



# Microwave-Assisted Camellia oleifera Abel Shell Biochar Catalyzed Fast Pyrolysis of Waste Vegetable Oil to Produce Aromatic-Rich Bio-Oil

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Xia M, Wang Y, Wu Q, Zeng Y, Zhang S, Dai L, Zou R, Liu Y and Ruan R (2022) Microwave-Assisted Camellia oleifera Abel Shell Biochar Catalyzed Fast Pyrolysis of Waste Vegetable Oil to Produce Aromatic-Rich Bio-Oil. Front. Energy Res. 10:837875. doi: 10.3389/fenrg.2022.837875 In this work, *Camellia oleifera* Abel shell was used as a feedstock to prepare biochar by HNO<sub>3</sub> impregnation and pyrolysis. The biochar was used for the catalytic pyrolysis of waste vegetable oil to prepare bio-oil. Experimental results showed that HNO<sub>3</sub> solution treatment had an important effect on the groups and structure of the biochar catalyst. When the solid/liquid ratio of pretreatment was 1:3, the Brunauer–Emmett–Teller specific surface area of the 1:3–600°C biochar is 392.65 m<sup>2</sup>/g, which is approximately 677 times higher than that of untreated biochar. Moreover, the biochar catalyst had a remarkable catalytic performance. The selectivity of the monocyclic aromatic hydrocarbon in the bio-oil was up to 78.82%, and the oxy-compound could be completely removed at the catalytic temperature of 600°C. However, the increase of the catalyst-to-waste vegetable oil ratio and catalytic temperature decreased the bio-oil yield.

Keywords: Camellia oleifera Abel shell, biochar, waste vegetable oil, pyrolysis, aromatic hydrocarbon

# INTRODUCTION

Fossil fuel depletion and the sustained growth of energy consumption result in the huge impact of the rise in energy prices on the global economy. In 2020, the combined consumption of oil, natural gas, and coal accounted for 83.10% of total primary energy consumption worldwide. Greenhouse effect aggravation and the improvement of people's awareness of environmental problems have prompted people to begin searching for alternative energy sources, and the demand for energy has led to great prospects to utilize renewable resources and their biorefinery (Ouyang and Lin, 2014; Hsiao et al., 2020; Khodadai et al., 2020; BP, 2021).

Waste oil can be divided into soapstock, acidified oil from refineries, nonedible woody oil, and waste catering oil (Wang et al., 2021). Edible oil is widely used in commercial activities, catering industry, and home cooking worldwide. More than 15 million tons of waste vegetable oil (WVO) are produced each year worldwide (Mahari et al., 2018; Fan et al., 2021). The disposal or incineration of WVO brings about environmental problems such as greenhouse gas emissions. Recycling and reuse of WVO can be converted into value-added products, reducing greenhouse gas emissions, and bringing about environmental, financial, and social benefits (Loizides et al., 2019). The main component of WVO is fatty acids, and its effective hydrogen-to-carbon ratio is approximately 1.50; thus, it belongs to materials with a high hydrogen-to-carbon ratio (Zhang et al., 2013). At

1

present, WVO is mainly used to prepare biodiesel through transesterification technology. Biodiesel is one of the most recognized alternative fuels because of its potential as an ecological fuel; however, the high content of free fatty acids in WVO inhibits transesterification and reduces biodiesel yield (Hsiao et al., 2020). Therefore, effective use of WVO must be determined.

