Converting pine sawdust to advanced biofuel over HZSM-5 using a two-stage catalytic pyrolysis reactor

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Abstract:

In this study, the pine sawdust thermal conversions over HZSM-5 catalyst were carried out under different reaction temperatures in a two-stage catalytic pyrolysis reactor. Higher temperatures in the catalytic reactor tended to decrease the yield of bio-oil and change the component of bio-oil. The results from the Gas chromatography–mass spectrometry (GC–MS) analysis showed that the pyrolysis reaction at 500 °C and catalytic reaction at 500 °C treatment obtained the highest hydrocarbon content (58.63%) and the highest C₈–C₁₂ content (48.03%) in the oil phase of the bio-oil. The X-ray Diffraction (XRD) and Selected-area-electron-diffraction (SEAD) characterization showed that the distortion of the ZSM-5 zeolite lattice occurred before and after use. The Brunauer–Emmett–Teller (BET) characterization indicated that the formation of coke increased as the catalytic temperature rose. The physical characterization of bio-oils, such as water content, density, viscosity, pH, and higher heating value (HHV) further demonstrated that HZSM-5 catalyst was beneficial in achieving low viscosity and higher HHV bio-oils. All the

results suggest that the two-stage catalytic pyrolysis reactor with HZSM-5 catalyst has a great potential for achieving advanced biofuel.

1. Introduction

Pyrolysis is a thermochemical decomposition for converting various biomasses to raw bio-oil at temperatures between 400 and 650 °C in the absence of O₂ [1, 2]. This process has been attracting much attention due to decreasing crude-oil reserves, growing demand for fuels worldwide and ever-increasing climate concerns on the use of fossil-based energy carriers [3-5]. Compared to finite reserves of fossil fuels, biomass is worldwide available and renewable. Biomass can be an alternative to fossil fuels for development of biofuels and valuable chemicals. Production of biofuels and chemicals from biomass is sustainable because it can help to reduce CO₂ emission in the natural carbon cycle [6]. Thus, exploration of methods for producing advanced bio-fuel to substitute conventional fuel is meaningful [7, 8].

Pyrolysis bio-oil consists of hydroxyaldehydes, hydroxyketones, carboxylic acids, furan and pyran ring containing compounds, anhydrosugars, phenolic compounds and oligomeric fragments of lignocellulosic polymers [9]. Catalytic upgrading can enhance the properties of raw bio-oil by removing oxygenated compounds via H₂O and CO₂, reducing molecular weight and altering chemical structures to resemble those of petrochemical products.[10] Many catalysts including MgO [11], NiCl₂ [12], K₂CO₃ [13], Ni/Al₂O₃ [14], Pt/Al₂O₃ [15], Ru/Al₂O₃ [16], Ni/C [17], Ru/C [18], Pd/C [19], Pt-Re/C [20], Ni/CeO₂ [14], Pt/SiO₂ [21], Pd/HY [22], Al/MCM-41 [23, 24] and Cu-Al/MCM-41[24] have been used to upgrade pyrolysis bio-oils into hydrocarbons in the range of gasoline [25-27].

A key disadvantage of pyrolysis bio-oil is its instability. The viscosity of pyrolysis bio-oil increases during storage before upgrading, due to slow polymerization and condensation

reactions [28]. Furthermore, large amounts of energy are consumed during the re-heating and re-gasifying of pyrolysis bio-oil during upgrading [15, 16, 18, 22, 25, 27].

Zeolite catalysts have robust catalytic cracking abilities which realize the deoxygenation by dehydration, decarboxylation, and decarbonylation reactions. [29] Zeolites have been successfully used for conversion of oxygenated organic compounds to hydrocarbons [30, 31]. However, the HZSM-5 catalysts deactivate very soon during the reactions due to the coking, which limit the application in industry.[32] In this study, we investigated the effect of temperature on the pine sawdust catalytic pyrolysis product distribution in a coupled reactor, discussed the possibilities to recycle the HZSM-5 catalysts. This not only avoided the disadvantage of denaturation during storage, but also saved energy. HZSM-5 catalysts was used in the two-stage catalytic pyrolysis reactor to obtain bio-oil. Results from various treatments were compared. GC-MS profiles of catalytic pyrolysis oil were obtained after each treatment to determine the composition of the bio-oil and optimal process conditions for producing higher quality biofuel.

