Microwave-assisted pyrolysis of vegetable oil soapstock: Comparative study of rapeseed, sunflower, corn, soybean, rice, and peanut oil soapstock

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Abstract: In this study, the effects of catalytic temperature and the type of soapstock on products from microwave-assisted pyrolysis were investigated. HZSM-5 was used as the catalyst to study the pyrolysis of six different soapstocks at 200°C, 300°C, and 400°C catalytic temperature. Results showed that the bio-oil yields initially increased and then decreased with the increase in catalytic temperature. When the catalytic temperature was 300°C, the bio-oil reached up to the maximum value (65.8 wt.%). Findings indicated that the composition of bio-oil was related to the degree of unsaturation of fatty acids sodium in the soapstocks. In the case of saturated fatty acid sodium, a series of alkanes was formed, whereas the pyrolysis of monounsaturated fatty acid sodium resulted mainly in cycloalkanes, the cycloalkenes obtained from bio-oil was produced by polyunsaturated fatty acid sodium.

Keywords: microwave pyrolysis vegetable oil soapstock, HZSM-5, bio-oil
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1 Introduction

The sudden increase in the need for energy is due to rapid increase in the world's population and development of technologies; however, the current energy resources with limited reserves are decreasing[1]. Soapstock, a byproduct of the refinement of vegetable oils, is another potential biodiesel feedstock. It consists of a heavy alkaline aqueous emulsion of lipids, containing about 50% water and the remaining consists of fatty acid soudium (FAS), phosphoacylglycerols, triacylglycerols, pigments, and other minor nonpolar soybean components[2]. The high H/C_{eff} value of soapstocks makes them useful as cheap and abundant hydrogen sources[3]. Several researchers have also converted soapstocks, which possesses the characteristics of low cost and high fatty acid content, into biodiesel[4-6]. Although edible oil can also be used for large-scale production of biodiesel, it is not as cheap as using waste oil/fat, which can be obtained easily[7]. At present, in the Chinese biodiesel and fatty acid industries, waste kitchen oil has exceeded 5 000 000 t/a and soapstock production has reached 1 500 000 t/a[7]. Unreasonable use of soapstocks or acid oils causes waste of resources and environmental pollution. Currently, numerous studies have used fast microwave-assisted catalytic pyrolysis of soapstocks to produce hydrocarbon-rich bio-oils[8,9].

Pyrolysis is a thermochemical process that can be used to break down certain materials into a liquid product called bio-oil[2]. Although pyrolysis is an old technology, it has been attracting increasing attention compared with other thermochemical processes as a result of significant progress in the past decade[10,11]. However, pyrolysis technology still exhibits many defects. In the traditional pyrolysis process, energy is diffused from the surface of the biomass to the inside; thus, biomass cannot be heated simultaneously, the pyrolysis rate is slow, and the yield and quality of the resulting liquid biofuel and the energy efficiency of the entire process must be improved[12,13]. Nevertheless, several approaches can solve these technical problems. Fast pyrolysis, which uses high heating rate, can reach the desired pyrolysis temperature instantaneously to reduce biomass carbonization and improve bio-oil yield and quality[14]. Recently, Ruan et al.[15] proposed the microwave-assisted catalytic fast pyrolysis (MACFP), which is a unique method that can bring many opportunities to

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biomass conversion. In contrast to traditional pyrolysis, MACFP can penetrate the material and generate energy internally; hence, the entire material can be heated simultaneously and not only externally[13]. MACFP has been used by many researchers due to its advantages of fast and even heating, easy control, and selective heating[16]. Wu et al.[17] concluded that microwave pyrolysis tends to produce less gas compared with conventional pyrolysis. Moreover, microwave radiation has the unique function of improving the process, modifying the selectivity, and performing the reaction that does not occur under traditional heating[18,19]. Microwave heating is also environmentally friendly because it reduces the formation of harmful products and minimizes the emission of pollutants[20].

At present, several studies have been conducted on the conversion of soapstocks using pyrolysis technology. Hilten et al.[21] studied the catalytic pyrolysis of an acidulated peanut oil soapstock (POS). Zhou et al.[13] investigated the co-pyrolysis of straw stalks and soapstocks, and Dai et al.[22] studied the co-pyrolysis of soapstocks and waste tires. Lappi and Alen[23] conducted a comparative experiment on pyrolysis based on various soapstocks under catalyst-free conditions. However, most of these studies studied the effect of only one type of soapstock during their experimental research.

The relationship between catalytic temperature and type of soapstock is rarely investigated. Therefore, in this study, we compared the effects of different catalytic temperatures on the pyrolysis of various soapstocks, thereby addressing the limitations of previous investigations and aiding future studies. Zhang et al.[24] suggested that a high pyrolysis temperature seriously affected the formation of aromatics. Zhou et al.[13] found that the optimum temperature range of MACFP was 500°C-550°C and a catalyst was used to remove oxygen in the pyrolysis reaction[25]. HZSM-5 zeolite exhibits excellent deoxygenating capacity and shape-selectivity for aromatics[26,27]. Dai et al.[9] suggested that the HZSM-5 catalyst enhanced the bio-oil yield. On the basis of the three conditions of the previously mentioned experiments, the pyrolysis temperature in the present study was fixed at 500°C, catalyst temperatures were set at 200°C, 300°C and 400°C, and HZSM-5 catalyst was used to study the pyrolysis of six types of soapstock, namely rapeseed oil soapstock (ROS1), soybean oil soapstock (SOS), corn oil soapstock (COS), sunflower seed oil soapstock (SSOS), rice oil soapstock (ROS2), and peanut oil soapstock (POS).