Last few years, researchers have focused on converting waste into hydrocarbon fuels through thermochemical pathways, such as pyrolysis. This endothermic decomposition process occurs in hightemperature environments and anoxic conditions to produce biochar, bio-oil, and syngas. Pyrolysis is mainly divided into four types, including flash pyrolysis, fast pyrolysis, medium pyrolysis, and slow pyrolysis. Fast pyrolysis, well known for having bio-oil as its main product, is considered the most feasible and economical way to produce bio-oil. The use of traditional heating methods for pyrolysis has not only lowheating efficiency, but also heat loss. Compared with traditional heating methods, microwave heating has the advantages of easy operation, uniform heating of materials, and rapid temperature rise, and the treatment time of microwave heating can usually be reduced to 1% of the time required to use in the electric heating method. Due to its fast heating speed, it may increase production speed, reduce power consumption, and reduce production costs (Hou et al., 2018; Putra et al., 2022). In addition, the aromatic hydrocarbons in the pyrolysis product produced by microwaveassisted catalytic pyrolysis of biomass are greater than those produced via traditional heating methods. Moreover, the coking rate of the catalyst decreases. Microwave-assisted pyrolysis is considered to be a promising technology for efficiently converting waste into clean energy (Mahari et al., 2018; Foong et al., 2020; Ryu et al., 2020; Li et al., 2021; Wang et al., 2021).

Carbon-neutral fuels can replace fossil fuels to produce chemicals, electricity, heat, and fuels. The bio-oil produced by pyrolysis contains more oxy-compounds than diesel and gasoline, and the high oxy-compound content leads to low calorific value, high viscosity, and unstable properties of bio-oil (Ryu et al., 2020; Gupta et al., 2021). Adding catalysts to the pyrolysis system can effectively improve the bio-oil quality; compared with catalysts such as metal oxides, inorganic salts, and zeolite, which are expensive or prone to deactivation, biochar as a catalyst provides added value by potentially reducing waste disposal cost (Feng et al., 2020; Qiu et al., 2020). Biochar exhibits high modification and good stability in acidic and alkaline media; however, untreated biochar has a limited surface area and porosity and relatively poor catalytic ability (Huang et al., 2020a; Shan et al., 2020). Therefore, using biochar after further treatment as a catalyst or catalyst carrier in the catalytic pyrolysis of waste oil has been studied, and its use for the catalytic reforming of bio-oil has presented good results (Lam et al., 2016; Duan et al., 2020).

Alkali metals and alkaline earth metals, functional groups and pore structure, abundant O-containing functional groups on the surface, and adsorption are the reasons why biochar is used as a bio-oil-reforming catalyst (Qiu et al., 2020). Compared with the modification of biochar, the pretreatment of raw materials before pyrolysis has the advantages of low cost, simple operation, and being suitable for large-scale production (Rizwan et al., 2020). Studies have shown that washing pretreatment is a promising pre-hydrolysis method, which is particularly effective for lignocellulosic biomass. It can destroy the structure of biomass before pyrolysis, remove part of inorganic matter, and improve the carbon content of biochar (Diao et al., 2021). Dilute acid pretreatment is a widely used chemical pretreatment method for biomass, and the commonly used acid solutions are H<sub>2</sub>SO<sub>4</sub>, HCl, HNO3, and so on. Studies have shown that acid solution pretreatment of biomass can change the form of biochar and increase biochar porosity (Nikkhah et al., 2020). As a cheap and easy-to-obtain raw material, agricultural and forestry waste has become the main raw material for preparing biochar. Camellia oleifera Abel shell (COAs) is a by-product of the processing of Camellia oleifera, and more than 3 million tons are produced every year (Zhang et al., 2018). Therefore, COAs is a kind of abundant biomass energy, and the valorization of nonfood residues could have a positive impact to some extent as long as the Camelia oleifera cultivation is sustainable. Biomass wastes with high lignin content and low water content are suitable as raw materials for preparing biochar. Compared with ryegrass, corn pericarp, miscanthus, rice husk, and millet husk, etc., the lignin content of COAs is higher, about 31.35-44.8%, and it is more suitable as a raw material for preparing biochar (Huang et al., 2020b; Li and Zhang, 2020).

However, studies on the application of biochar prepared after pretreatment of biomass in the catalytic pyrolysis of WVO are few. Therefore, in this study, the effects of the solid-to-liquid ratio of COAs pretreatment by HNO<sub>3</sub>, carbonization temperature of COAs, the ratio of the feedstock to catalyst, and catalytic temperature on the composition and yield of bio-oil from microwave-assisted fast pyrolysis of WVO have been investigated.

