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Characterization Studies for Derived Biodiesel from the Fluid Catalytic Cracking (FCC) of Waste Cooking Oil through a Fixed Fluidized Bed (FFB)

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Abstract: Biodiesel production through transesterification or catalytic hydrogenation using vegetable oil is a sustainable method, but it has the downsides of by-product generation and a higher cost. Therefore, in this study, waste cooking oil was selected as a raw material, and fluidized catalytic cracking was carried out on the catalyst (LDO-75) through a fixed-fluidized-bed (FFB) reactor. The effects of the reaction temperature, catalyst–oil ratio and weight hourly space velocity (WHSV) on the yield of pyrolysis gas, gasoline, diesel and heavy oil fractions were studied. The composition of the pyrolysis gas was determined by gas chromatography (GC), the composition of the gasoline fraction was analyzed by gas chromatography-mass spectrometry (GC-MS), and the characteristics of the diesel and heavy oil fractions were determined by nuclear magnetic resonance (NMR). The results show that light olefins are the main products of pyrolysis gases, and the liquid products are mainly composed of aromatic compounds. In addition, the catalytic cracking process of waste cooking oil fluid is proposed, indicating that the process of the catalytic cracking of waste cooking oil fluid includes deoxygenation, oligoaromatization and hydrodeoxygenation. The results of this study will provide a basis for the high value-added utilization of waste cooking oil.

Keywords: waste cooking oil; FCC; fraction; reaction pathway

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1. Introduction

In recent years, with increasingly stringent environmental regulations and the increasing shortage of petroleum resources, researchers around the world are actively looking for a new sustainable energy sources [1]. Compared with petroleum, vegetable oil—a renewable energy source—contains almost no S, N, or metal substances. Vegetable oil is a clean raw material and is considered to be one of the important sources of biomass fuel production. In addition, vegetable oil is also receiving wide attention due to its lower net CO_2 emissions [2].

The annual production rate of waste cooking oil in China is up to 5 million tons; therefore, the use of waste cooking oil with high added value is an important research subject. The main methods of producing biomass fuel from vegetable oil are transesterification, catalytic hydrogenation and FCC. The transesterification of vegetable oils is the main production process used to produce biodiesel, which is a mixture of fatty acid methyl esters (FAMEs). However, this reaction also produces glycerin as a byproduct, which will not only lead to a decline in the quality of oil products but also reduce the market price of biodiesel [3,4]. Otherwise, it has the drawbacks of byproduct generation and a higher cost. Catalytic hydrogenation is performed at a moderate temperature (300–600 °C) and high hydrogen pressure (10–20 MPa), over a variety of catalysts, with the removal of oxygen as H_2O, CO_2 or CO. Nonetheless, due to the use of high pressure and hydrogen, its investment

and operation cost are relatively high. Therefore, more researchers are paying attention to the study of biodiesel production from FCC vegetable oil [5].

The catalysts used for the FCC of animal and vegetable oils are mainly include molecular sieve catalysts (HZSM-5 [6,7], USY [8], MCM-41 [9]), amorphous catalysts (activated alumina gamma-Al_2O_3 [10], and alkaline catalysts (CaO, Na_2CO_3 [11]), etc. Thanh-An [12] used waste cooking oil as a raw material and carried out FCC experiments in a fixed-bed microreactor. The results showed that by using HZSM-5 as a catalyst, the aromatics contents—such as benzene, toluene and xylene—were higher in the liquid products. Atsushi Ishihara [13] used ZSM-5 zeolite-containing silica-aluminas as a catalyst; by comparison, ZSM-5 zeolite showed the highest yield of aromatics among the three types of zeolite.

In the aspect of reactor selection, most researchers choose a fixed-bed microreactor as the FCC reactor [14–16]. However, the fixed-fluidized-bed (FFB) reactor will have better commercial characteristics. FCC, the most important technology in petrochemical industry, can transform high-molecular-weight hydrocarbons to more gasoline products [17,18]. Its units are usually designed for the treatment of complex and heavy feeds [19]. According to the characteristics of FCC, it is possible for it to be used for the upgrading of waste cooking oil. The direct feeding of bio-oil in a FCC unit has been considered to be infeasible. Attempts to directly upgrade bio-oil have reported significant amounts of char, coke and water as the main products [20–23]. Bio-oil's immiscibility with hydrocarbons has also been singled out as an impediment to its direct introduction into the FCC process [24].