2 Material and methods

2.1 Materials

Soapstock was used as the research object in this study (Yihai Kerry Oils and Foodstuffs Co. Ltd., Jiangxi, China). It was saponified with slightly excessive NaOH and then dried under an anaerobic environment at 90°C for 48 h. Thereafter, the dried soapstock was mechanically pulverized and sieved to less than 2 mm. Proximate and elemental analyses were conducted to determine the fundamental characteristics of soapstock powders (Table 1). In the pyrolysis experiments, silicon carbide (SiC) particles with a grit size of 30 were used as the microwave absorbent. The HZSM-5 zeolite (Si/Al ratio = 25; Catalyst Plant of Nankai University, China) was calcined at 550°C for 4 h to stabilize the structure.

2.2 Analytical methods and experimental instruments

2.2.1 Elemental analysis

The contents of carbon and hydrogen elements in the six soapstocks was determined via element analyzer (Elementar Vario EL III, Germany), and the content of oxygen element was determined by difference. Calculating higher heating value (HHV) and the effective hydrogen index (H/C_{eff}) through elemental analysis, the results were showed in Table 1.

Table 1 Ultimate and proximate analysis of six soapstocks

Characteristics	ROS1	SSOS	COS	SOS	ROS2	POS
A^a	16.00	16.67	16.82	16.88	17.22	17.82
C	63.11	67.62	62.75	67.48	67.54	67.49
H	10.03	11.45	10.05	9.95	11.20	10.93
O	10.86	4.26	10.38	5.69	4.04	3.76
HHV^b/MJ·kg^{-1}	32.88	36.83	32.83	34.78	36.51	36.19
$H/C_{eff}{}^c$	1.65	1.94	1.67	1.64	1.90	1.86

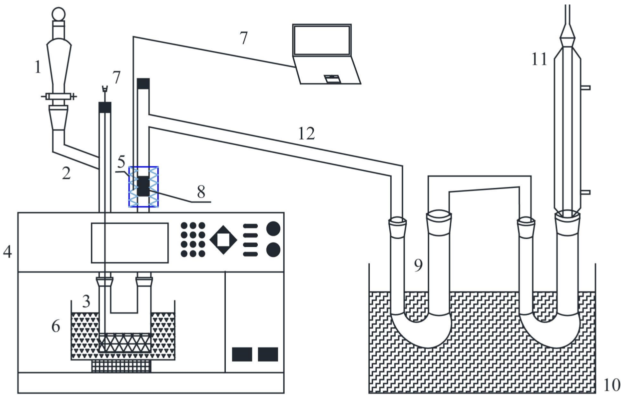
Note: A: ash content; ^{a} Dry basis;
^{b} Higher heating value, HHV(MJ/kg)=34.1C+123.9H-9.85O+6.3N+19.1S[8];
^{c} The effective hydrogen index (H/C_{eff})= (H-2O-3N-2S)/C[38].

2.2.2 Bio-oil analysis

After filtering using a 0.22 μm organic syringe membrane, the bio-oil was analyzed by gas chromatography–mass spectrometry, equipped with a chromatographic column (HP-5ms; 30 m× 0.25 mm × 0.25 μm). The conditions were as follows. Helium was selected as the carrier gas, and the flow rate was set to 1.0 mL/min. The sampling size was 0.2 μL, and the split ratio was 20:1. The column temperature was heated to 60°C for 2 min, increased to 280°C at a rate of 10°C/min, and then kept at 280°C for 10 min. The vaporizer temperature was 250°C. The temperatures of the ion source and detector interface were 230°C and 280°C, respectively. The analysis mode was the scan mode. We identified the components in the bio-oil by comparing their mass spectra with those from the National Institute of Standards and Technology Mass Spectral Data Library. We used a semi-quantitative method to determine the relative content of each component in the bio-oil by calculating the chromatographic area percentage.

2.2.3 Experimental installation

The apparatus used in the experiment is shown in Figure 1. The system comprises (1) Semi-continuous biomass feeder; (2) feed inlet; (3) quartz reactor; (4) microwave device; (5) heating jacket; (6) microwave absorbent (SiC) bed; (7) K-type thermocouple to measure the pyrolysis temperature; (8) catalyst bed; (9) U-type condenser; (10) tap water of 2°C; (11) connection for vacuum pump; (12) quartz connector.



1. Semi-continuous biomass feeder 2. Feed inlet 3. Quartz reactor 4. Microwave device 5. Heating jacket 6. Microwave absorbent (SiC) bed 7. K-type thermocouple to measure the pyrolysis temperature 8. Catalyst bed 9. U-type condenser 10. Tap water of 2°C 11. Connection for vacuum pump 12. Quartz connector

Figure 1 Schematic diagram of external catalytic co-pyrolysis

2.3 Experimental scheme

The experiment aims to study pyrolysis of six soapstocks at different catalytic temperatures. Each type of soapstock was set at three catalytic temperatures (200°C, 300°C, and 400°C). The raw materials were pyrolyzed in the microwave oven (MAX, CEM) at 800 W power and 2450 MHz frequency. 10 g of soapstock and 5 g of HZSM-5 catalyst (soapstock:catalyst = 2:1) were weighed and placed the quartz reactor in a quartz beaker. Then 900 g of SiC was buried; the height of SiC from the reactor nozzle is 3-5 cm. Subsequently, the quartz beaker was placed into the microwave instrument and the experimental device was set up according to the diagram. The catalytic and pyrolysis temperatures were set to 500°C and then began heating. When the temperature of microwave oven reached 500°C and waiting for 1-2 min, the soapstock was added into the quartz reactor from the feeder. The power of the vacuum pump should be adjusted appropriately to ensure the smooth operation of the experiment. A stable temperature was kept during the reaction until no obvious white gas was evident and then heating was stopped. Gas condensation was achieved by adding ice water to the beaker that contained the condenser. After the reaction, the liquid in the condenser was collected as bio-oil; the solid material accumulated on the catalyst HZSM-5 was called coke, whereas the solid residue accumulated in the quartz reactor was called bio-char. The four material yields are calculated as follows[28]:

$$Y_{oil}\,(\text{wt\%}) = \frac{W_2 - W_1}{W} \times 100 \qquad (1)$$

$$Y_{char}\,(\text{wt\%}) = \frac{W_4 - W_3}{W} \times 100 \qquad (2)$$

$$Y_{coke}\,(\text{wt\%}) = \frac{W_6 - W_5}{W} \times 100 \qquad (3)$$

$$Y_{gas}\,(\text{wt\%}) = 100\% - Y_{oil} - Y_{char} - Y_{coke} \qquad (4)$$

where, W is the weight of the soapstock; W_1 is the weight of empty collector; W_2 is the weight of the collector after the reaction; W_3 is the weight of the empty reactor; W_4 is the weight of the reactor after the reaction; W_5 is the weight of catalyzer before the reaction; and W_6 is the weight of the catalyzer after the reaction.

3 Results and discussion

3.1 Elemental analysis, HHV and H/C$_{\text{eff}}$ of soapstock

The elemental analysis, HHV and H/C$_{\text{eff}}$ of six soapstocks is shown in Table 1. From the table, the carbon contents of SSOS, SOS, ROS2, POS have a close content of about 67%, and the ROS1 and COS have similar carbon contents, which are 63.11% and 63.75% respectively. The hydrogen content of six soapstocks is close to 10%, and the lowest hydrogen content is 9.95% (SOS), the highest is 11.45% (SSOS). ROS1 and COS contain higher oxygen, which are 10.86% and 10.38% separately, and the remaining soapstocks have a low oxygen content (less than 6%), the order of the remaining soapstocks in terms of oxygen content is SOS > SSOS > ROS2 > POS. The ash content of soapstock is close to between 16% and 18%. Ash content of ROS2 and POS are slightly higher than other soapstocks. In a way, it is beneficial to use agricultural resources with higher content of ash as catalysts for thermal conversion experiment[29]. Among all the soapstocks, SSOS shows the highest higher heating value (HHV) of 36.83 MJ/kg, and COS has the lowest HHV of 32.83 MJ/kg.

3.2 Analysis of pyrolysis product distribution

ROS1, SSOS, COS, SOS, ROS2, and POS were pyrolyzed at catalytic temperatures of 200°C, 300°C, and 400°C, the pyrolysis products yield obtained from them are showed in Table 2, which is consisted of gas, bio-char, coke and bio-oil.

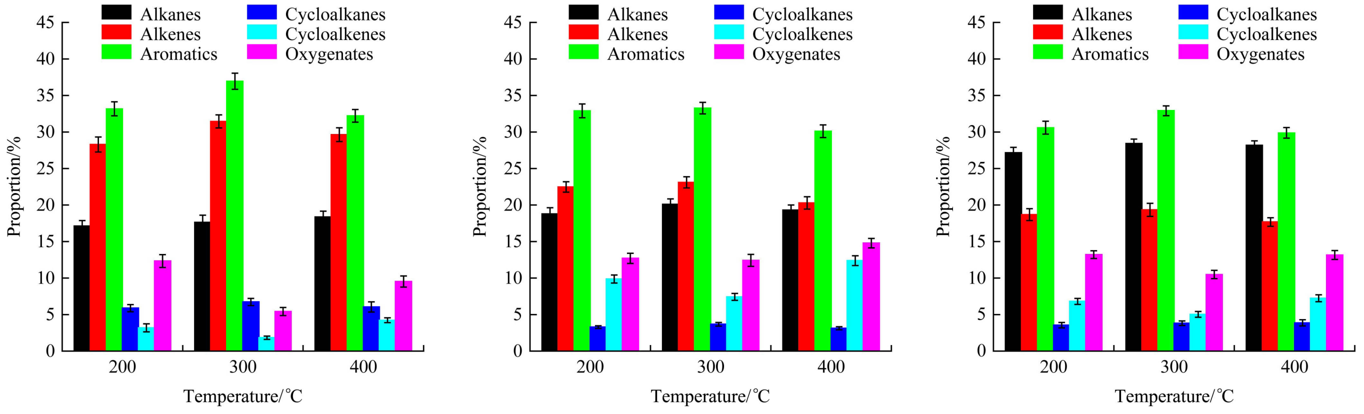
As catalytic temperature rose from 200°C to 400°C, the gas yields of six soapstocks all initially decreased and then increased, where ROS1 gas yield was lower than others. The bio-oil yield initially increased and then decreased with the increase in catalytic temperature from 200°C to 400°C and reached the maximum at 300°C. The maximum yield of bio-oil of ROS1, SSOS, COS, SOS, ROS2, and POS were 65.8%, 57.9%, 58.1%, 60.4%, 60.1%, and 55.3% respectively. The bio-char yields of six soapstocks had no obvious change with different catalytic temperature, they all keep in about 21%, this phenomenon may be related to the ex situ catalysis[24], since the temperature in microwave reactor was a specific 500°C, the change in external catalyst temperature did not affect biochar production. The coke yields of six soapstocks decreased successively with the increase in catalytic temperature. This result was possibly due to the cracking of vapors on catalytic sites and desorption of heavy compounds; the polymerization of aromatics with oxygenates to form coke also occurred at a low catalytic temperature[30,31]. The highest coke yield was 4.8% (200°C, ROS1) and the lowest was 1.9% (400°C, SOS). From Table 2, the product distribution obtained by pyrolysis of these soapstocks at different catalytic temperatures indicates that the catalytic temperature was closely related to the yield of bio-oil. The maximum bio-oil yield can be obtained by pyrolysis of each soapstock at a specific catalytic temperature.

