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Orthogonal test design to optimize products and to characterize heavy oil via biomass hydrothermal treatment

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ABSTRACT

The key parameters for biomass hydrothermal treatment were optimized for product distribution in this study on the basis of a L16 (45) orthogonal experiment design. Results showed that biomass species, particle size, and hydrothermal temperature significantly affected heavy oil yield. By contrast, the effect of biomass concentration was negligible. The maximum heavy oil yield was 28.00 wt.% at the optimal condition (biomass species, pine sawdust; 250 °C; 80–150 mesh; 15 min; 10 g/110 g). In addition, cotton straw yielded the most liquid in the agricultural straws, although ash content was low. The influences of temperature, residence time, catalysts, and the size of cotton straw particles on product distribution were investigated as well. The results of analysis with GC–MS (gas chromatography–mass spectroscopy) indicated that the liquid product contained organic components, namely, acids, esters, aldehydes, ketones, and phenols. Among these components, acids, esters, phenols, and their derivatives were dominant. The addition of catalysts increased oil yield and also affected the oil components. Specifically, acids and ketones were reduced and the pH value of the oil increased. As a result, its quality improved to a certain extent. This research provides a reference for biomass hydrothermal treatment.

1. Introduction

Unlike solar, wind, and other renewable resources, biomass is the sole material that contains carbon and can be used in the large-scale production of liquid fuel. The liquid fuel derived from biomass is expected to replace fossil fuels, such as natural gas, gasoline, and diesel, as the main transportation fuel in the future. Thus, this fuel has broad application prospects [1]. Biomass resources are scattered, with low energy density and high collection and transportation costs. Thus, the processing system of distributed biomass must be developed according to local conditions by converting biomass resources into the bio-oil of intermediate products to improve energy density and to reduce transport cost. The bio-oil of intermediate products is then collected from bio-refinery factories to improve and modify quality for the preparation of high-grade liquid biofuels [2,3]. Supercritical fluid technology has been widely applied in material preparation, chemical reaction, and many other fields given its excellent heat and mass transfer capability and controllability. This technology has also been used successfully in biofuel production [4–6].

The technology for biomass hydrothermal treatment processes biomass by considering the properties of subcritical/supercritical water. This topic is popular in current research on biomass resource degradation and transformation. All conditions that can affect the properties of water during hydrothermal reaction are regarded as influential factors in this reaction. These conditions mainly include reaction temperature, pressure, residence time, and catalyst [7].

Reaction temperature, pressure, and time are important parameters in hydrothermal treatment. Therefore, their settings directly affect the treatment goals and effect. In particular, the settings of temperature and pressure influence the properties and role of water in hydrothermal treatment firsthand. This effect is the focus of recent research [8–10]. The temperature and pressure requirements for hard-degradation biomass are generally high. By contrast, those for cellulose, hemicelluloses, and lignin are low [11,12]. When temperature and pressure increase, the hydrothermal reaction becomes increasingly exhaustive as well. The material

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reacts quickly, and the reaction process is usually completed within a few seconds. This procedure produces CO_2 and water. Nonetheless, the pressure of the hydrothermal reaction is generally determined by the temperature setting during actual treatment research.

Residence time is another important factor that affects the influence of hydrothermal treatment. Terminating the reaction at the appropriate time can not only generate a good treatment effect but can also save energy; thus, this factor is also a hot topic in the research on hydrothermal treatment [13,14]. Residence time is determined based on the raw materials, temperature, and pressure applied during the treatment, as well as the desired product. In particular, the temperature and pressure of the treatment are negatively related to this factor. In other words, residence time is shortened accordingly if temperature and pressure increase when the same kinds of materials are treated and when the desired results are similar.

The use of catalysts is another influential factor in hydrothermal treatment. The addition of suitable catalysts can not only accelerate the reaction rate but can also change the reaction route. Furthermore, new desired products are generated, thereby improving treatment effect and efficiency. The catalysts studied in relation to hydrothermal reaction technology can be categorized into oxidant and chemical catalysts. The former is investigated by adding peroxides such as hydrogen. Research confirms that the incorporation of oxidant catalysts can improve treatment efficiency and can change the reaction route. At present, studies on this aspect mainly focus on the added amount and residence time of oxidants. The scope of research on chemical catalysts mainly includes dilute acid [15,16], dilute alkaline solution [17], and neutral or basic salt and metal [18,19].

Gao et al. discussed the influence of reaction temperature on the distribution of the gas products of heavy oil, solid residue, and light oil from hydrothermal treatments conducted on cellulose. As per analysis results, heavy oil yield is high when cellulose temperature is within the range of 250 °C–350 °C and residence time ranges from 5 min to 30 min [20]. Therefore, the liquid product prepared within this range is suitable for the characteristics and high-value application of products derived from the yield. Yin et al. studied the pyrolysis behavior of cow manure in subcritical water and determined that its oil yield is maximized at 48.38 wt.% when hydrolyzed at 310 °C given a residence time of 15 min and an atmosphere of CO. The main ingredients are toluene, ethylbenzene, and xylene, as in gasoline and diesel. The average heat value of the oil is 35.53 MJ/kg [21]. Cheng et al. investigated the hydrothermal liquefaction of switch grass with an 11 ml hydrothermal reactor in subcritical water. They determined that the conversion rate of biomass can exceed 90 wt.% when the temperature is between 250 °C and 350 °C, pressure is 20 MPa, and residence time ranges from 1 s to 300 s. This finding indicated that the hydrothermal reaction is successful in the conversion of biomass to liquid fuel oil under the rapid reaction condition [22]. Huang et al. studied the hydrothermal characteristics of straw, microalgae, and sludge at 350 °C and a residence time of 20 min. Despite the low content of organic matter in sludge, the yield of bio-oil reached 39.5 ± 1.16 wt.%. Moreover, the calorific value was 36.14 MJ/kg, which was significantly higher than those of straw (21.1% ± 0.93%) and microalgae (34.5% ± 1.31%). GC–MS (gas chromatography–mass spectroscopy) results showed that the bio-oil of straw mainly contained phenols, whereas those of sludge and microalgae primarily consisted of esters [23]. Akalin et al. conducted a hydrothermal treatment on cherry stones at reaction temperatures of 200 °C, 250 °C, and 300 °C and residence times of 0, 15, and 30 min. Oil yield is high at 28.00 wt.% under temperatures of 250 °C and 300 °C, as well as a residence time of 0 min. Solid residue yield gradually decreases with temperature and residence time. Furthermore, the heat values of light and heavy oils are 23.86 and 28.35 MJ/kg, respectively. The light oil mainly contained furfural, phenol, and vanillin. In heavy oil, the concentration of linoleic acid is maximal at 250 °C and 300 °C [24]. To improve oil yield and quality, catalysts can be added to the hydrothermal reaction by restraining the condensation reaction from oil to coke. Song et al. conducted a liquefaction experiment that incorporates catalysts and determined that oil yield increases from 33.4 wt. % to 47.2 wt. % when 1 wt. % of Na_2CO_3 is added [25].