## MATERIALS AND METHODS

### **Experimental Materials**

COAs was obtained from Jinshu Ecological Camellia Professional Cooperative, Shangyou County, Ganzhou City, Jiangxi Province. HNO<sub>3</sub>, of domestic analytical pure, was obtained from Xilong Scientific Co., Ltd. SiC spheres with a diameter of 5 mm were purchased from Xinli Wear-Resistant Materials Co., Ltd. The WVO from a fried shop was filtered and then stored in a 4-°C refrigerator with shading for further experiments. The WVO was 1.0 ml, and n-hexane 5 ml and NaOH–methanol solution (0.5M) 2.5 ml were added, and the solution was refluxed in a 70°C water bath for 10 min. Then, the solution was cooled to room temperature. Then, it was transferred to a graduated test tube, and deionized water was added to make it 20 ml for ultrasonic extraction for 10 min, and the supernatant was taken for GC–MS analysis after centrifugation. The predominant fatty acid composition of WVO is shown in **Table 1**.

## Experimental Process Catalyst Preparation

The COAs was dried in a WF-22G drying oven (WIGGENS, United States, 2019) at 105°C for 24 h, then crushed using a small

Predominant fa	atty acid o	composition	of WV/O
		Johnposition	01 00 00.

	Linoleic (18:2)	Oleic (18:1)	Palmitic (16:0)	Stearic (18:0)	Others
Content (%)	46.36	35.58	13.00	4.69	0.37



grinder, and screened through a 40-mesh sieve for use. The COAs powder and HNO<sub>3</sub> (0.2 mol/L) solution were thoroughly mixed according to M/V (1:1, 1:2, and 1:3) and underwent impregnation for 12 h. Then, the impregnated COAs powder was washed with deionization water until neutral and dried in the drying oven at 105°C. After drying, the material was crushed using the grinder and stored through a 40-mesh sieve for standby. Then, it was calcined in a tubular furnace (OFT-1200X, Hefei Keijing material technology Co., Ltd., China, 2019) at different temperatures (800, 700, 600, and 500°C) for 0.5 h. The carbon was finally collected and stored for the next experiment. The catalyst was named X-T (X: pretreatment M/V; T: carbonization temperature).

### Catalyst Characterization

The functional groups were analyzed by Fourier transforminfrared spectroscopy (FTIR) (Thermo Fisher Nicolet iS5, United States, 2007). The recording range of each sample was  $400-4,000 \text{ cm}^{-1}$ , and the resolution was  $4 \text{ cm}^{-1}$ . A total of 64 scans were performed. The morphology of biochar samples was determined by scanning electron microscopy (SEM) (JEOL JSM-6701F, Japan, 2012). Before the determination, the samples were precoated with gold. N<sub>2</sub> adsorption/desorption isotherms were measured using a specific surface analyzer (Micromeritics ASAP2460, United States, 2018) to evaluate the structural characteristics of biochar. The pore volume and specific surface area were calculated using the t-plot method and Brunauer-Emmett-Teller (BET) theory, respectively.

### Pyrolysis Process of WVO

As shown in Figure 1, the experimental device was a refitted MAS-II microwave oven (SINEO Microwave Chemical Technology Co. Ltd., China, 2015). The microwave absorbent used was 5-mm-diameter SiC spheres (200 g). High-purity nitrogen was added to the system as a carrier gas and protective gas at a flow rate of 5 ml/min. Then, the microwave oven and electric heating belt began to work after nitrogen was introduced into the quartz reactor for 5 min. The catalytic bed temperature reached the set value. The entire heating program of the refitted MAS-II microwave oven was set at 800 W for 5 min and then to 300 W until the end of the reaction process. The heating curve of the microwave absorbent bed and SiC temperature measurement method diagram are shown in Supplementary Figures S1, S2 (Supplementary material). After the refitted MAS-II microwave oven was heated for 5 min, WVO (4 g) was added to the reactor. During the reaction, condensable gas was collected in two U-tubes placed in a mixture of ice and water for subsequent product analysis. According to the quality difference before and after the system, the bio-oil yield was calculated, and the yield of char was negligible. Therefore, the char yield is not discussed in this article.