Table 2 Product yields of pyrolysis of six soapstocks at different catalytic temperatures

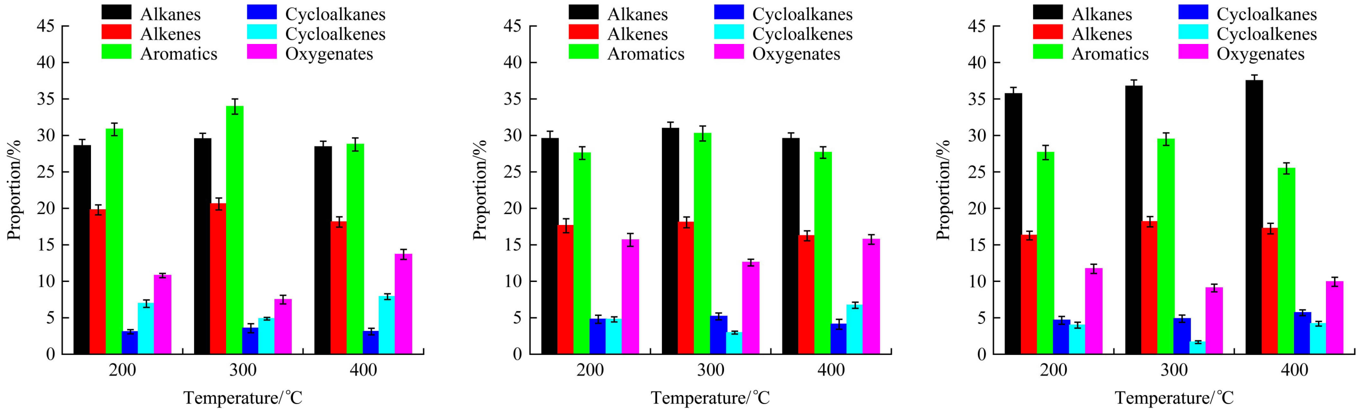
Temperature/°C	Bio-oil/wt%	Bio-char/wt%	Gas/wt%	Coke/wt%
ROS1-200	58.9	20.3	16.0	4.8
ROS1-300	65.8	21.0	9.6	3.6
ROS1-400	62.1	20.8	14.5	2.6
SSOS-200	53.4	21.3	21.6	3.7
SSOS-300	57.9	21.0	18.5	2.6
SSOS-400	56.6	21.3	20.1	2.0
COS-200	51.4	20.1	24.8	3.7
COS-300	58.1	20.7	18.2	3.0
COS-400	57.0	20.3	20.7	2.0
SOS-200	54.8	21.0	20.3	3.9
SOS-300	60.4	20.6	16.0	3.0
SOS-400	58.3	20.4	19.4	1.9
ROS2-200	53.9	20.2	22.1	3.8
ROS2-300	60.1	20.6	16.2	3.1
ROS2-400	57.2	21.7	18.7	2.4
POS-200	50.1	21.0	25.7	3.2
POS-300	55.3	20.3	21.5	2.9
POS-400	51.8	20.7	25.4	2.1

3.3 Effect of catalytic temperature on bio-oil composition

In order to investigate the effect of catalytic temperature on compounds of bio-oil, GC-MS was used to analyze the bio-oil obtained from pyrolysis of soapstocks at different catalytic temperatures, and the results are shown in Figure 2. With the catalytic temperature increasing, the proportion of cycloalkenes and oxygenates of all the soapstocks initially decreased and then increased, reaching the minimum at 300°C. Duan et al.[39] had explained the cause of oxygenates change. When the vapor generated from pyrolysis passed through HZSM-5, deoxidation and cracking reactions occurred. And catalytic temperature higher than 300°C inhibited deoxygenation and aromatization, resulting in an increase in oxygenates. Alkanes content of SOS, SSOS, ROS2, COS, cycloalkanes of SOS, SSOS, ROS2, ROS1, COS, and the alkenes, aromatics of all the soapstocks firstly increased and then decreased, reaching the maximum at 300°C. Zhang et al.[24] indicated that as the catalytic temperature changes from 249°C to 375°C, the proportion of monocyclic aromatic hydrocarbons of bio-oil in low-density polyethylene increases due to the enhanced hydrogen transfer reaction. When the catalytic temperature exceeded 375°C, the increasing catalytic temperature promoted pyrolysis steam cracking reaction and reducing the aromatic yield. In addition, the dealkylation of aromatics was also facilitated at the elevated catalytic temperatures, resulting in an increase of simple aromatic hydrocarbons[30,32]. As the catalytic temperature increased, the alkane content of ROS1 and the alkane and cycloalkane contents of POS increased, the different result may be related to the type and compound of the soapstocks. If the oxygenates and N-counting compounds occupied a high proportion in bio-oil, the value of bio-oil application would be reduced[25]. From the analysis and induction of the above data, 300°C was the most suitable catalytic temperature for pyrolysis.