The hydrothermal liquefaction of biomass converts the active group in the biomass to liquid organic material to maximize its use. Thus, the reaction route of the liquefaction of the main biomass component, the method of generating the active group, and the structure and distribution of liquefied products must be clarified. This clarification is the theoretical basis for controlling the liquefaction path. In the current study, the hydrothermal method is first applied in an orthogonal experiment. The optimal process conditions are determined for different target products. Among the agricultural straws, cotton straw displays the highest liquid yield. However, ash content is low. Thus, the quality of bio-oil is relatively high. Cotton straw is used as the raw material in this study. Furthermore, the production distribution during the hydrothermal reaction of biomass is investigated according to different influential factors, such as the reaction temperature, residence time, catalyst, and particle size of biomass samples. It is also examined by separating and analyzing products effectively. The formation process and chemical composition of the oil phase products are analyzed as well.

2. Material and method

2.1. Samples

Rice straw, cotton straw, pine sawdust, and water hyacinth were utilized as the raw materials in the experiment. The samples were collected from the city of Wuhan, which is located south of China. The samples were dried at 55 °C for 8 h after crushing and screening. They were then sealed in the drying tower. The solvents (acetone) and bases [NaOH, Na_2CO_3, KOH, K_2CO_3, and $Ca(OH)_2$] were purchased from Shenshi Chemicals, China and were used as received.

2.2. Experiment procedure and analysis

The biomass was dried at 105 °C for 12 h. It was hydrothermally treated in a high-temperature (maximum working temperature of 600 °C) and high-pressure (maximum pressure of 40 MPa) CWYF-type batch reactor manufactured by Haian Scientific Research Devices Co., Ltd. (Jiangsu, China). This reactor was equipped with a 500 cm^3 vessel made of 316 L stainless steel, was 150 mm high, had an internal diameter of 65 mm, and possessed 2 mm-thick walls. It also contained with a 1000 rev/min magnetic mixer, a manometer, and an internal cooler in the form of a U-loop. A thermo-coupler was also placed in the vessel within the reactor. The temperature was controlled at 5 °C, and the pressure was measured at an accuracy of 2%.

In the typical catalytic hydrothermal experiment, the reactor was loaded with 8 g (dry basis) of cotton straw and 110 ml of 1 M alkaline solutions [NaOH, Na_2CO_3, KOH, K_2CO_3, and $Ca(OH)_2$]. In the thermal run, the reactor was loaded with a certain amount of biomass and deionized water once the raw materials swelled completely. After the air was displaced, the autoclave was heated to the desired reaction temperature and set to the specified residence time. Then, it was cooled to room temperature with an electric fan and the internal cooling U-loop. In a flow-through process, the biomass was subjected to a typical temperature cycle for a 500 mL autoclave reactor, that is, 300 °C with a 20 min residence time. This condition is shown in Fig. 1.

Once the reaction was completed, the gas was vented. Thus, the pressure is reduced to an atmospheric level. The solid and liquid mixtures were removed from the autoclave for separation. This procedure is depicted in Fig. 2. Then, the acetone extracts were dried in the rotary evaporator at 45 °C and 0.006 MPa. The corresponding fraction was weighed and designated as heavy oil. The solid residue was defined as the acetone insoluble fraction and dried at 105 °C. The yields of the heavy oil, solid residue, and light oil + gas were defined as the weight percentages to the raw material.

$$\text{Heavy oil yield (wt.\%)} = (\text{weight of heavy oil}) \times /(\text{weight of raw material}) \times 100\%$$

$$\text{Solid residue yield (wt.\%)} = (\text{weight of solid residue})/ \times (\text{weight of raw material}) \times 100\%$$

$$\text{Light oil} + \text{gas yield (wt.\%)} = 100 - \text{heavy oil yield (wt.\%)} - \text{solid residue yield (wt.\%)}$$

Each experiment was repeated thrice, and the relative errors were within 9%.

The elemental compositions of biomass, namely, C, H, S and N, were analyzed with a Series II CNHS/O 2400 elemental analyzer (PerkinElmer instruments). O content was determined based on differences. The HHV (higher heating value) of each product was calculated using Dulong formula: HHV (MJ/kg) = 0.3383C + 1.422 (H–O/8) [26]. FTIR (Fourier transform infrared spectroscopy) (Bruker's VERTEX-70) analysis was performed as described previously [27]. The process was run before each measurement to establish a background with KBr. In this study, the infrared spectra between 4000 and 500 cm^{-1} were recorded with a resolution of 4 cm^{-1}. To produce a pellet, approximately 1 mg of dried sample was mixed with 100 mg KBr (Merck, spectroscopy grade). The resultant mixture was pressed successively at 10 $tons/cm^2$ for 5 min under vacuum. The Van Soest method was applied to determine the contents of hemicellulose, cellulose, and lignin in biomass using the ANKOM 2000 Fiber Analyzer.

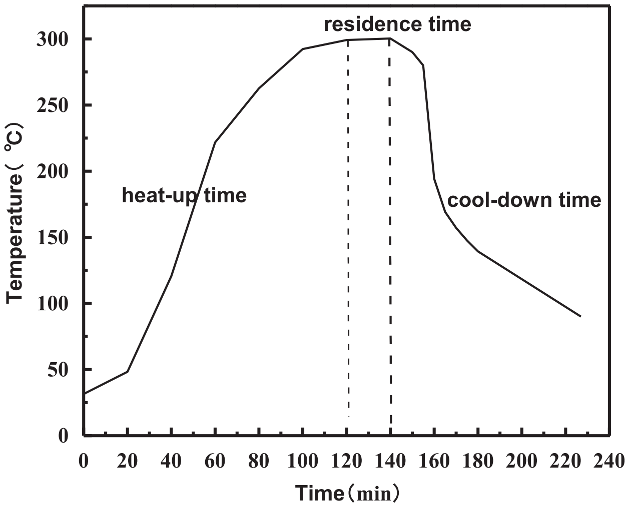

Fig. 1. Schematic diagram of a typical temperature cycle for 500 mL autoclave reactor to 300 °C with 20 min residence time.