In this study, the effects of the carbonization temperature of COAs (800, 700, 600, and 500°C), the solid-to-liquid ratio (M/V) (untreated, 1:1, 1:2, and 1:3) in the pretreatment process, the ratio of the feedstock and catalyst (without catalyst, 8:1, 4:1, 2:1, and 1: 1), and the catalytic temperature (600, 550, 500, 450, and 400°C) on the chemical composition and yield of bio-oil were studied.

## **Product Analysis**

Gas chromatography–mass spectrometry (7890B-7000D, Agilent Technologies, United States, 2017) was used to analyze the bio-oil obtained from the pyrolysis of WVO. The analytical conditions were consistent with the previous study (Wu et al., 2020). The GC–MS conditions are as follows: Column: HP-PONA (50 m × 0.200 mm × 0.50 µm); Carrier gas: helium; Vaporizer temperature: 280°C; Ion source temperature: 230°C; Injection mode: split (50:1); Target temperature: 180°C, Heating rate: 5°C/min, and Hold time: 2 min; Target temperature: 280°C, Heating rate: 8°C/min, and Hold time: 3 min.

## **RESULTS AND DISCUSSION**

## **Characterization of the Biochar Catalyst**

The FTIR results of untreated COAs biochar and pretreated COAs biochar are shown in **Figure 2**. Untreated COAs biochar and pretreated COAs biochar show a similar peak shape. In particular, 790, 830, and 870 cm<sup>-1</sup> are caused by aromatic C–H bending. C–H around 1,419 cm<sup>-1</sup>, C=C around 1,577 cm<sup>-1</sup>, and the C=O bond at 2,346 cm<sup>-1</sup> may be caused by the presence of the aldehyde or ketone. The band strength at 3,446 cm<sup>-1</sup> is related to the tensile vibration of the O–H group. The increase of the liquid-to-solid ratio results in a slight increase of the group peak, and its peak value decreases with the increase of carbonization temperature (Wang et al., 2020; Zhang et al., 2021). The group signal peak in biochar after HNO<sub>3</sub> treatment is clearer than that in untreated biochar. However, C=C, C=O, O–H, and other groups were obviously missing when the carbonization

temperature reaches 800°C; thus, high temperature promotes the decomposition of functional groups (Zhang et al., 2021). This scenario indicates that the high temperature is harmful to the groups. This result is consistent with the study of Zhang et al. (2020).

The COAs biochar has a lamellar structure and rough surface, as shown in **Figure 3**. This feature is caused by the COAs structure itself and the devolatilization and breakdown of biomass during carbonization (Shi, 2018; Duan et al., 2020). The increase of the liquid-to-solid ratio and carbonization temperature results in the increase of the lamellar structure and appearance of pore structure. This result is consistent with the N<sub>2</sub> adsorption/desorption isotherm. Acid solution has a corrosive effect. It can destroy and dissolve the cellulose and other substances in the biomass and remove some metals. The removal of metals creates new pores, which is conducive to the volatilization analysis. Moreover, the evaporation degree of volatile substances increases with the increase in carbonization temperature, resulting in the increase in surface area and pore structure formation (Nikkhah et al., 2020).

The results in **Table 2** show that HNO<sub>3</sub> pretreatment significantly affects the specific surface area of the COAs biochar catalyst. The untreated biochar has a very low BET surface area  $(0.58 \text{ m}^2/\text{g})$ . However, the BET surface area increases significantly with the decrease of the solid-to-liquid ratio. Moreover, the specific surface area of the 1:3–600°C biochar is as high as 392.65 m<sup>2</sup>/g, which is approximately 677 times larger than that of the untreated biochar. Furthermore, 1:3–600°C biochar has a relatively high micropore area of  $323.34 \text{ m}^2/\text{g}$ . These findings may be caused by the removal of alkali and alkaline earth metals and some inorganic substances in biomass by HNO<sub>3</sub> pretreatment (Wang et al., 2020). The larger the specific surface area of the biochar, the more the contact surface area and active sites can be provided in the catalytic system (Yang et al., 2020).