a. Rapeseed oil soapstock (ROS1) b. Sunflower seed oil soapstock (SSOS) c. Corn oil soapstock (COS)



d. Soybean oil soapstock (SOS) e. Rice oil soapstock (ROS2) f. Peanut oil soapstock (POS)

Figure 2 Proportion of different compositions

3.4 Effect of soapstocks properties on bio-oil composition

3.4.1 GC-MS of bio-oil at 300°C catalytic temperature

Bio-oil obtained from pyrolysis of soapstock using HZSM-5 as a catalyst had been analyzed by GC-MS in order to study the effect of catalytic temperature on bio-oil compounds. The results were shown in Table 3. Based on the conclusions of previous analysis, Table 4 only showed the analysis of the compounds under the catalytic conditions of 300°C. Usually, the bio-oil from cmicrowave-assisted pyrolysis of soapstock contains alkane, alkenes, aromatics, and a part of oxygenates, a small amount of a nitrogen-containing compound. Among them, alkanes, alkenes, and aromatics roduced by pyrolysis and aromatization of fatty acid salts are the main components of bio-oil. As can be seen from Table 3, the alkanes in bio-oil of ROS1, SSOS, COS, SOS, ROS2, POS mainly include octane, nonane, decane, alkanes of C11-C14 and cycloalkanes, all the soapstocks contain a low relative content of pentadecanes. The tridecane, dodecane and cycloalkenes have high levels in all soapstocks. The total alkane content was up to 41.62 area% (POS) and the lowest was 23.78 area% (SSOS). About alkenes, the C15 and C17 alkenes content was highly reflected in all soapstocks, as well as nonene, nonadiene and isomers, decene, undecene and alkenes of C13 and C14 also account for a proportion. Most of the alkenes are monoalkene, which was one of the typical products of sodium oleate[33]. The total alkenes content was highest in ROS1 (33.42%) and lowest in POS (19.83%). The aromatics are mainly composed of ethylbenzene, xylene, trimethylbenzene and its isomers, methylnaphthalene, butylbenzene, pentylbenzene, hexylbenzene and their isomers, and some of them contain certain indene (SOS, POS). The highest content of aromatic was found in ROS1 (36.94%) and the lowest was reflected in POS (29.48%). An obvious feature can be observed that these aromatics mainly include C8-C12 aromatics, Ayanoglu and Yumrutas[34] indicated that the aromatics of C8-C12 are the main components of gasoline. As for oxygenates, it can be seen from Table 3 that the higher oxygenates in the bio-oils of ROS1, SSOS, COS, SOS, ROS2, POS are alcohols and ketones. The oxygen content can reach up to 12.57% (ROS2) and the lowest was 5.43% (ROS1). The oxygen content can reflect the utilization value of bio-oil, and it is beneficial that the bio-oil has lower oxygen content. In addition, it is worth noting that the chemical instability of biofuels and other undesirable physical properties of biofuels are affected by the presence oxygenated components.

Table 3 Relative content (area%) of the chemical compositions presented in the bio-oil at a catalytic temperature of 300°C

Compounds identified in bio-oil	Molecular formula	Area%					
		ROS1	SSOS	COS	SOS	ROS2	POS
Alkanes selectivity/%							
Octane	C_8H_{18}	1.59	1.62	1.08	0.87	1.11	2.32
Nonane	C_9H_{20}	2.27	2.11	3.79	2.96	2.89	3.56
Decane	$C_{10}H_{22}$	2.29	2.84	2.29	3.59	4.13	3.94
Undecane	$C_{11}H_{24}$	2.96	3.88	3.88	4.04	3.92	5.88
Dodecane	$C_{12}H_{26}$	3.26	4.11	8.37	8.06	7.84	7.06
Tridecane	$C_{13}H_{28}$	3.37	4.26	6.91	7.13	8.61	9.78
Tetradecane	$C_{14}H_{30}$	1.89	1.15	2.11	2.56	2.13	3.36
Pentadecane	$C_{15}H_{32}$	0	0.13	0	0.32	0.33	0.85
Cycloalkanes	$C_8 - C_{16}$	6.73	3.68	3.81	3.56	5.18	4.87
Alkanes overall yields/%		**24.36**	**23.78**	**32.24**	**33.09**	**36.14**	**41.62**
Olefins selectivity/%							
Octadiene	C_8H_{16}	0.95	0.56	0.12	0.35	0.41	0.35
Nonene	C_9H_{18}	2.11	1.54	0.37	0.68	0.56	0.51
Nonadiene and isomers	C_9H_{16}	2.24	1.68	1.75	1.41	1.06	0.82
Decene	$C_{10}H_{20}$	2.38	1.72	0.94	1.03	1.21	1.37
Undecene	$C_{11}H_{22}$	3.77	2.09	1.98	1.69	1.38	1.45
Dodecene	$C_{12}H_{24}$	1.17	0.58	0.93	0.86	0.74	0.59
Tridecene	$C_{13}H_{26}$	2.67	1.39	1.28	1.57	1.27	1.46
Tetradecene	$C_{14}H_{28}$	4.09	2.44	1.65	1.88	1.39	1.58
Tetradecadiene	$C_{14}H_{26}$	0	0	0	0	0.13	0.23
Pentadecene	$C_{15}H_{30}$	7.15	6.55	5.18	5.63	5.01	4.76
Heptadecene	$C_{17}H_{34}$	3.95	3.48	4.07	3.95	3.43	3.95
Octadecene	$C_{18}H_{36}$	0	0	0	0.18	0.25	0.38
Nonadecene	$C_{19}H_{38}$	1.11	1.07	1.07	1.37	1.23	0.72
Cycloolefins	C_9- C_{15}	1.83	7.43	5.03	4.87	2.96	1.66
Olefins overall yields/%		**33.42**	**30.53**	**24.37**	**25.47**	**21.03**	**19.83**
Aromatics selectivity/%							
Ethylbenzene	C_8H_{10}	3.41	3.11	2.01	1.99	2.62	1.73
Xylene and isomers	C_8H_{10}	6.83	5.09	5.18	4.73	3.48	2.96
Trimethylbenzene and isomers	C_9H_{12}	7.32	6.83	5.96	7.02	5.86	5.12
Indene	C_9H_{10}	1.82	1.96	2.13	3.31	2.27	3.03
Methylindene	$C_{10}H_{12}$	0.94	0.94	0.55	0.29	0.19	0.31
Butylbenzene and isomers	$C_{10}H_{14}$	3.42	4.44	5.36	6.17	5.46	5.63
Pentylbenzene and isomers	$C_{11}H_{16}$	2.72	2.36	1.29	1.12	1.03	0.97
Methylnaphthalene	$C_{11}H_{10}$	5.79	4.11	4.96	5.74	5.43	5.71
Dimethylindene	$C_{11}H_{14}$	0.28	0.16	0.16	0.28	0.59	0.82
Hexylbenzene and isomers	$C_{12}H_{18}$	2.03	2.45	3.61	2.11	1.84	1.79
Heptylbenzene and isomers	$C_{13}H_{20}$	1.55	1.23	1.23	1.07	1.37	1.16
Octylbenzene	$C_{14}H_{22}$	0.83	0.59	0.47	0.13	0.12	0.25
Aromatics overall yields/%		**36.94**	**33.27**	**32.91**	**33.96**	**30.26**	**29.48**
Oxygenates selectivity/%							
Alcohols		2.38	4.98	3.62	1.94	3.13	2.81
Aldehydes		0.69	2.17	1.96	2.17	3.87	2.43
Ketones		2.04	3.93	4.02	3.16	5.13	3.18
Carboxylic acids		0.32	1.34	0.88	0.21	0.44	0.65
Oxygenates overall yields/%		**5.43**	**12.42**	**10.48**	**7.48**	**12.57**	**9.07**