2. Experimental

2.1. Materials

2.1.1. Feedstock

The feedstock used in the experiments was pine sawdust produced by the Rushmore Forest Products, Inc. in Rapid City South Dakota. The sawdust was further ground into powder with a particle size less than 2 mm using a hammer mill.

2.1.2. Catalysts

The HZSM-5 with Si/Al = 30 was purchased from Zeolite Company and formed into cylindrical extrudate with guar gum and boehmite as binders. The catalyst was prepared with a

length of 3-5 mm and calcined at 550 °C for 5 h before use. In each test, 20 g of HZSM-5 was used.

2.2 Catalysts characterizations

2.2.1 BET

The BET specific surface area and porosity texture of each sample were determined by nitrogen adsorption measurements at 77.2 K with an automatic Micromeritics ASAP 2020 apparatus. The samples were first degassed at 573 K for approximately 6 h and then studied with a static volumetric technique. The specific surface area of the catalysts was computed according to the Brunauer–Emmett–Teller (BET) method, and the total pore volume was determined at a relative pressure $P/P_0 = 0.995$. Density functional theory (DFT) was used to characterize the micropore, mesopore and pore size distribution.

2.2.2 XRD

XRD was used for phase identification and determination of the relative crystallinity. XRD measurements were carried out using Cu K α radiation on a RIGAKU SMARTLAB. The X-ray tube was operated at 40 kV and 44 mA and the X-ray pattern was scanned with a step size of crystallite sizes of 0.02° (2 θ) from 5 to 50° (2 θ) and counting time of 1 s per step.

2.2.3 TEM

TEM was performed on a JEM 2100 with an accelerating voltage of 300 kV. SEAD technique was used to obtain electron diffraction patterns from individual grains of powder. A few mg of the powdered samples was suspended in 2 ml ethanol, and the suspension was sonicated for 1 h. Then, the suspension was allowed to settle for 15 min, before a drop was taken and dispersed on a 300 mesh copper grid coated with holey carbon film.

2.3. Product characterizations

The pH value of bio-oil was measured by a pH meter (AB15, Accumet Company) at room temperature. The instrument was calibrated with liquid calibration standards of pH 4 and 7 prior to the measurement. The viscosity analyzer (REOLOGICA Instruments AB Company Dynamic Viscosity) was used to measure dynamic viscosity at 20 °C. The samples' elemental compositions of carbon, hydrogen, nitrogen, and oxygen were determined by the CE-440 Elemental Analyzer. The HHV of samples were determined by the bomb calorimeter (Parr Instrument Company 1341). The moisture contents of samples were measured by the Karl Fischer Titrator V20 (Mettler Toledo Company). Syngas analysis was carried out on a GC (Agilent GC-7890A (Hp-5 column: 30 m × 0.25 mm × 0.25 μm)) with a combined TCD and FID. Standard gas mixtures were used for calibration, and argon was used as the carrier gas. GC-MS (Agilent GC-7890A (DB-5 column: 30 m × 0.25 mm × 0.25 μm)) and MSD-5975C (Electron ionization at 70 eV, mass range of 50–5000 m/z, semi-quantitation based on TIC, mass chromatograms)) was used to analyze the chemical composition of samples.

The gas chromatograph was programmed at 60 °C for 1 min, followed by ramp 1 at 3 °C/min to 260 °C and ramp 2 at 5 °C/min to 280 °C. The temperature was held for an additional 10 min after each ramp. The injector temperature was 300 °C, and the injection size was 1 μL. The flow rate of carrier gas (hydrogen) was 1 mL/ min. The compositions were identified based on the NIST Mass Spectral Library and literatures [11, 12, 33, 34, 35].

2.4 Experimental apparatus and procedure

The catalytic pyrolysis system is a novel coupled reactor configuration which includes a pyrolysis fixed-bed reactor, a catalytic fixed-bed reactor and a condenser system. The diameter and the length of the pyrolysis reactor is 12.7 cm and 27.9 cm. The diameter and the length of the catalytic reactor is 5.1 cm and 45.7 cm. Both of the reactors consist of a temperature controlled

furnace and a fixed bed tube. Reaction products travel through a condenser, and liquid product is collected in a flask. The gas product composition was determined by a GC. The schematic diagram of the two-stage catalytic pyrolysis system is shown in Fig. 1.