## Effects of Carbonization Temperature and Solid-to-Liquid Ratio During the COAs Pretreatment on the Bio-Oil

The effects of the solid-to-liquid ratio (M/V) (untreated, 1:1, 1:2, and 1:3) and carbonization temperature (800, 700, 600, and 500°C) on bio-oil constituents were studied. The feedstock-to-catalyst ratio was 8:1, and the catalytic temperature was kept at  $450^{\circ}$ C.

The distribution of pyrolysis products under different biochar catalyst conditions is shown in **Figure 4**. The main components of bio-oils were divided into five categories, as shown in **Figure 4B**:  $C_{20+}$  hydrocarbons, green diesel ( $C_{13}$ – $C_{20}$ ), green gasoline ( $C_{10}$ – $C_{12}$ ), green naphtha ( $C_5$ – $C_9$ ), and oxy-compound (Khodadadi et al., 2020). The content of green naphtha was significantly higher than that of untreated COAs biochar with the increase of the liquid-to-solid ratio. Compared with that obtained under the untreated biochar catalyzed condition, the selectivity of green naphtha in the liquid product obtained under the catalyzed condition of 1:3–600°C biochar greatly increased from 36.01 to 67.17%. The reason is that



#### TABLE 2 | BET results of COAs biochar.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>micro</sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm³/g)	
Untreated-600°C	0.58	0.33	0.00	0.00	
1:1-600°C	173.36	72.77	0.11	0.03	
1:2-600°C	333.47	228.18	0.19	0.10	
1:3–600°C	392.65	323.34	0.17	0.13	

the active groups, surface structure levels, and BET surface area of biochar prepared from COAs pretreated with HNO3 were increased, which was beneficial to the catalytic performance of biochar; this scenario enhanced catalytic cracking of decarboxylation and decarbonylation of long-chain fatty acids, alcohols, and esters in the process of catalytic pyrolysis and accelerated the Diels-Alder reaction to convert alkenes to aromatics (Duan et al., 2020). Moreover, the content of aromatics was increased, and the content of oxy-compound in bio-oil was decreased. The presence of oxy-compound in bio-oil can cause it to be chemically unstable and corrosive and reduce its calorific value (Nikkhah et al., 2020). As shown in Figure 4A, compared with those under untreated biochar condition, the content of the monocyclic aromatic hydrocarbon (MAH) in the bio-oil under the catalyzed condition of 1:3-600°C biochar increased significantly, and the selectivity of MAH increased from 46.08 to 66.86%. Moreover, the content of polycyclic aromatic hydrocarbon (PAH) was reduced, and the selectivity dropped

from 37.26 to 15.90%. When the solid-to-liquid ratio was 1:2 and 1:3, the MAH content first increased and then decreased with the increase of carbonization temperature, and the PAH content first decreased and then increased. The increase of carbonization temperature resulted in the increase of the release of volatile substances in biomass, formation of the pore structure, and increase in the specific surface area. Moreover, the microporous structure inhibited the formation of high molecular weight aromatic hydrocarbons. However, the pore structure of biochar was destroyed when the carbonization temperature was excessively high, and the inhibitory effect was reduced (Zhang et al., 2021). Increasing MAH content and reducing PAH content can be considered the advantages of HNO<sub>3</sub> pretreatment for biochar preparation. According to the results of catalytic pyrolysis experiments, when 1:3-600°C COAs biochar was used as a catalyst, the content of MAH is the highest, and the content of PAH is the lowest, and the content of green naphtha is also the highest in terms of carbon number



classification. Therefore, 1:3–600°C COAs biochar was used in the following experiments.

# Effects of the Feedstock-to-Catalyst Ratio on the Bio-Oil Composition and Yield

The solid-to-liquid ratio of the pretreatment was 1:3, the catalytic temperature was fixed at 450°C, and the carbonization temperature was 600°C to study the effects of the feedstock-to-catalyst ratio (catalyst free, 8:1, 4:1, 2:1, and 1:1) on the bio-oil composition and yield. The bio-oil yields at different feedstock-to-catalyst ratios are shown in **Figure 5A**. The pyrolysis of WVO without catalyst had the highest bio-oil yield (82.50%). The bio-oil yield decreased with the increase of catalyst amount.