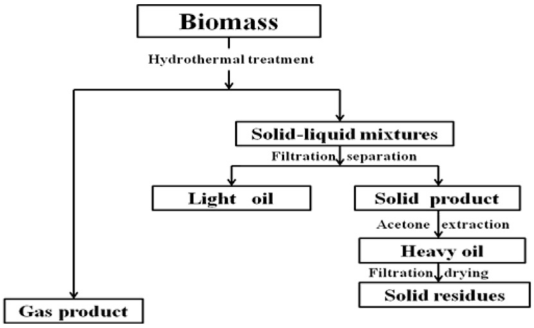

Fig. 2. Products separation after hydrothermal treatment.

The chemical compositions of heavy oil were identified with GC–MS (HP7890 series GC with an HP5975 MS detector that is equipped with a DB-WAX chromatographic column). The film in the column was composed of bonded 5% phenyl and 95% methyl siloxane. Moreover, the GC–MS operating conditions were as follows: 45 °C for 5 min, increased to 250 °C at a rate of 5 °C/min, and finally maintained at 250 °C for 10 min. In each trial, 1 μL volume of heavy oil dissolved in acetone at a split ratio of 5:1 was injected. A micro filter was used to remove the particles in the heavy oil prior to injection into GC–MS. The flow rate of helium was 1 ml/min for the column.

2.3. Experimental design

According to research on the hydrothermal process of cellulose [20], rising temperature decomposes the heavy oil produced during this process and enhances the production of solid residue and gas. However, an excessively high temperature results in the secondary decomposition of heavy oil. This procedure reduces the yield. In addition, the composition of heavy oil is complicated, and the extended residence time limits the yield of heavy oil. Thus, the current study mainly identified the distribution and characteristics of hydrothermal products at temperatures ranging between 250 °C and 350 °C and with residence times ranging from 5 min to 30 min. The experimental conditions are summarized in Table 1. The factors that may affect hydrothermal conversion were determined primarily through an orthogonal experiment, and they included biomass, temperature, residence time, concentration, and particle size. Then, the factors that influence the characteristics of hydrothermal products were selected on the basis of the same experiment to conduct the single-factor test.

3. Result and discussion

3.1. Biomass characterization

The results of the ultimate, elemental and calorific value analyses of biomass are presented in Table 2. V (volatile) content was high in agricultural straw and in pine sawdust. The ash content in pine sawdust was the lowest at 0.20 wt.%. Moreover, pine sawdust had high C and fixed carbon contents at 51.01 and 14.19 wt.%, respectively. Therefore, pine sawdust has a maximum calorific value of 18.16 MJ/kg. Nonetheless, the contents of N and S were low in agricultural straw and pine sawdust. The oxygen and V contents were low in water hyacinth at 22.68 and 49.92 wt.%, respectively. By contrast, the contents of N and S were significantly higher in this biomass than in the other three biomasses, as was ash content.

Table 1
Summary of experimental conditions.

	Biomass	Temperature (°C)	Residence time (min)	Sample/water (g/g)	Particle size (mesh)	Catalyst
Orthogonal	Rice straw	250	5	7/110	80	–
	Cotton Straw	275	10	8/110	80–150	–
	Pine sawdust	300	15	9/110	150–200	–
	Water hyacinth	325	20	10/110	200	–
Single-factor	Cotton Straw	250–350 °C	20	8/110	80	–
	Cotton Straw	300	5 −30min	8/110	80–150	–
	Cotton Straw	300	20	8/110	150–200	–
	Cotton Straw	300	20	8/110	200	K_2CO_3, KOH et al.

Table 2
Main characteristics of the biomass (wt.%).

Sample	Elemental analysis, d					Ultimate analysis, ad					Chemical analysis(%)		
	N	C	S	O[a]	H	M	V	A	FC	HHV (MJ/Kg)	cellulose	Hemicellulose	Lignin
Cotton straw	1.15	45.22	0.34	46.94	6.34	5.10	72.98	3.09	16.73	15.97	46.2	18.7	25.4
Rice straw	0.86	37.52	0.14	42.78	5.92	5.04	82.12	7.74	5.10	13.51	37.5	32.8	16.0
Pine sawdust	0.10	51.01	0.02	42.90	6.00	15.30	70.40	0.20	14.19	18.16	55.3	10.1	27.2
Water hyacinth	2.03	29.75	0.33	22.68	5.41	5.69	49.92	38.11	6.28	13.73	23.5	33.6	8.6

[a] The oxygen (O) content was determined by difference; ad: on air dried basis; d: on dry basis.

To clarify the internal chemical structure of biomass and its three components, FTIR analysis was conducted on five dried biomasses. As per Fig. 3, the chemical component of biomass mainly included different oxygen functional groups, such as ether, aromatic, alkanes [OH (3400–3200 cm^{-1}), C=O (1765–1715 cm^{-1}), C–O (1050 cm^{-1}, 1270 cm^{-1}), ketone, and alcohol (3000–2800 cm^{-1} and 900–700 cm^{-1})]. Given that the contents of cellulose, hemicelluloses, and lignin differed in straw, in pine sawdust, and in water hyacinth, they exhibited varying infrared absorption properties as well. According to literature [28], a strong absorption peak was observed at 1732 cm^{-1} in the biomass. This peak was the C=O stretching vibration that corresponded to the existence of hemicellulose. The peaks at 1648 and 1515 cm^{-1} were aromatic hydrocarbon, which characterized the typical absorption peak of lignin. The absorption peak of β-glucosidic bond vibration at 899 cm^{-1} was characteristic of cellulose. Moreover, the absorption peak of aromatic hydrocarbon was higher in pine sawdust than in the other three biomasses because pine sawdust contained the most lignin. Water hyacinth displayed the maximum C=O absorption peak because its hemicellulose content is the highest among the studied biomasses.