In each test, 200 g of sawdust was added into the pyrolysis reactor, then 20 g of HZSM-5 was loaded as the catalyst. Nitrogen was injected into the system to remove the air with 10 ml/min flow rate for 30 min. The catalytic reactor was heated to a preset temperature at the beginning of the experiment. The nitrogen flow rate was set at 3 ml/min. After that, the catalytic reactor furnace was opened and heated at a rate of 20 °C/min to 500 °C. When the catalytic reactor reached 500 °C, the gas started to be collected and analyzed. The pyrolysis reactor temperature was kept at 500 °C for 1 hour, then the furnaces were shut off. Four groups of reactions were carried out in the two-stage catalytic pyrolysis reactor with different reaction conditions. The reaction conditions were pyrolysis reaction at 500 °C and no catalyst (P500+NC), pyrolysis reaction at 500 °C and catalytic reaction at 400 °C (P500+C400), pyrolysis reaction at 500 °C and catalytic reaction at 500 °C (P500+C500), and pyrolysis reaction at 500 °C and catalytic reaction at 600 °C (P500+C600). After each test, the system was allowed to cool for 2 hours. And then, the bio-oil was collected from the condenser. Bio-char was got by disassembling the pyrolysis reactor. The syngas was calculated by subtracting the bio-char and bio-oil weights from the original feedstock weight.

In order to get the objective experiment results, each test was performed in duplicate. All observations were recorded in triplicate and average values were reported. All the data were rounded to two decimals.

3. Results and discussion

3.1. Feedstock characterization

Moisture content, particle size distribution, elemental analysis and HHV analysis of the sawdust used for two-stage processes are presented in Table 1. The reactivity and combustion behavior of biomass is strongly affected by surface area [36]. In the biomass conversion processes, smaller particle sizes of the biomass increase heating transfer rate, which contributes to high-quality bio-oils. With the aid of the software (Nano-measurer 1.2), the particle size distribution of sawdust was achieved (Fig. 2), and the mean particle size is 0.48 mm.

3.2 Characterization of catalysts

BET parameters of the various samples are summarized in Table 2. The BET surface area, Langmuir surface area and total pore volume gradually decreased with an increasing catalytic treatment temperature. DFT model simulation results (Fig. 3) indicated that the fresh and used HZSM-5 catalysts contain micropores and mesoporous with a distribution of sizes between 1 and 20 nm. The HZSM-5 catalysts treated by higher temperature have less incremental volume for pore size between 1 and 20 nm. All these results indicates that the higher catalytic temperature is beneficial to the formation of coke in the pores of HZSM-5.

In order to further determine whether or not coke is present inside the catalysts, the XRD patterns of the fresh and used HZSM-5 catalysts in the angle region ($5-50^\circ$) were measured, and the results are shown in Fig. 4. For the fresh catalyst, the two peaks appearing at 23.1° and 23.7° can be found in the XRD patterns. For the used HZSM-5 after P500+C400 treatment, the two peaks appearing at 23.1° and 23.4° can be found in the XRD patterns. However, the two peaks collapse into one at 23.3° for HZSM-5 catalysts after P500+C500 and P500+C600 treatment. The intensities in the angle region ($<10^\circ$) change for different treatments to HZSM-5 catalyst. According to the research of Bibby [37] and Bao [38], the changes in the relative positions and intensities of the peaks in the XRD spectra of the coked ZSM-5 zeolite could be attributed to a

displacive transformation from monoclinic to orthorhombic caused by deposition of coking within HZSM-5 pores. SEAD characterization (Fig. 5) also indicated that used HZSM-5 catalysts are still polycrystalline even if the distortion of HZSM-5 zeolite lattice, which supports the XRD analysis result.

3.3. Evaluation of two-stage catalytic pyrolysis process

3.3.1 Product yield

Bio-oil, syngas and bio-char yields were determined at four treatments: P500+NC, P500+C400, P500+C500, P500+C600. The bio-char and bio-oil are obtained by weighing the components before and after experiments. The syngas is calculated by subtracting the bio-char and bio-oil weights from the original feedstock weight. The product distribution of the bio-char, bio-oil and syngas are shown in Fig. 6. It is illustrated that the yield of syngas increases and the yield of bio-oil decreases with the increase of catalytic reaction temperature. This outcome may be due to more efficient cracking reactions at high temperatures, which produce many small molecules ($<C_4$). The formation of bio-char is only concerned with the pyrolysis temperature. Since all the pyrolysis reactions occurred at 500 °C, there is no significant disparity in the bio-char yields for the different treatments in the catalytic reactor.