Therefore, the increase of catalyst amount provides abundant catalytic active sites, prolongs the catalytic reaction time, promotes the secondary fracture of pyrolysis steam, and forms considerable noncondensable vapor, leading to the decline of bio-oil yield from 82.50 to 41.25% (Jin et al., 2018).

The composition of bio-oil collected at different feedstock-tocatalyst ratios are shown in **Figure 5B**. The area percentage of oxy-compound decreased significantly from 66.00% (catalystfree) to 2.96% (8:1). The oxy-compound in the bio-oil produced without catalysis mainly consists of acids, alcohols, esters, and ketones. The selectivity of green naphtha, green gasoline, and green diesel was all lower than 15.00%, which limits its use in industry. The small amount of oxy-compound in the bio-oil produced by the catalyst was mainly alcohols, esters, and ketones. The area percentage of acids, alcohols, and esters decreased obviously with catalysis. The contents of green naphtha and gasoline were significantly increased with the use of the catalyst. However, the selectivity of  $C_5$ – $C_9$  was significantly inhibited, and the selectivity of  $C_{13}$ – $C_{20}$ ,  $C_{20+}$  hydrocarbons,



**FIGURE 5** | Effect of the feedstock-to-catalyst ratio on bio-oil. (A) Area percentage of the bio-oil containing oxy-compound, hydrocarbon (alkene and alkane), MAH, PAH, the total aromatics, and the bio-oil yield; (B) area percentage of oxy-compound,  $C_{20+}$  hydrocarbons, green diesel ( $C_{13}-C_{20}$ ), green gasoline ( $C_{10}-C_{12}$ ), and green naphtha ( $C_{5}-C_{9}$ ) in bio-oil.



and oxy-compound increased with the increase of catalyst dosage (more than 1 g). Long-chain fatty acids, alcohols, and esters were catalyzed to decarboxylation and decarbonylation and dehydrogenation/hydrogenation to form short-chain hydrocarbons, which then formed olefins or further cyclization and aromatization to alicyclic compounds and aromatic hydrocarbons (Lam et al., 2016). As a result, the area percentage of oxy-compound and hydrocarbons decreased considerably, whereas the area percentage of PAH and MAH increased considerably. The area percentage of hydrocarbons decreased and reached the lowest of 9.76% at 4:1 with the decrease of the feedstock-to-catalyst ratio. The further decrease of the feedstock-to-catalyst ratio slightly increased the hydrocarbon content. Olefins can be converted to aromatic hydrocarbons by the Diels-Alder reaction, a kind of a cycloaddition reaction (Lam et al., 2016). The area percentage of MAH increased from 5.10% (catalyst-free) to 69.21% (4:1). The area percentage of PAH increased from 0.00% (without catalyst) to 20.30% (2:1). High catalyst usage can hinder the passage rate of volatile substances, thus prolonging the catalytic reaction time. This scenario leads to the secondary fracture reaction and repolymerization reaction. As a result, the hydrocarbon content decreased, and the contents of MAH and PAH increased (Balasundram et al., 2018). PAHs have harmful biological effects, such toxicity, mutagenicity, as carcinogenicity, and adverse environmental effects. They are also precursors of carbon deposits, which greatly affect catalyst activity, and the high oxygen content of bio-oil affects the bio-oil quality (Zhang et al., 2014; Sun et al., 2021). It is worth noting that when the feedstock-to-catalyst ratio was 8:1 to 4:1, the increase rate of MAH and total aromatics was lower than that of the catalyst (Ding et al., 2018). Therefore, it is not economically feasible to increase the aromatics content by simply increasing the amount of the catalyst. Therefore, by analyzing the yield and composition of bio-oil, the feedstock-to-catalyst ratio of 8:1 was chosen for subsequent experiments.