LDO-75 is a kind of industrial catalyst. It has been widely used in heavy-oil FCC. The experimental results show that a high liquid yield can be obtained by using LDO-75 as the catalyst in heavy-oil FCC. Thus, in this paper, LDO-75 was selected as a catalyst, waste cooking oil was selected as a raw material, and a fixed fluidized bed was selected as a reactor to study waste cooking oil FCC characterization. The effect of the temperature, catalyst–oil ratio, and weight hourly space velocity (WHSV) on the yield of product was investigated. The formation and distribution of products in the FCC of waste cooking oil were analyzed by gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), and nuclear magnetic resonance (NMR).

2. Material and Methods

2.1. Materials

The crude waste cooking oil was purchased from a local supermarket, and was used without any further treatment. The crude waste cooking oil was mainly composed of C_{16}–C_{20} unsaturated fatty acids, and a small quantity of saturated fatty acid was detected using gas chromatography–mass spectrometry (GC–MS): hexadecanoic acid (7.53%), 9-octadecenoic acid (32.94%), octadecanoic acid (3.13%), 9,12-octadecadienoic acid (52.46%), arachidic acid (0.57%), 12-octadecenoic acid (0.82%), and α-linolenic acid (2.55%).

The industrial catalyst LDO-75 produced by petroChina Lanzhou Petrochemical company (Lanzhou, China) catalyst plant was used in this research. The catalyst characterization was as follows: pore volume 0.38 $mL \cdot g^{-1}$, specific surface area 267 $m^2 \cdot g^{-1}$, and mean pore size 3.82 nm. The catalyst was calcinated for 6 h at 600 °C before experiment.

2.2. Cracking Reaction

The experiment was carried out in a fluidized bed reactor system. The device is shown in Figure 1. Firstly, the water was pumped into the preheater and heated to 350 °C. Then, the steam formed in the reactor and contacted with the catalyst at a high temperature in the reactor to form fluidization. Secondly, the waste cooking oil was extracted by the oil pump and injected into the preheater; then, the preheated waste cooking oil entered the reactor and reacted with the catalyst in the fluidized state. After the reaction, the oil gas was condensed and cooled from the reactor; the heavy oil entered the heavy oil receiving bottle, the light oil entered the light oil receiving bottle, and the remaining oil and gas are absorbed into the liquefied gas by the liquefied gas absorption bottle with industrial

ethanol, and then enters the wet flow meter to measure the dry gas. The effects of the reaction temperature (400–550 °C), catalyst–oil ratio (3–6), and weight hourly space velocity (WHSV) (6–22/h) on the yield of products were investigated. However, in this experiment, steam was used as a carrier, such that the water content produced by the FCC of waste cooking oil cannot be accurately measured during the experiment.

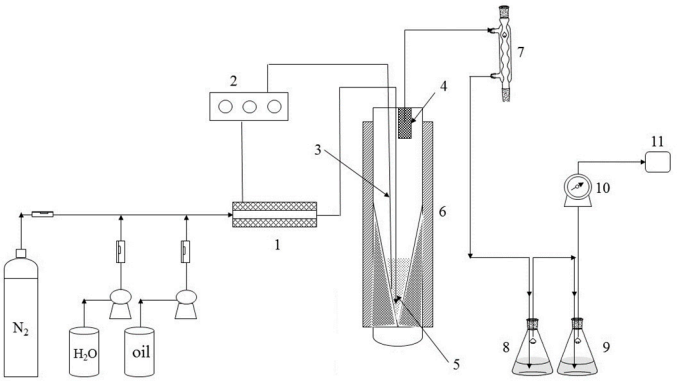


Figure 1. Schematic diagram of the FFB facility. 1, Preheating unit; 2, temperature displaying instrument; 3, electric couple thermometer; 4, filter unit; 5, catalyst; 6, fluidifying unit; 7, condensation unit; 8, ice-water bath; 9, alcohol bath; 10, wet-type gas flowmeter; 11, gas collection.