3.3.2 Effect of the different treatments on the bio-oils

During the pine sawdust conversion process, multiple reactions occurred, including hydrogenation, hydrogenolysis, decarboxylation, decarbonylation, hydrocracking and polymerization [39]. The products after the two-stage process included many compounds such as esters, ketones, phenols, aldehydes, alcohols, ethers and hydrocarbons. In order to evaluate the two-stage catalytic pyrolysis process, the physical properties were combined with organic

compounds of treated bio-oil to analyze. The typical GC-MS spectroscopy in Fig. 7 shows that separation of all the components from two-stage process bio-oil was successful.

The bio-oils from all these treatments included two phases. The top phase was the aqueous phase, while the bottom was the oil phase. The physical properties of the two phases are presented in Table 3. From Table 1 and 3, it is noted that the HHVs of bio-oils were around 23 MJ/kg, much higher than that of pine sawdust (19.28 MJ/kg), which indicated the effectiveness of the two-stage process. With an increase in catalytic reaction temperature, the density of the oil phases would decrease slightly. Compared to the viscosity of oil phase from P500+NC treatment, the viscosities from P500+C400, P500+C500 and P500+C600 treatments decreased significantly. This suggested that the HZSM-5 increased the production of small molecules, which contributed to a lower viscosity.

The relative content (GC-MS) of typical organic compounds in the oil phase of bio-oil are shown clearly in Table 4. The bio-oil was mainly composed of esters, ketones, phenols, aldehydes, alcohols, ethers and hydrocarbons. The composition of bio-oils from different treatments in the two-stage reactor was similar and it implied there were similar transformation pathways for typical compounds. These chemicals originate from the degradation of cellulose, hemicellulose, lignin and extractives present in pine sawdust. Around 48 peaks were judged to be crucial and selected for analysis. These are presented in Table 4 showing the total peak areas for the different chemical groups for both non-catalytic and catalytic sawdust bio-oils from two-stage process.

When the catalytic reaction temperature increased, the contents of phenols, aldehydes, alcohols, ketones and ethers decreased and the conversion of ethers was maximized at the catalytic temperature of 500 °C. The aldehydes were totally converted by HZSM-5 at the

temperature of 400 °C, 500 °C and 600 °C. The amount of hydrocarbons increased greatly from 10.76% in P500+NC treatment bio-oil to a maximum of 58.63% in P500+C500 treatment bio-oil. These results indicated that HZSM-5 catalysts are efficient in converting oxy-compounds to hydrocarbons.

Achieving bio-oils with a high hydrocarbon content is the ultimate aim for biomass conversion. The hydrocarbon distributions of the oil phase in bio-oils were shown in Fig. 8. Compared to the non-catalytic treatment, the catalytic treatments increased the hydrocarbon contents immensely. The highest total hydrocarbon content in the oil phase of bio-oil was achieved from P500+C500 treatment. Meanwhile, the production of C₈-C₁₂ had a maximizing value (48.03%). In addition, most of the composition in C₈-C₁₂ were aromatic compounds. This result indicated the HZSM-5 was an active catalyst in aromatization, which is consistent with the research of Abu Bakar [34]. The content of heavy hydrocarbons (C₁₇-C₂₀) decreased as the catalytic reaction temperature increased. It indicated that HZSM-5, under high temperature, has a strong ability to crack heavy hydrocarbon molecules into light hydrocarbon molecules. These results demonstrated pine sawdust conversion in the two-stage process under HZSM-5 as an effective way to get high content hydrocarbon bio-oils.

3.3.3 Effect of the different treatments on the syngas

For the experiments, the gaseous products mainly contain carbon dioxide and carbon monoxide small quantities of hydrogen, methane and C₂₋₄ hydrocarbon gases. According to Fig. 9, with an increase in catalytic reaction temperature, the contents of carbon dioxide, carbon monoxide and C₂₋₄ hydrocarbon gases increased, methane content had almost no change and hydrogen content decreased, the trend of carbon dioxide and carbon monoxide production is consistent with the Baker's research [40]. The research suggested that decarbonylation reactions,

which produce carbon monoxide, were favored in the presence of HZSM-5. The most preferable way to remove oxygen is to form carbon dioxide during upgrading reactions.³⁴ Therefore, the higher carbon dioxide in syngas is beneficial.