3.4.2 Relationship between soapstocks and composition of bio-oil

Fatty acid in vegetable oil reacts with sodium hydroxide to form a fatty acid sodium, which is the main component of soapstock. According to the above experimental data and analysis, relationship between the properties of soapstocks (content of fatty acid sodium) and chemical components in bio-oil has been investigated. The analysis is mainly based on Table 4 and Figure 3. Fatty acid composition was analyzed using GC-MS after methyl esterification to obtain the content of fatty acid sodium in ROS1, SSOS, COS, SOS, ROS2, and POS. The saturated fatty acid sodium (SFAS), monounsaturated fatty acid sodium (MFAS) and polyunsaturated fatty acid sodium content of all the soapstocks has been listed in Table 4. It can be observed that the saturated fatty acid sodium in these soapstocks is below 20%, which is less than MFAS and PFAS. The order of SFAS is POS > ROS2 > SOS > COS > SSOS > ROS1. The MFAS content ranges from 20% to 65%, with the highest occurring at ROS1 (64.8%) and the lowest at SSOS (20%). The PFAS content of the six soapstocks is ranked as SSOS > SOS > COS > ROS2 > POS > ROS1, it is interesting that this arrangement is opposite to MFAS. Furthermore, the PFAS of SSOS, ROS1 are 67%, and 28%, respectively.

Table 4 Fatty acid sodium composition

FA composition/%	ROS1	SSOS	COS	SOS	ROS2	POS
Saturate fatty acid sodium	7.2	13	15	16	18.7	20
Monounsaturate fatty acid sodium	64.8	20	32	25	40.3	44
Polyunsaturate fatty acid sodium	28	67	53	59	41.1	36