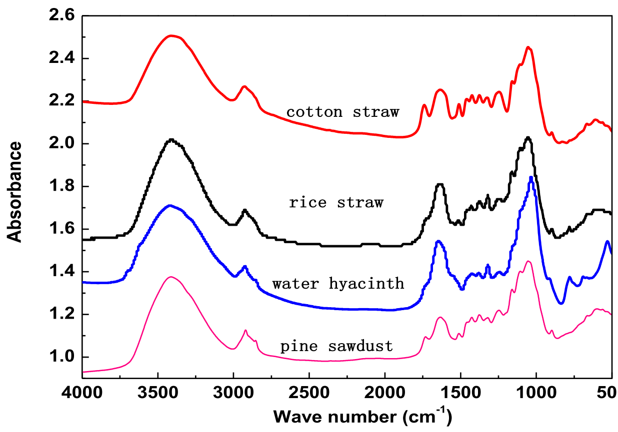

Fig. 3. FTIR spectra of different biomass.

3.2. Optimization of hydrothermal product yield using orthogonal design method

As mentioned previously, many factors affect the yield of the hydrothermal products of biomass, including biomass type, residence time, reaction temperature, concentration, and particle size [29,30]. To control experiment conditions and to improve yield effectively, a five-factor, two-level orthogonal experiment was performed (Table 3). The influence of the reaction factors on the test results is depicted in Table 4.

On the basis of the data and Range R results, the influence of five factors on heavy oil yield can be ranked as follows: A > E > B > C > D. Therefore, the difference in raw materials influenced yield the most, followed by the particle size of the raw material, the temperature, the residence time, and the concentration. The table also presents the influence of these factors on the yields of solid residue, light oil, and gas.

Fig. 4 depicts the effects of reaction conditions on the yield of orthogonal experiment products. Specifically, Fig. 4(a) indicates that pine sawdust yielded the largest amount of heavy oil among the four biomasses in the experiment. Rice straw displayed the highest solid residue yield. Although water hyacinth yielded the least solid residue and heavy oil, it yielded the most light oil and gas. This result is mainly due to the different content levels of the three components (cellulose, hemicelluloses, and lignin) and of the ash in biomass. Tables 1 and 2 suggest that the ash content in pine sawdust is low, whereas those of cellulose and lignin were high at 55.3% and 27.2%, respectively. Thus, the amount of organic matters in the hydrothermal reaction that takes place in pine sawdust was higher than that in other biomasses. As a result, heavy oil yield is high. Fig. 4(b) illustrates that a decrease in particle size reduces this yield. Moreover, the increasing trend of solid residue was insignificant. The yields of light oil and gas initially increased and then decreased. As a result of the dissolution and swelling of raw materials and water during hydrothermal conversion, small particles can promote contact between raw materials and water, can accelerate the hydrolysis and degradation of biomass, and can inhibit the condensation and polymerization of decomposed products. In the process, the yield of light oil increases and the yields of heavy oil and residue are reduced. According to Fig. 4(c), the increase in temperature from 250 °C to 325 °C first increased and then reduced

Table 3
Orthogonal experiment list $L_{16}(4^5)$.

Level	Factors				
	Biomass A	Temperature B (°C)	Residence time C (min)	Concentration D(g/g)	Particle size E(mesh)
1	Rice straw	250	5	7/110	80
2	Cotton straw	275	10	8/110	80–150
3	Pine sawdust	300	15	9/110	150–200
4	Water hyacinth	325	20	10/110	200

heavy oil yield. The yields of light oil and gas exhibited a trend of significant increase, whereas that of solid residue decreased with the increase in reaction temperature. Biomass was hydrolyzed to produce glucose and dimmer at low temperature. Simultaneously, the hydrolysis product was decomposed and degraded. Complex reactions such as condensation and polymerization produced a small amount of heavy oil. Part of the biomass did not participate in the reaction in solid residue. Its concentration increased with the increase in temperature, and the heavy oil yield was maximized at 300 °C. Meanwhile, the part that did not participate in the reaction in solid residue was thoroughly decomposed. This process may be induced by the direct decomposition of the intermediates or the liquid products. The rising temperature promoted the secondary reactions in solid residue and heavy oil. These products were soluble in water, thereby reducing yield. By contrast, the yields of light oil and gas increased. According to Fig. 4(d), the yield of hydrothermal products did not change significantly when reaction time increased. Furthermore, the conversion rate of biomass was usually high. The target product yield increased when the reaction time increased. If this time is adequately long, then the concentration of the reactant is reduced and the conversion rate decreases. As shown in Fig. 4(e), solid residue yield increased significantly with the increase in concentration. However, the yields of liquid and gas did not vary considerably. This finding may be attributed to the fact that the increased concentration limited the contact opportunities of raw materials and solvent. As a result, the reaction of reactants was incomplete. Solid residue yield increased in the process and did not promote the production of other products effectively. Hence, yield is low. If heavy oil yield is the desired product, the optimal process conditions include the use of pine sawdust as the raw material and adopting a temperature of 250 °C, a residence time of 15 min, a concentration of 10 g/110 g, and a biomass particle size of 80–150 mesh. Under these conditions, the heavy oil yield of pine sawdust was 28.00 wt.% on dry basis. If solid residue yield is the desired product, then the ideal process conditions include the employment of rice straw as the raw material and the application of a temperature of 250 °C, a residence time of 5 min, a concentration of 7 g/110 g, and a biomass particle size of 80 mesh. If the yields of light oil and gas are the desired products, then the best process conditions include the application of water hyacinth as the raw material and the adoption of a temperature of 275 °C, a residence time of 15 min, a concentration of 7 g/110 g, and a biomass particle size of 200 mesh.

3.3. Effect of temperature

To understand the influence of various factors on the hydrothermal process and to identify the hydrothermal conversion characteristics of biomass, the sensitive factors were prioritized in the experimental study. First, cotton straw was examined in line with the research objective. The other conditions were fixed to determine the influence of temperature, time, particle size, and catalyst on the yield of this product. The products generated by hydrothermal conversion were heavy oil, solid residue, and light oil + gas. The high content of water in the light oil affected the utilization of organic chemicals. The gas product yield was low enough to be neglected. Moreover, heavy oil and solid residue were extracted from the solid product with acetone. The solid residue was composed of inorganic materials and small amounts of low-quality organic ones. Thus, the heavy oil was of high quality. The characteristics of heavy oil were analyzed to employ these products in the hydrothermal conversion process with high quality. If no

Table 4
Product yield of biomass in $L_{16}(4^5)$ matrix.