2.3. Product Collection, Calculation and Characterization

The pyrolysis gases included dry gas (H_2, CO, CO_2 and C_1–C_2 hydrocarbons) and liquefied gas (C_3–C_5 hydrocarbons). The dry gas was calculated using a wet-gas flowmeter; the calculation of the dry-gas yield was performed according to the ideal gas equation of state. The liquefied gas was absorbed by industrial alcohol (95 wt%).

After the removal of the water, the liquid products collected from the separation system were subjected to a reduced-pressure Engler distillation experiment. The liquid products were divided into gasoline (<205 °C), diesel (205–350 °C) and heavy oil (>350 °C) fractions according to the distillation range. The coke deposited on the catalyst surface was calculated by the charred difference method.

The gas components and their percentages were determined by GC analysis (GC 950), equipped with a Porapak-Q column (3 m × 3 mm) and a TDX-01 column (3 m × 3 mm). The C_1∼C_5 hydrocarbons were detected by a FID using nitrogen as a carrier gas, and the H_2 and CO_x were detected by a TCD using helium as a carrier gas, respectively. The qualitative and quantitative analysis of the pyrolysis gas were determined by the external standard method with a standard gas.

The characterization parameters of the diesel and heavy oil fractions were identified by NMR. The ^{13}C NMR curve was obtained at 100.62 MHz by a Bruker AVANCEIII−400 MHz with a 5-mm probe insert and TMS as the internal standard. In order to guarantee the total solution organic matter, $CDCl_3$ was used as the solvent. The acquisition time of the ^{13}C spectra was 3 s. MestReNova 6.1.1 was used to analyze the NMR spectra and quantify the relative proportion of different carbon and hydrogen types in the liquid product samples.

GC-MS was performed with ACION TQ (Bruker) in order to determine the composition of the gasoline fraction. The type of chromatographic column was an HP-5MS (30 m × 0.25 mm × 0.25 μm) fused silica capillary column. The oven temperature was maintained at 20 °C for 5 min and then slowly increased to 280 °C at a rate of 10 °C min^{-1}, followed by holding the pyrolysis temperature for 20 min. The analysis was performed using a Qual Browser and Technology mass spectra library search. In order to quantitatively analyze the peaks in the total ion chromatogram, the curves were compared with the spectra in the National Institute of Standards and Technology (NIST) [25,26].

3. Results and Discussion

3.1. The Yield of the Catalytic Cracking Products

In this section, the yields of FCC products—as affected by the catalyst–oil ratio, WHSV and temperature—were investigated.

3.1.1. Products Distribution

As shown in Figure 2, the temperature, catalyst–oil ratio and WHSV will all affect the product yield, of which temperature has the greatest impact. The yield of dry gas and liquefied gas increases with the increasing temperature, and the yield of liquefied gas is more obvious. Katikaneni [16] indicated that the fatty acid ester FCC has two steps: firstly, the fatty acid esters initial crack and deoxidate on the surface of the catalyst; secondly, the intermediates, such as oxygen-containing derivatives, spread into the catalyst channel for the secondary cracking, and most of the oxygen-containing derivatives will be removed in the form of H_2O, CO and CO_2.