3.3.3 Effect of the different treatments on the bio-chars

The physical properties of bio-char are also depicted in Table 5. Since all the treatments had the same temperature in pyrolysis reactor, the HHV and carbon content of bio-char have no big difference.

4. Conclusion

The sawdust conversion to bio-oil under HZSM-5 on the two-stage catalytic pyrolysis reactor has been studied over P500+NC, P500+C400, P500+C500 and P500+C600 reaction conditions. The physical characterization of bio-oils showed that the two-stage catalytic pyrolysis treatments were beneficial in achieving low viscosity and high HHV bio-oils. The GC–MS analysis of the liquid products in the oil phase showed that P500+C400, P500+C500 and P500+C600 treatments exhibited relatively high hydrocarbon content in the bio-oils compared to the P500+NC treatment. The highest hydrocarbon content (58.63%) and the highest C₈–C₁₂ content (48.03%) in the oil phase was obtained by P500+C500 treatment. The BET analysis indicated that the formation of coke increased with the increasing catalytic temperature. Besides, the deposition of coke into pores of HZSM-5 resulted in the distortion of zeolite lattice according to the XRD and SEAD analysis.

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363

364 **Fig. 1.** Schematic diagram of two-stage catalytic pyrolysis equipment

365 **Fig. 2.** Particle size distribution of the pine sawdust

366 **Fig. 3.** Pore size distribution of fresh and used HZSM-5 catalysts

367 **Fig. 4.** X-ray diffraction patterns of (a) fresh HZSM-5, (b) HZSM-5 after P500+C400 treatment,
368 (c) HZSM-5 after P500+C500 treatment, (d) HZSM-5 after P500+C600 treatment.

369 **Fig. 5.** SEAD image of the samples (a) fresh HZSM-5, (b) HZSM-5 after P500+C400 treatment,
370 (c) HZSM-5 after P500+C500 treatment, (d) HZSM-5 after P500+C600 treatment

371 **Fig. 6.** The products distributions of the bio-char, bio-oil and syngas

372 **Fig. 7.** The typical GC-MS spectroscopy of the bio-oil by P500+C500 treatment

373 **Fig. 8.** The hydrocarbon distributions of the oil phase of bio-oils

374 **Fig. 9.** The distribution of syngas from different treatments

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Table 1

Characterizations of the pine sawdust

Analysis	Data
Moisture Content (wt %)	7.15
Elements Analysis (wt %)	Carbon 47.75
	Hydrogen 6.30
	Nitrogen 1.27
	Oxygen 44.37
	Rest 0.31
HHV (MJ/kg)	19.28

Table 2

BET parameters of the various samples

Sample	Surface area (m ² /g)		Pore volume(cm ³ /g)		
	BET	Langmuir	Total ^a	Micropores ^b	Mesopores ^c
Fresh HZSM-5	423.40	506.00	0.34	0.15	0.17
HZSM-5 (P500 + C400)	322.50	389.60	0.33	0.14	0.08
HZSM-5 (P500 + C500)	302.70	366.50	0.32	0.13	0.07
HZSM-5 (P500 + C600)	188.50	229.90	0.27	0.10	0.04

^a Total pore volume, measured at P/P₀ = 0.995.
^b Micropore volume, derived from NLDFT model.
^c Mesopore volume, derived from NLDFT model.

Table 3

Properties of catalytic and non-catalytic bio-oils in two-stage catalytic pyrolysis reactor

Treatment	HHV, MJ/kg	Mass, g		MC, %		pH		Density, g/ml		Viscosity, cP	
	OP	AP	OP	AP	OP	AP	OP	AP	OP	AP	OP
P500 + NC	21.29	61.32	38.12	81.48	4.12	3.30	3.48	1.07	1.10	2.02	162.00
P500 + C400	23.37	60.79	30.93	85.65	5.22	3.17	3.38	1.04	1.06	2.14	4.80
P500 + C500	24.80	53.69	34.25	78.40	4.77	3.18	3.13	1.03	1.05	2.02	3.43
P500 + C600	22.89	48.77	32.85	75.47	5.09	3.21	3.41	1.04	1.02	1.99	3.07
AP: Aqueous phase; OP: Oil phase; Catalyst: 20.00 g HZSM-5; Feedstock: 200.00 g pine sawdust											

