis offers a simpler and potentially less costly option that is beneficial for straightforward biochar production, it falls short in terms of conversion efficiency and product quality, as seen in the lower carbon and energy values in catalyst-free trials. Catalytic pyrolysis, employing catalysts such as Al and Fe metal powders, and MCM-41/Al and MCM-41/Fe, considerably enhances the breakdown of biomass into high-value liquid and gas products with increased conversion rates.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s13399-024-05772-2>.

Author contributions Halil Durak planned the study, determined the study parameters, analyzed the data, and wrote the article. Salih Genel conducted the trials and analyzed product.

Funding Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK). This research was supported by the Van Yuzuncu Yıl University Research Fund. (No. FHD-2021–9710).

Declarations

Ethics approval and consent to participate Not applicable.

Competing interests The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Durak H (2023) Comprehensive assessment of thermochemical processes for sustainable waste management and resource recovery. *Processes* 11. <https://doi.org/10.3390/pr11072092>
- Vakulchuk R, Overland I, Scholten D (2020) Renewable energy and geopolitics: a review. *Renew Sustain Energy Rev* 122:109547. <https://doi.org/10.1016/j.rser.2019.109547>
- Galan-Martin A, Tulus V, Diaz I et al (2021) Sustainability footprints of a renewable carbon transition for the petrochemical sector within planetary boundaries. *One Earth* 4:565–583
- Chen W-H, Lin B-J, Lin Y-Y et al (2021) Progress in biomass torrefaction: principles, applications and challenges. *Prog Energy Combust Sci* 82:100887. <https://doi.org/10.1016/j.pecs.2020.100887>
- Seo MW, Lee SH, Nam H et al (2022) Recent advances of thermochemical conversion processes for biorefinery. *Bioresour Technol* 343:126109. <https://doi.org/10.1016/j.biortech.2021.126109>
- Genel S, Durak H (2023) Comparison of catalytic efficiency of MCM-41/metal and metal powder catalysts in *Crambe orientalis* pyrolysis. *Biomass Convers Biorefin*. <https://doi.org/10.1007/s13399-023-04354-y>
- Genel S, Durak H, Genel Y (2023) Catalytic effect of metal powder and MCM-41/metal catalysts on the pyrolysis of cellulose. *Environ Prog Sustain Energy* n/a:e14225. <https://doi.org/10.1002/ep.14225>
- Park HJ, Heo HS, Jeon J-K et al (2010) Highly valuable chemicals production from catalytic upgrading of radiata pine sawdust-derived pyrolytic vapors over mesoporous MFI zeolites. *Appl Catal B* 95:365–373. <https://doi.org/10.1016/j.apcatb.2010.01.015>
- Valizadeh S, Pyo S, Kim Y-M et al (2022) Production of aromatics fuel additives from catalytic pyrolysis of cow manure over HZSM-5, HBeta, and HY zeolites. *Chem Eng J* 450:137971. <https://doi.org/10.1016/j.cej.2022.137971>
- Corma A (1997) From microporous to mesoporous molecular sieve materials and their use in catalysis. *Chem Rev* 97:2373–2420. <https://doi.org/10.1021/cr960406n>
- Adam J, Antonakou E, Lappas A et al (2006) In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials. *Microporous Mesoporous Mater* 96:93–101. <https://doi.org/10.1016/j.micromeso.2006.06.021>
- Dobrzynski P, Fabbri D, Torri C et al (2009) A novel hydroxy functionalized polyester obtained by ring opening copolymerization of L-lactide with a pyrolysis product of cellulose. *J Polym Sci A Polym Chem* 47:247–257. <https://doi.org/10.1002/pola.23149>
- Melo RAA, Giotto MV, Rocha J, Urquieta-González EA (1999) MCM-41 ordered mesoporous molecular sieves synthesis and characterization. *Mater Res* 2:173–179. <https://doi.org/10.1590/S1516-14391999000300010>
- Xue J, Zhuo J, Liu M et al (2017) Synergetic effect of Co-pyrolysis of cellulose and polypropylene over an all-silica mesoporous catalyst MCM-41 using thermogravimetry–Fourier transform infrared spectroscopy and pyrolysis–gas chromatography–mass spectrometry. *Energy Fuels* 31:9576–9584. <https://doi.org/10.1021/acs.energyfuels.7b01651>
- McNeil SJ, Sunderland MR, Leighs SJ (2017) The utilisation of wool as a catalyst and as a support for catalysts. *Appl Catal A Gen* 541:120–140. <https://doi.org/10.1016/j.apcata.2017.04.021>
- Yarbay Şahin RZ (2022) A comparative study on dark adsorption of dyes using mesoporous MCM-41 catalyst. *Res on Chem Int* 48:541–553. <https://doi.org/10.1007/s11164-021-04631-3>
- Lu Q, Shi X, Hu H et al (2016) Research progress on the chemical constituents and bioactivity of *Aesculus chinensis* Bunge var. *chinensis*. *Northwest Pharm J* 31:651–654
- Liu Z (2012) Research progress and exploitation of *Aesculus chinensis* Bunge. *J Anhui Agric Sci* 40:5986–5988
- Li Y, Shaheen SM, Rinklebe J et al (2021) Pyrolysis of *Aesculus chinensis* Bunge seed with Fe₂O₃/NiO as nanocatalysts for the production of bio-oil material. *J Hazard Mater* 416:126012. <https://doi.org/10.1016/j.jhazmat.2021.126012>
- Zaman F, Akhtar N, Guan Y, Huang Y (2020) Thermal degradation kinetic analysis and conversion of *Aesculus indica* to porous carbon. *Ind Crops Prod* 153:112555. <https://doi.org/10.1016/j.indcrop.2020.112555>
- Zaman F, Ishaq MW, Munawar A et al (2023) *Aesculus indica*-derived heteroatom-doped carbon as an electrode material for super-capacitor. *Carbon Lett*. <https://doi.org/10.1007/s42823-023-00565-5>
- Choa E-J, Moonb J-K, Leec C-G, Parka S-J (2022) Removal of triclosan from aqueous solution using biochar derived from seed shell of *Aesculus turbinata*. *Desalination Water Treat* 266:256–267
- Dyjakon A, Noszczyk T (2020) Alternative fuels from forestry biomass residue: torrefaction process of horse chestnuts, oak acorns, and spruce cones. *Energies (Basel)* 13. <https://doi.org/10.3390/en13102468>
- Brems A, Baeyens J, Beerlandt J, Dewil R (2011) Thermogravimetric pyrolysis of waste polyethylene-terephthalate and polystyrene: a critical assessment of kinetics modelling. *Resour Conserv Recycl* 55:772–781. <https://doi.org/10.1016/J.RESCONREC.2011.03.003>
- Van de Velden M, Baeyens J, Brems A, Janssens B, Dewil R (2010) Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renew Energy* 35(1):232–242

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.