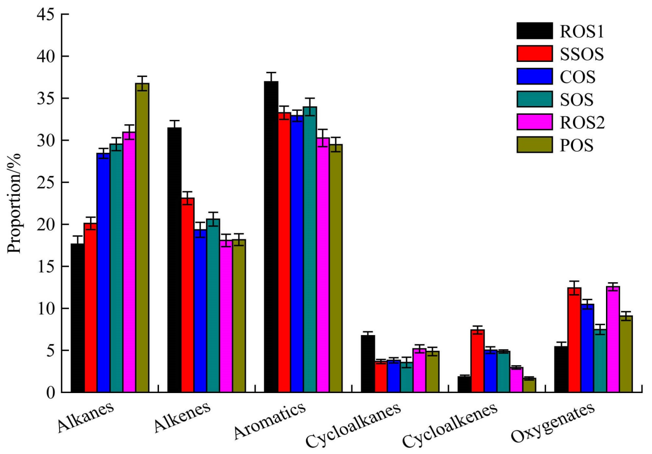


Figure 3 Composition of bio-oil at a catalytic temperature of 300°C

Figure 3 compares the composition of bio-oil at a catalytic temperature of 300°C. It can be seen that the alkane content older in bio-oil is POS > ROS2 > SOS > COS > SSOS > ROS1, which is consistent with the SFAS content of these soapstocks. As for other components, the highest content of alkenes, aromatics and cycloalkanes all appear in bio-oil of ROS1. The highest cycloalkenes and oxygenates are SSOS and ROS2 respectively. The lowest alkenes, cycloalkanes and oxygenates are separately present in ROS2, SOS. ROS1. POS contains the lowest aromatics and cycloalkenes. The content of cycloalkenes is arranged as SSOS > COS > SOS > ROS2 > ROS1 > POS. This order is very close to PFAS in soapstocks, which means that the pyrolysis products of PFAS are mainly cycloalkenes. There lies a similar correspondence which can be found between cycloalkanes and MFAS, but it is unconspicuous. Finally, combining the previous analysis, it can be concluded that the composition of bio-oil is related to the degree of unsaturation of fatty acid sodium of soapstock, because the unsaturation of fatty acid carbon chain affects the pyrolysis reaction[35]. In this study, the most common saturated fatty acids are palmitic (C16:0) and stearic (C18:0), which can be found at a small amount in every vegetable oil[33]. Similarly, oleic (C18:1) was the most common monounsaturated fatty acid, and all of the vegetable oils contained highly linoleic acid (C18:2)[36]. Therefore, in order to facilitate the analysis of bio-oil component formation pathway, sodium stearate, sodium oleate and sodium linoleate are respectively used as typical representatives of SFAS, MFAS and PFAS in soapstocks.

In the process of microwave pyrolysis, the carbon anion carbanion intermediate formed by dissociation of fatty acid sodium will be combined with oleic acid, linoleic acid and linolenic acid. Wang et al.[33] pointed out that the double bond in sodium oleate can form a P-π conjugated system with the carbanion to facilitate decarboxylation, terminal olefination, isomerization and aromatization. The Diels-Alder reaction in the course of the reaction forms cycloalkanes and cycloalkenes, and the cycloalkenes can form aromatic hydrocarbons through further reaction. The experiment[37] about pyrolysis of *Mesua ferrea* L. seed oil indicated that the formation of hydrocarbons was due to decomposition of fatty acids, and aromatic hydrocarbons were mainly produced from oleic acid and linoleic acid. Production of vegetable oil-based biofuels[35] showed that alkane and olefin were mainly produced by stearic acid. In a word, the results obtained in this study were in line with previous studies.

4 Conclusions

Among the three different catalytic temperatures, 300°C is the optimum. Bio-oil production (wt.%) of the soapstocks at 300°C is 55.3% (POS) < 57.9% (SSOS) < 58.1% (COS) < 60.1% (ROS2) < 60.4% (SOS) < 65.8% (ROS1). The highest bio-oil production was derived from rapeseed oil (65.8%, 300°C). The fatty acid sodium saturation of the soapstocks is closely related to the compounds in the bio-oil obtained by pyrolysis. The change rules of the contents of alkenes, aromatics, cycloalkenes, and oxygenates in the six soapstocks are the same, and those of alkanes and cycloalkanes are slightly identical.

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[References]

[1] Isahak W N R W, Hisham M W M, Yarmo M A, Yun Hin T. A review on bio-oil production from biomass by using pyrolysis method. Renewable and Sustainable Energy Reviews, 2012; 16(8): 5910–5923.

[2] Mahinpey N, Murugan P, Mani T, Raina R. Analysis of bio-oil, bio-gas and biochar from pressurized pyrolysis of wheat straw using a tubular reactor. Energy & Fuels, 2009; 23(5): 2736–2742.

[3] Duan D, Ruan R, Lei H, Liu Y, Wang Y, Zhang Y, et al. Microwave-assisted co-pyrolysis of pretreated lignin and soapstock for upgrading liquid oil: Effect of pretreatment parameters on pyrolysis behavior. Bioresource Technology, 2018; 258: 98–104.

[4] Li Y, Zhang X, Sun L. Fatty acid methyl esters from soapstocks with potential use as biodiesel. Energy Conversion and Management, 2010; 51(11): 2307–2311.

[5] Guo F, Xiu Z, Liang Z. Synthesis of biodiesel from acidified soybean soapstock using a lignin-derived carbonaceous catalyst. Applied Energy, 2012; 98: 47–52.

[6] Su E, Wei D. Improvement in biodiesel production from soapstock oil by one-stage lipase catalyzed methanolysis. Energy Conversion &

Management, 2014; 88: 60–65.

[7] Tang Q, Zheng Y, Liu T, Ma X, Liao Y, Wang J. Influence of vacuum pressure on the vacuum pyrolysis of plant oil asphalt to pyrolytic biodiesel. Chemical Engineering Journal, 2012; 207-208: 2–9.

[8] Wang Y, Dai L, Wang R, Fan L, Liu Y, Xie Q, et al. Hydrocarbon fuel production from soapstock through fast microwave-assisted pyrolysis using microwave absorbent. Journal of Analytical and Applied Pyrolysis, 2016; 119: 251–258.

[9] Dai L, Fan L, Duan D, Ruan R, Wang Y, Liu Y, et al. Production of hydrocarbon-rich bio-oil from soapstock via fast microwave-assisted catalytic pyrolysis. Journal of Analytical and Applied Pyrolysis, 2017; 125: 356–362.

[10] Scott D, Jan P. The continuous flash pyrolysis of biomass. Canadian Journal of Chemical Engineering, 1984; 62(3): 404–412.

[11] Mohan D, Pittman C, Steele P. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy & Fuels, 2006; 20(3): 848–889.

[12] Yin C. Microwave-assisted pyrolysis of biomass for liquid biofuels production. Bioresource Technology, 2012; 120(17): 273–284.

[13] Zhou Y, Wang Y, Fan L, Dai L, Duan D, Liu Y, et al. Fast microwave-assisted catalytic co-pyrolysis of straw stalk and soapstock for bio-oil production. Journal of Analytical and Applied Pyrolysis, 2017; 124: 35–41.

[14] Bridgwater A, Peacocke G. Fast pyrolysis processes for biomass. Renewable & Sustainable Energy Reviews, 2000; 4(1): 1–73.