Table 4

Chemical composition of the oil phases in bio-oils

Compounds		Molecular formula	Relative content (%)			
			P500 + NC	P500 + C400	P500 + C500	P500 + C600
Esters			25.26	12.07	10.93	20.41
	Cyclooctanecarboxylic acid, 4-methyl-ethyl ester	$C_{12}H_{22}O_2$	0.38			
	9-Octadecenoic acid methyl ester,	$C_{19}H_{36}O_2$	1.91	1.05	0.92	0.97
	Methyl Dehydroabietate	$C_{21}H_{30}O_2$	19.97	8.64	8.32	16.67
	7-Oxodehydroabietic acid, methyl ester	$C_{21}H_{28}O_3$	3.00	2.38	1.69	2.77
Phenols			27.36	17.88	12.37	9.08
	Phenol	C_6H_6O			1.46	
	2-methyl-phenol	C_7H_8O			3.49	
	2-methoxy-phenol	$C_7H_8O_2$	5.66			
	2-methoxy-4-methyl-phenol	$C_8H_{10}O_2$	11.05	10.83	3.20	8.50
	4-ethyl-2-methoxy-phenol	$C_9H_{12}O_2$	9.56	5.73	3.70	
	2-methoxy-4-(1-propenyl)-phenol	$C_{10}H_{12}O_2$	1.09	1.32	0.52	0.58
Aldehydes			0.94			
	5-methylfurfural	$C_6H_6O_2$	0.94			
Alcohols			6.71	5.38	4.82	4.11
	2-Benzofurancarboxaldehyde	$C_9H_6O_2$	0.62	0.69		
	Eugenol	$C_{10}H_{12}O_2$	4.76	4.15	4.66	3.47
	7-Dehydrocholesterol	$C_{27}H_{44}O$	0.25			
	Ergost-5,8(14)-dien-3-ol	$C_{28}H_{46}O$	1.08	0.54	0.16	0.64

Ketones			10.75	6.94	5.71	6.82
	2-methyl-2-Cyclopenten-1-one	C ₆ H ₈ O			0.03	
	4-Hydroxy-2-methylacetophenone	C ₉ H ₁₀ O ₂	0.49	0.19		
	3,4-Dimethoxytoluene	C ₉ H ₁₂ O ₂	0.28	0.31		0.18
	2',4'-Dihydroxy-3'-methylpropiophenone	C ₁₀ H ₁₂ O ₃		0.21		
	1-[1,1'-biphenyl]-3-yl-Ethanone	C ₁₄ H ₁₂ O			2.88	
	S-Indacen-1(2H)-One,3,5,6,7-T	C ₁₈ H ₂₄ O	9.98	6.23	2.80	6.47
Ethers			10.92	9.19	5.73	8.77
	Benzofuran	C ₈ H ₆ O			2.44	
	2-Methylbenzofuran	C ₉ H ₈ O		0.75		
	3,4-Dimethylanisole	C ₉ H ₁₂ O	0.24	0.52		
	2-Tolyloxirane	C ₉ H ₁₀ O	4.45	0.90		0.24
	Dibenzofuran	C ₁₂ H ₈ O				0.17
	4'-Phenoxyacetophenone	C ₁₄ H ₁₂ O ₂	0.37	3.89	0.27	
	9,10-Dimethoxy-Anthracene	C ₁₆ H ₁₄ O ₂				1.18
	Lincomycin 2,7-diacetate	C ₁₆ H ₁₄ O ₂	5.32	3.13	3.02	4.12
	Dimethyl-Bisphenol A	C ₁₇ H ₂₀ O ₂				3.06
	Methyl abietate	C ₂₁ H ₃₂ O ₂	0.54			
Hydrocarbons			10.76	43.51	58.63	40.63
	1,6-Dimethylcyclohexene	C ₈ H ₁₄			0.10	
	Indene	C ₉ H ₈	0.44	0.40	2.02	1.32
	5-Methyl-3-Octyne	C ₉ H ₁₆			0.10	
	α-Methylstyrene	C ₉ H ₁₀			0.18	
	1,3,5-Trimethylbenzene	C ₉ H ₁₂	0.38			
	3-Ethyltoluene	C ₉ H ₁₂	0.23	3.7		1.51