	Trial NO.	Heavy oil yield (wt.%)	Solid residue yield (wt.%)	Light oil + gas yield (wt.%)
1	11,111	19.29	33.0	47.71
2	12,222	14.88	27.50	57.63
3	13,333	14.11	28.56	57.33
4	14,444	12.90	30.30	56.80
5	21,234	19.22	32.67	48.11
6	22,143	18.20	27.90	53.90
7	23,412	21.00	23.86	55.14
8	24,321	19.88	23.00	57.13
9	31,342	28.00	29.50	42.50
10	32,431	27.67	25.89	46.44
11	33,124	27.75	24.38	47.88
12	34,213	25.74	22.29	52.00
13	41,423	7.13	22.13	70.75
14	42,314	5.71	17.86	76.43
15	43,241	12.10	17.60	70.30
16	44,132	8.33	17.22	74.44
Range	A	18.97	11.14	25.78
	B	2.13	6.12	7.83
	C	1.47	0.90	2.37
	D	0.60	2.07	2.47
	E	3.44	1.78	3.10
The affect order		A > E > B > C > D	A > B > D > E > C	A > B > E > D > C

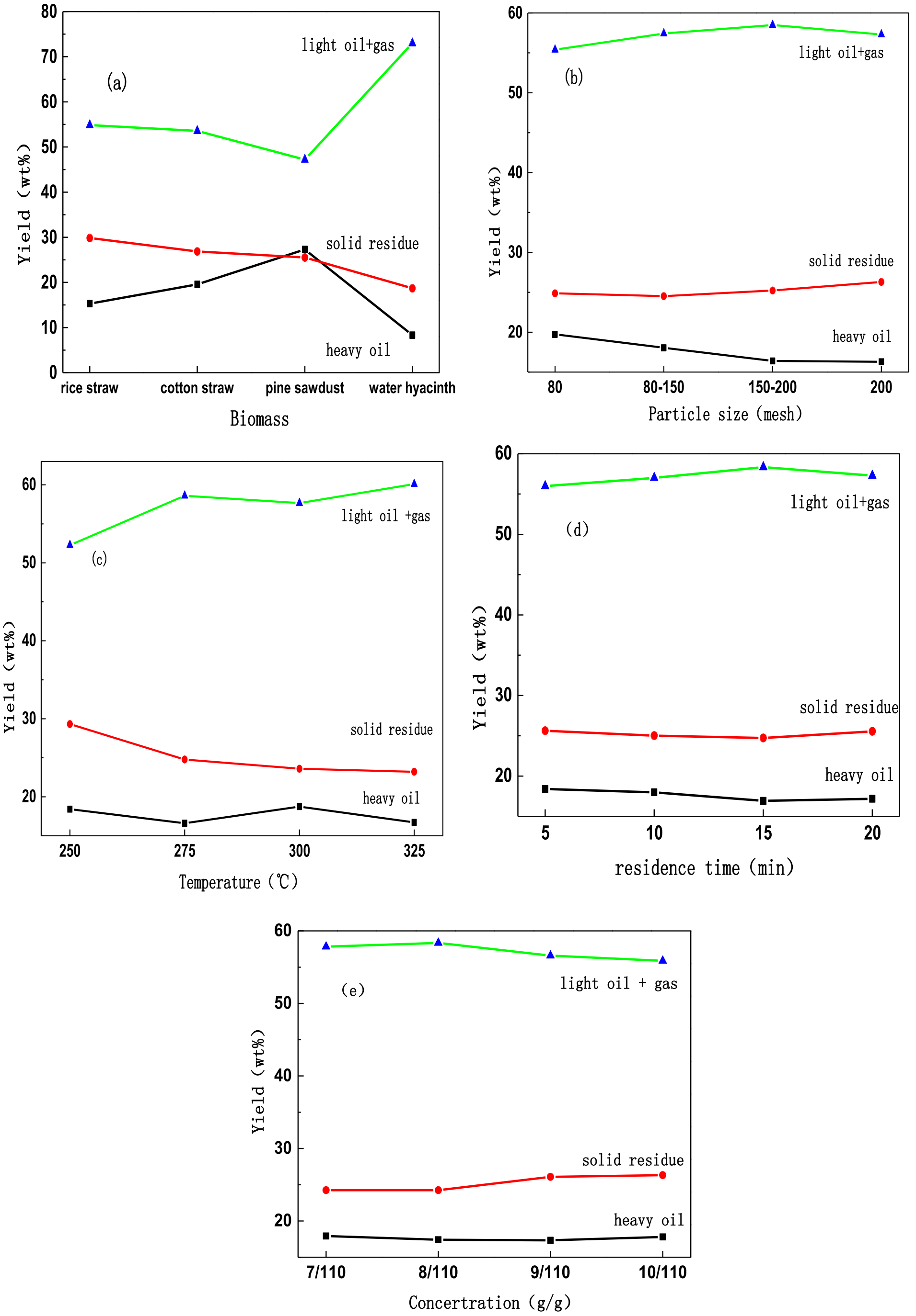

Fig. 4. The effects of reaction conditions on the yield of the products.

special instruction was provided, the conditions of the hydrothermal reaction were set as follows: reaction time of 20 min, temperature of 300 °C, concentration of 8 g/110 g, particle size 80–150 mesh.

Hydrothermal temperature is the key factor that affects the hydrothermal process of biomass and the distribution of products. As per the results of the orthogonal experiment, the heavy oil yield of cotton straw through hydrothermal conversion was maximized at approximately 300 °C. Thus, the temperature in this study ranged from 250 °C to 350 °C.

Fig. 5 illustrates the effect of temperature on the product distribution of cotton straw. The increase in temperature reduced solid residue yield. Moreover, the heavy oil yield first increased and then decreased. The yields of light oil and gas increased. Specifically, the yield of heavy oil was 16.98 wt.% at 250 °C; it was then maximized at 19.57 wt.% given a temperature of 275 °C. At this point, the solid residue yield decreased from 32.14 wt.% to 23 wt.%. When the temperature range was between 275 °C and 325 °C, the yields of heavy oil and solid residue did not change significantly. When the temperature reached 350 °C, the heavy oil yield was 8.99 wt.%. The yield of both light oil and gas was 67.87 wt.%. The reaction mainly involved the hydrolysis of cellulose and hemicellulose to generate glucose and dimmer when the temperature was below 275 °C. Thus, heavy oil yield was low. The materials that did not participate