[15] Ruan R, Chen P, Hemmingsen R, Morey V, Tiffany D. Size matters: small distributed biomass energy production systems for economic viability. Int J Agric & Biol Eng, 2008; 1(1): 64–68.

[16] Hu Z, Ma X, Chen C. A study on experimental characteristic of microwave-assisted pyrolysis of microalgae. Bioresource Technology, 2012; 107: 487–493.

[17] Wu C, Budarin V, Gronnow M, Bruyn M, Onwudili J, Clark J, et al. Conventional and microwave assisted-pyrolysis of biomass under different heating rates. Journal of Analytical & Applied Pyrolysis, 2014; 107(5): 276–283.

[18] Huang Y-F, Cheng P-H, Chiueh P-T, Lo S-L. Leucaena biochar produced by microwave torrefaction: Fuel properties and energy efficiency. Applied Energy, 2017; 204: 1018–1025.

[19] Su S, Chase H. A review on waste to energy processes using microwave pyrolysis. Energies, 2012; 5(10): 4209–4232.

[20] Li J, Dai J, Liu G, Zhang H, Gao Z, Fu J, et al. Biochar from microwave pyrolysis of biomass: A review. Biomass & Bioenergy, 2016; 94: 228–244.

[21] Hilten R, Speir R, Kastner J, Das KC. Production of aromatic green gasoline additives via catalytic pyrolysis of acidulated peanut oil soap stock. Bioresource Technology, 2011; 102(17): 8288–8294.

[22] Dai L, Fan L, Duan D, Ruan R, Wang Y, Liu Y, et al. Microwave-assisted catalytic fast co-pyrolysis of soapstock and waste tire for bio-oil production. Journal of Analytical and Applied Pyrolysis, 2017; 125: 304–309.

[23] Lappi H, Alén R. Pyrolysis of vegetable oil soaps-Palm, olive, rapeseed and castor oils. Journal of Analytical and Applied Pyrolysis, 2011; 91(1): 154–158.

[24] Zhang X, Lei H, Zhu L, Qian M, Zhu X, Wu J, et al. Enhancement of jet fuel range alkanes from co-feeding of lignocellulosic biomass with plastics via tandem catalytic conversions. Applied Energy, 2016; 173: 418–430.

[25] Dai L, Fan L, Liu Y, Ruan R, Wang Y, Zhou Y, et al. Production of bio-oil and biochar from soapstock via microwave-assisted co-catalytic fast pyrolysis. Bioresource Technology, 2017; 225: 1–8.

[26] Czernik S, Bridgwater A. Overview of applications of biomass fast pyrolysis oil. Energy & Fuels, 2004; 18(2): 590–598.

[27] Liu S, Xie Q, Zhang B, Cheng Y, Liu Y, Chen P, et al. Fast microwave-assisted catalytic co-pyrolysis of corn stover and scum for bio-oil production with CaO and HZSM-5 as the catalyst. Bioresource Technology, 2016; 204: 164–170.

[28] Biswas B, Pandey N, Bisht Y, Singh R, Kumar J, Bhaskar T. Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk. Bioresource Technology, 2017; 237: 57–63.

[29] Kenney K, Smith W, Gresham G, Westover T. Understanding biomass feedstock variability. Biofuels, 2013; 4(1): 111–127.

[30] Xue Y, Kelkar A, Bai X. Catalytic co-pyrolysis of biomass and polyethylene in a tandem micropyrolyzer. Fuel, 2016; 166: 227–236.

[31] Zhang X, Lei H, Zhu L, Zhu X, Qian M, Yadavalli G, et al. Optimizing carbon efficiency of jet fuel range alkanes from cellulose co-fed with polyethylene via catalytically combined processes. Bioresource Technology, 2016; 214: 45–54.

[32] Zhang H, Nie J, Xiao R, Jin B, Dong C, Xiao G. Catalytic co-pyrolysis of biomass and different plastics (polyethylene, polypropylene, and polystyrene) to improve hydrocarbon yield in a fluidized-bed reactor. Energy & Fuels, 2014; 28(3): 1940–1947.

[33] Wang Y, Liu Y, Ruan R, Wen P, Wan Y, Zhang J, et al. microwave-assisted decarboxylation of sodium oleate and renewable hydrocarbon fuel production. Chemical Industry & Engineering Progress, 2013; 15(3): 19–27.

[34] Ayanoğlu A, Yumrutaş R. Production of gasoline and diesel like fuels from waste tire oil by using catalytic pyrolysis. Energy, 2016; 103: 456–468.

[35] Lappi H, Alén R. Production of vegetable oil-based biofuels-Thermochemical behavior of fatty acid sodium salts during pyrolysis. Journal of Analytical and Applied Pyrolysis, 2009; 86(2): 274–280.

[36] Demirbaş A. Diesel fuel from vegetable oil via transesterification and soap pyrolysis. Energy Sources, 2002; 24(9): 835–841.

[37] Konwer D, Taylor S, Gordon B, Otvos J, Calvin M. Liquid fuels from *Mesua ferrea* L. seed oil. Journal of the American Oil Chemists Society, 1989; 66(2): 223–226.

[38] Chen N, Degnan T, Koenig L. Liquid fuel from carbohydrates. Chemtech, 1986; 16(8): 506–511.

[39] Duan D, Wang Y, Dai L, Ruan R, Zhao Y, Fan L, et al. Ex-situ catalytic co-pyrolysis of lignin and polypropylene to upgrade bio-oil quality by microwave heating. Bioresource Technology, 2017; 241: 207–213.