Propylbenzene	C ₉ H ₁₂	0.42	0.11	0.33	
2-Ethyltoluene	C ₉ H ₁₂		0.42		
4-Ethyltoluene	C ₉ H ₁₂		0.16		
1,2,4-trimethylbenzene	C ₉ H ₁₂	4.45	5.06		
1,2,3-trimethylbenzene	C ₉ H ₁₂				1.59
1,3,5-trimethylbenzene	C ₉ H ₁₂	0.38	13.10	11.3	9.49
2-propenylbenzene	C ₉ H ₁₀	0.88			
4-Allyltoluene	C ₁₀ H ₁₂	0.84	0.70		
1,2,3,5-tetramethylbenzene	C ₁₀ H ₁₄	0.97			
<i>o</i> -Cymene	C ₁₀ H ₁₄	1.00	0.86	1.11	0.96
1-methylindene	C ₁₀ H ₁₀	0.24	3.14	3.70	1.44
Naphthalene	C ₁₀ H ₈	1.11	1.34	8.22	6.74
3-Carene	C ₁₀ H ₁₆	0.52			0.80
2-Methylnaphthalene	C ₁₁ H ₁₀	2.16	3.85	6.81	7.67
(1-ethyl-1-propenyl)-benzene	C ₁₁ H ₁₄	0.47			
1-(2-butenyl)-2,3-dimethyl-benzene	C ₁₂ H ₁₆	0.17	0.20		
1-Ethyl-naphthalene	C ₁₂ H ₁₂	1.01	1.07		1.08
2,7-Dimethylnaphthalene,	C ₁₂ H ₁₂	1.77			1.25
1,3-Dimethylnaphthalene	C ₁₂ H ₁₂	0.46			
2-Vinylnaphthalene	C ₁₂ H ₁₂		2.05		
1,6-Dimethylnaphthalene	C ₁₂ H ₁₂				1.17
Acenaphthylene	C ₁₂ H ₈		4.72		
1-(1-methylethyl)-Naphthalene	C ₁₃ H ₁₄		2.53		
3-(2-Methyl-propenyl)-1H-indene	C ₁₃ H ₁₄	0.67			
1-Propylnaphthalene	C ₁₃ H ₁₄	0.20			

2,3,6-Trimethyl-naphthalene	C ₁₃ H ₁₄	0.59			
3-Phenyltoluene	C ₁₃ H ₁₂		1.69		
α-ionene	C ₁₃ H ₁₈	1.27		0.27	
1-Methylfluorene	C ₁₄ H ₁₂	0.18		0.39	
Phenanthrene	C ₁₄ H ₁₀		2.21	0.81	
(+)-Longifolene	C ₁₅ H ₂₄		2.43		
2-Phenylindene	C ₁₅ H ₁₂			1.01	
Methylanthracene	C ₁₅ H ₁₂			0.73	
1,3,5-Cycloheptatriene, 6-methyl-1-	C ₁₆ H ₁₈	0.51	0.30		0.32
(6-methyl-1,3,5-cycloheptatrien-1-yl)-					
1,2,3,4,4a,9,10,10a.α-tetrahydro-1,1,4a.β-trimethyl-Phenanthrene	C ₁₇ H ₂₄	0.90	0.72		0.80
1-methyl-7-(propan-2-yl)-1,2,3,4-tetrahydrophenanthrene	C ₁₈ H ₂₂			0.26	
Dehydroabietine	C ₁₉ H ₂₈	1.18	0.83	0.74	0.95
Heptamethyl-3-phenyl-1,4-cyclohexadiene	C ₁₉ H ₂₆			0.31	
Phenanthrene,7-ethenyl-1,2	C ₂₀ H ₃₂	1.71	0.92	0.43	

Chemical composition of the oil phases in bio-oils

Table 5

The properties of bio-char from different treatments

	Bio-char			
	P500 + NC	P500 + C400	P500 + C500	P500 + C600
HHV	28.74	28.55	28.68	28.89
Carbon content %	78.30	79.10	78.60	78.90

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

The two-stage catalytic pyrolysis system

The hydrocarbons distributions of the oil phases of bio-oils