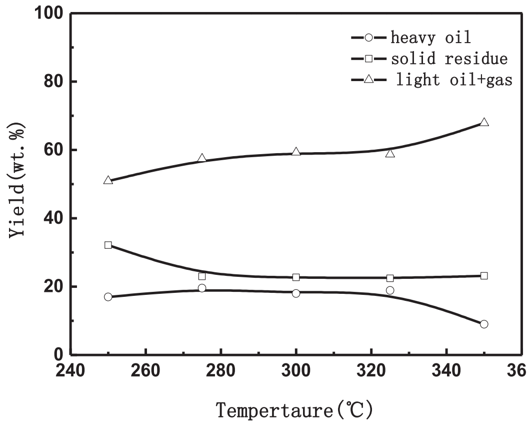

Fig. 5. Effect of temperature on product distribution of cotton straw.

in the reaction in solid residue yielded little gas. Furthermore, the organic carbon content in light oil was high. The increase in temperature enhanced decomposition rate. In addition, the biomass was hydrolyzed. The amount of macromolecule compounds increased gradually, and these compounds were combined into macromolecular compounds. Lignin was also hydrolyzed at this point to generate a large amount of phenolic compounds, thereby increasing heavy oil yield and reducing solid residue yield. Lignin is difficult to decompose. When the temperature exceeded 325 °C, heavy oil yield decreased and the yields of light oil + gas increased continuously. This result indicates that increases in temperature did not promote the hydrolysis of biomass considerably. However, it enhanced the occurrence of secondary reactions, the degradation of heavy oil, and the generation of gas phase products through glucose gasification.

The main composition of the heavy oil obtained through the hydrothermal processing of cotton straw under different temperatures is shown in Table 5. Under this experimental condition, 25 types of compounds were detected in the heavy oil derived from cotton straw. These compounds include fatty acid, ethyl esters, other esters, ketones, and phenolic derivatives. The relative contents of some compounds were less than 0.1 wt.%; these contents are expressed as "-" in the table. The contents of acids, aldehydes, and phthalic acid [namely, mono-(2-ethylhexyl) ester] measured 9.77, 6.76, and 57.36 wt.%, respectively, in the heavy oil at 250 °C. Among these compounds, ester content was the highest. This part of the esters was obtained through the reaction of organic acids and alcohols in the converted products. Moreover, the contents of ketones and phenols were low because the low temperature was conducive to biomass hydrolysis. Cellulose was first hydrolyzed to generate glucose and fructose. Then, sugar monomers were hydrolyzed, depolymerized, and degraded further to produce small molecule compounds. The contents of acids, aldehydes, and esters in heavy oil decreased significantly at 300 °C in heavy oil. By contrast, those of ketones, phenols, and benzenes increased to 9.75, 29.79, and 7.60 wt.%, respectively. These amounts were conducive to the use of these compounds as chemicals. The content of guaiacol and its derivatives measured roughly 11.03 wt.% in these chemicals. Guaiacol was primarily the product of lignin hydrolysis, thus indicating that lignin was hydrolyzed at high temperatures. Hydrolysis products were decomposed at this point, and the heavy oil was subject to secondary decomposition to generate the compounds when temperature increased. The content of phenols decreased to 22.71 wt.% when the temperature reached 350 °C, and those of ketones and benzenes were 14.63 and 6.86 wt.%, respectively.

3.4. Effect of residence time

Both residence time and hydrothermal temperature also affected the distribution of hydrothermal products. A long residence time reduced heavy oil yield. Therefore, the typical residence time was between 20 and 40 min. In this study, the influence of residence time on the hydrothermal conversion of cotton straw was investigated at 5, 10, 15, 20, 25, and 30 min. The temperature of hydrothermal conversion was 300 °C. Furthermore, particle size ranged from 80 to 150 mesh, and the material ratio was 8 g/110 g.

Table 5
GC/MS analysis results of the heavy oil from different temperatures with cotton straw for 20 min.

		Area (wt.%)		
		250 °C	300 °C	350 °C
Acids	Acetic acid	7.39	5.88	2.55
	n-Hexadecanoic acid	2.38	3.55	2.45
Aldehydes	Furfural	1.53	0.78	0.51
	2-Furancarboxaldehyde, 5-methyl-	2.95	–	–
	Vanillin	2.28	1.65	–
Esters	Phthalic acid, mono-(2-ethylhexyl) ester	57.36	7.52	13.07
Phenols	Guaiacol	1.48	5.51	3.56
	4-Ethylguaiacol	0.81	5.52	7.02
	2-methoxy-4-propyl-Phenol	0.22	2.25	2.58
	2,3-Xylenol	–	2.26	3.74
	2,6-Dimethoxyphenol	3.05	7.07	2.59
	(e)-isoeugenol	1.44	2.98	1.44
	Phenol,2,6-dimethoxy-4-(2-propen-1-yl)-	1.82	2.83	–
	Phenol	0.46	1.37	1.78
Ketones	4-Hydroxy-4-methyl-2-pentanone	1.41	2.29	2.62
	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	1.69	1.07	0.74
	5-Methyl -2-(1-2- Cyclohexene -1-one)	0.48	1.76	2.91
	2-Hydroxy-5-methyl acetophenone	0.63	1.48	1.78
	3-Methyl -2-(1 , 3-Dodecenyl)-2- cyclopentenone	1.01	0.77	1.99
	2-Hydroxy −3 , 4 dimethyl -2- cyclopentenone	–	2.38	4.59
Phenyl	2,3-Dimethylfluorobenzene;	–	1.44	1.86
	4-Propylbiphenyl	0.5	2.79	2.77
	4-Ethylbiphenyl	–	3.37	2.23
Alkanes	cis-9-Tricosene	–	2.49	3.47
	15-Crown-5	0.66	6.16	3.36

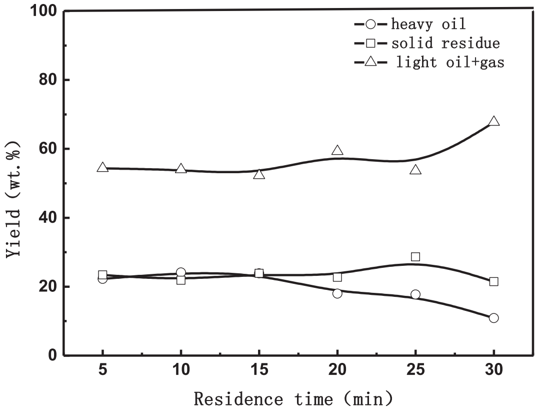

Fig. 6. Effect of residence time on product distribution of cotton straw.