# Influence of Catalytic Temperature on the Bio-Oil Composition and Yield

The effects of catalytic temperature (600, 550, 500, 450, and 400°C) on the composition and yield of bio-oil were studied. The catalyst was 1:3-600°C biochar, and the feedstock-to-catalyst ratio was 8:1. The bio-oil components and yield distributions at different catalytic temperatures are shown in **Figure 6**.

As shown in **Figure 6A**, the yield of bio-oil decreased with the increase of catalytic temperature, and the maximum yield was 50.00 wt% at 400°C. Pyrolysis is an endothermic reaction, which can be promoted by a high temperature. High catalytic temperature (the temperature in the current study exceeded 400°C) can provide much energy, promoting long-chain compound fracture and small molecule compound formation. The condensable part of the small molecule compounds after condensation formed bio-oil. However, the secondary pyrolysis of the pyrolysis vapor was promoted when the catalytic temperature was further increased, and considerable noncondensable vapor was generated, leading to the bio-oil yield decrease (Wang et al., 2018). This scenario was also the main reason for the decrease of bio-oil yield as the catalytic temperature increased from 400 to 600°C.

The results showed that when the catalytic temperature increased from 400 to 600°C, the oxy-compound content decreased from 2.63 to 0.00%. The high catalytic temperature promoted the deoxidation reaction and reduced the oxy-compound content. The area percentage of the hydrocarbon decreased from 15.15% (400°C) to 6.03% (550°C). The area percentage of the MAH increased from 66.86% (450°C) to 78.82% (600°C). The high catalytic temperature also promoted PAH formation, and the area percentage of PAH increased from 10.15% (400°C) to 16.07% (550°C); the total aromatics content was up to 93.27% when the catalytic temperature was 550°C. This occurrence was due to the increase of temperature, which caused short-chain alkene oligomerization to produce mixtures of long-chain alkenes and alkanes; aromatic hydrocarbons were produced by aromatization, alkylation, and isomerization of long-chain

alkenes and alkanes (Wu et al., 2020). Therefore, high temperature promotes deoxidation and aromatization at the expense of oxycompound and olefins, and this finding is consistent with the results of Duan et al. (2020). However, the area percentage of MAH and hydrocarbons showed an opposite trend to PAH when the catalytic temperature was further increased to 600°C, indicating that the high catalytic temperature reduced PAH production. As shown in Figure 6B, the green naphtha content increased from 67.17 to 76.32% when the catalytic temperature was increased from 450 to 600°C, and the area percentage of C<sub>10+</sub> hydrocarbons decreased significantly. This result was attributed to the catalytic fast pyrolysis process. The high catalytic temperature promoted the cracking reaction of long-chain fractions (C<sub>10+</sub> hydrocarbons) (Duan et al., 2020). When the catalytic temperature was 600°C, the area percentage of MAH was up to 78.82%, and the area percentage of green naphtha was 76.32%, and also the oxycompound content was the lowest, so the best catalytic temperature was 600°C.

## CONCLUSION

In this study, COAs biochar was proposed for microwave-assisted catalytic pyrolysis of WVO to produce aromatic-rich bio-oil. The micropore area and BET surface area of  $1:3-600^{\circ}$ C biochar were 323.34 and 392.65 m<sup>2</sup>/g, respectively. The high carbonization temperature caused the loss of O–H and C–O groups. High catalytic temperature and catalyst dosage could promote deoxidation but also reduce the bio-oil yield. The oxy-compound significantly decreased by 63.04% from no catalysis to the feedstock-to-catalyst ratio of 8:1, thus showing significant deoxygenation capacity. The total aromatics content was up to 93.27% when the catalytic temperature was 550°C.

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## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**; further inquiries can be directed to the corresponding author.

## **AUTHOR CONTRIBUTIONS**

MX: conceptualization, methodology, data curation, and writing-original draft; YW: resources, supervision, project administration, and funding acquisition; QW: writing-review and editing; YZ: investigation and visualization; SZ: validation; LD: software; RZ: formal analysis; YL: project administration; and RR: funding acquisition.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenrg.2022.837875/full#supplementary-material

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