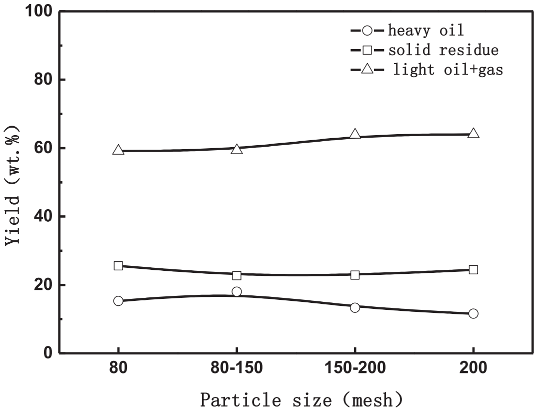

Fig. 7. Effect of particle size on product distribution of cotton straw.

Fig. 6 displays the effect of residence time on the product distribution of cotton straw. When residence time was less than 15 min, heavy oil yield first increased and then decreased. This yield peaked at 24.14 wt.% when the residence time was 10 min. In addition, the solid residue yield first decreased and then increased. The yields of light oil and gas did not change considerably. When the residence time was extended to 30 min, the heavy oil yield decreased to 10.86 wt.%. The solid residue yield first decreased and then increased. Furthermore, this yield reached 28.67 wt.% when residence time was 25 min. The yields of light oil and gas increased in the process. When the reaction temperature was 300 °C, cotton straw was hydrolyzed at low temperatures. The hydrolyzed straw and its products were degraded further to generate liquid products. Under this condition, the extension of residence time can inhibit the production of the intermediates of cotton straw degradation. It can also promote the generation of glucose decomposition products, such as acids, aldehydes, alcohols, and other small molecular compounds. However, this extension cannot enhance hydrothermal reaction. The hydrolysis products of cotton straw experienced secondary decomposition. Moreover, the thermal decomposition or agglomeration of liquid products generated coke and other insoluble materials. As a result, the yields of heavy oil and solid residue decreased, whereas the yields of light oil and gas increased.

Table 6 shows that the components of heavy oil were similar and did not change significantly given different residence times. The heavy oil was mainly composed of acids, aldehydes, ketones, phenols, and esters. When residence time increased to 30 min, the content of phthalic acid [mono-(2-ethylhexyl) ester] peaked at 36.53 wt.%. The contents of aldehydes, ketones, and acids decreased, whereas those of phenols and their derivatives increased. Due to the certain oxidation of subcritical water, the small molecular compounds generated during the hydrothermal conversion of cotton straw were oxidized to organic acids and phenolic derivatives. This process lowered the pH value of heavy oil because of the acidity and corrosivity. Esters were generated by the esterification initiated between organic acids and alcohols. Therefore, residence time influenced heavy oil yield significantly, but it affected chemical composition only slightly.

Table 6
GC/MS analysis results of the heavy oil from different residence time with cotton straw for 300 °C.

		5 min	15 min	25 min	30 min
Acids	Acetic acid	4.09	3.46	3.99	4.03
	Benzenecarboxylic acid	1.09	1.57	1.17	–
	4-Hydroxy-3-methoxyphenylacetic acid	1.41	1.23	1.05	0.67
	Stearic acid	1.01	0.66	1.29	–
	n-Hexadecanoic acid	4.30	3.32	4.19	5.95
Aldehydes	Furfural	1.19	0.78	1.02	0.74
	4-Hydroxy-3,5-dimethoxybenzaldehyde	1.11	0.88	1.2	0.67
	2-(2- furfuryl)-5-methylfuran	1.47	1.05	1.28	2.00
	Vanillin	2.01	1.65	1.34	–
Esters	phthalic acid, mono-(2-ethylhexyl) ester	13.85	9.69	6.18	36.53
Phenols	Guaiacol	4.45	3.77	5.29	5.90
	4-Methyl guaiacol	1.15	1.32	1.56	1.98
	4-Ethylguaiacol	3.18	2.53	3.30	4.43
	2-methoxy-4-propyl-Pheno	1.78	1.52	2.05	2.73
	Eugenol	1.78	1.20	0.90	1.37
	2,3-Xylenol	4.76	3.47	–	–
	2,6-Dimethoxyphenol	6.75	5.89	9.38	7.35
	2,6-Dimethoxy-4-allylphenol	1.32	1.27	1.24	–
	Phenol	1.21	1.06	0.94	1.27
Ketones	4-Hydroxy-4-methyl-2-pentanone	2.43	3.32	3.08	3.62
	5-Methyl-2-(1-2- Cyclohexene -1-one)	1.83	1.45	1.71	1.94
	3-Methyl-2-(1 , 3- pentadienyl)-2- Cyclopentenone	1.47	1.05	1.28	–
	4′-Methylthioacetophenone	1.60	1.05	1.07	–
Phenyl	4-Propylbiphenyl;	2.48	2.25	3.24	3.08
	4-Ethylbiphenyl	3.33	2.94	3.47	3.31
Others	3-Pyridinol	1.53	1.13	1.16	0.76
	6-Dimethyldibenzothiophene	0.19	0.25	1.53	0.87

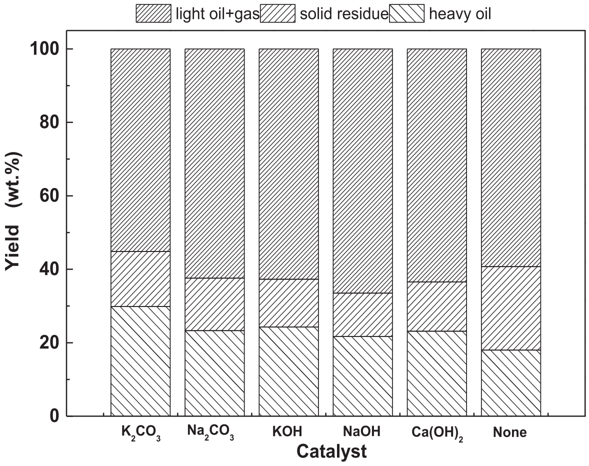

Fig. 8. Effect of catalysts on product distribution of cotton straw.

3.5. Effect of particle size

In this study, the influence of the particle size of raw materials on hydrothermal products was investigated. The particle size ranges were 80, 80 to 150, 150 to 200, and 200 mesh. The results are depicted in Fig. 7. Particle size had little influence on the hydrothermal conversion of cotton straw relative to reaction temperature and time. The experiment results indicated that an increase in particle size first improved and then reduced heavy oil yield. Solid residue initially decreased and then increased, whereas the yields of light oil and gas displayed an increasing trend. Heavy oil yield peaked at 18 wt.% when particle size was between 80 and 150 mesh. When the particle size of the reactant decreased, the cellulose and hemicellulose in the cotton straw dissolved easily. This condition was conducive to the conversion of the degradation products into light and gaseous products. Thus, production yield increased. Heavy oil yield decreased gradually, thereby indicating that a small particle did not promote the production of heavy oil. Particle size mainly affected the secondary reaction. When the temperature was 300 °C and the residence time was 20 min, a small raw material particle was conducive to the miscibility of cotton and water, thus accelerating the hydrothermal reaction. Given the rapid low-temperature hydrolysis and high-temperature pyrolysis reactions, the polymeric products generated through condensation and pyrolysis transformed into solid residue while the heavy oil was subject to the secondary reaction. The yield decreased as well.

3.6. Effect of catalyst

As indicated in Fig. 8, the addition of catalysts increased heavy oil yield and reduced that of solid residue. The yields of light oil and gas did not change significantly. The influences of catalysts on heavy oil yield were ranked as follows: $K_2CO_3 > KOH > Na_2CO_3 > Ca(OH)_2 > NaOH$. When K_2CO_3 was used as the catalyst, heavy oil yield increased from 18 wt.% to 29.86 wt.%. By contrast, residue yield decreased from 22.71 wt.% to 15.00 wt.%. Moreover, those of light oil and gas dropped from 59.29 wt.% to 55.14 wt.%. When NaOH was the catalyst, the yield of residue was minimal at only 11.80 wt.%. The catalysts that contained K^+ facilitated the positive development of the reaction. These catalysts can increase heavy oil yield and reduce solid residue yield at the same time because K^+ displays strong polarity and because the polarity of potassium is close to that of water. In sum, alkaline catalysts can promote the hydrothermal decomposition of cotton straw, can increase heavy oil yield, can inhibit the promotion of cotton thermal decomposition in water simultaneously, can improve heavy oil production rate, and can inhibit condensation. Furthermore, K_2CO_3 exerts a good catalytic effect.

The compositions of heavy oil produced after adding K_2CO_3 and KOH are analyzed through GC–MS. Table 7 indicates that the heavy oil generated without catalysts mainly contained acetic acid, hexadecanoic acid, phthalic acid [mono-(2-ethylhexyl) ester], guaiacol, (4-ethylguaiacol), and 2,6-Dimethoxyphenol. When the catalyst used was K_2CO_3, the content of phthalic acid [mono-(2-ethylhexyl) ester] was 18.52 wt.%. Its content peaked at 28.53 wt.% when the catalyst applied was KOH. Thus, catalysts can promote etherification. Once they were added, the heavy oil also contained 4-methylphenol, 1-hydroxy-2-methoxy-4-propen-1-yl benzene, 2,5-xylenol, and 2-methoxy-4-propenylphenol. This finding indicated

Table 7
GC/MS analysis results of the heavy oil from different catalysts with cotton straw for 300 °C , 20 min.

		Area (wt.%)		
		No catalyst	K_2CO_3	KOH
		Heavy oil	Heavy oil	Heavy oil
Acids	Acetic acid	5.88	4.82	5.11
	n-Hexadecanoic acid	3.55	4.85	3.98
Esters	phthalic acid, mono-(2-ethylhexyl) ester	7.52	18.52	28.53
Phenols	Guaiacol	5.51	4.81	6.04
	Pyrocatechol	–	–	–
	3-methoxy-2-benzenediol	–	–	–
	4-ethyl guiacol	5.52	3.99	4.10
	4-Methylphenol	–	2.02	1.04
	2-Methoxy-4-propylphenol	2.25	3.30	2.56
	2-Methoxy-4-propenylphenol	–	2.67	1.12
	2,5-Xylenol	–	2.39	0.42
	2,6-Dimethoxyphenol	7.07	9.75	8.38
	2-Methoxy-4-propenylphenol	–	4.50	3.34
	2,6-Dimethoxy-4-allylphenol	2.83	2.82	4.75
Ketones	4-Hydroxy-4-methyl-2-pentanone	2.29	2.59	3.61
	5- methyl -2-(1-2- cyclohexene -1-one)	1.76	2.43	1.35
	Methyl-cyclopentenolone	0.83	0.81	1.04
	2-Hydroxy-3-methyl-2-cyclopentene-1-one	0.65	0.78	0.76
Phenyl	4-Propylbiphenyl	2.79	4.42	3.55
	4-Ethylbiphenyl	3.37	4.82	3.72
Others	3-Pyridinol	0.99	2.16	1.00

that the addition of catalysts increases the contents of esters and phenols in heavy oil. This increase is conducive to the use of these compounds as chemicals. Furthermore, the β-aromatic and ether bonds in lignin were deconstructed by the incorporation of catalysts to generate phenols. These compounds were decomposed further to produce diphenol and its derivatives. Therefore, the addition of catalysts can promote etherification and accelerate the decomposition of lignin.

4. Conclusion

In this study, an orthogonal experiment was conducted on the hydrothermal conversion process of biomass to determine the optimal conditions of different hydrothermal product yields. If heavy oil yield is the target product, then the optimal process condition involved the use of pine sawdust as the raw material and the adoption of a temperature of 250 °C, a residence time of 15 min, a concentration of 10 g/110 g, and a particle size of 80 mesh–150 mesh. Under these conditions, the heavy oil yield of pine sawdust is 28.00 wt.% on dry basis.

From among the factors that significantly affect heavy oil yield in the orthogonal experiment, cotton straw was selected as the raw material for the study on the influence of different reaction conditions (temperature, time, particle size, and catalyst). In the experiment without catalysts, heavy oil yield was maximized at 24.14 wt.%. When the reaction temperature was 300 °C, the residence time was 10 min, and the particle size was between 80 and 150 mesh. Therefore, the addition of catalysts not only enhanced heavy oil yield significantly, but it also inhibited the generation of solid residue. In particular, the incorporation of K_2CO_3 effectively increased heavy oil yield. Following GC–MS analysis, liquid product was derived from the cotton straw. This product included almost all of the following organic components: acids, esters, aldehydes, ketones, and phenols. Among these components, acids, esters, phenols, and their derivatives were dominant. Therefore, the addition of catalysts increased oil yield and affected the oil components as well. The concentrations of acids and ketones decreased, and the pH value of oil increased. As a result, oil quality improved to a certain extent.

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