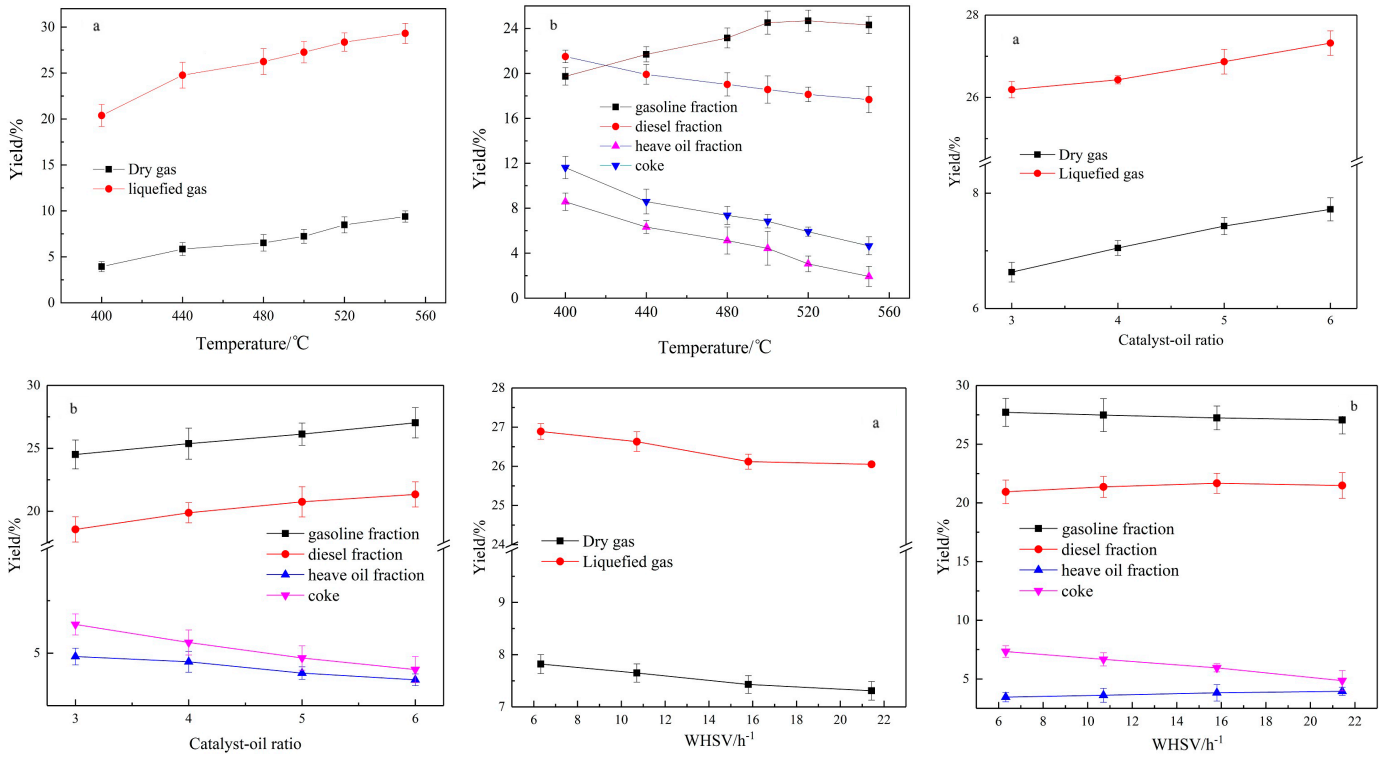


Figure 2. Product yield of FCC waste cooking oil in different process conditions. (**a**) Pyrolysis gases; (**b**) liquid products and coke.

The yield of the gasoline fraction increases gradually from 19.73% at 400 °C to 24.30% at 550 °C. To the contrary, the yields of diesel, the heavy oil fraction and coke decrease with the increasing temperature. The results show that the higher the temperature is, the higher the yield of light components is. In the cracking process, the thermal and FCC reactions occur at the catalyst's surface to produce light compounds, then the light compounds will produce heavier alkane and aromatic hydrocarbons through oligomerization and aromatization, respectively [27]. The degree of thermal cracking will deepen with the increase of the reaction temperature. Not only the coke but also some tar components will attach to the catalyst. When the reaction temperature rises, the relatively heavy molecular weight of the tar components will volatilize into the product collection device.

With the increase of the catalyst–oil ratio, the yields of dry gas and liquefied gas also gradually increase; at the same time, the yields of the gasoline and diesel fractions gradually increase from 24.51% and 18.56% of the catalyst–oil ratio 3 to 27.03% and 21.34% of catalyst–oil ratio 6, respectively. On the contrary, the yields of heavy oil fractions and coke decrease with the increase of the catalyst–oil ratio. The results showed that with the increase of the catalyst–oil ratio, the number of active catalyst bits per unit of feed molecule was increased, which promoted the secondary cracking reaction, deepened the reaction, and made more products move to small molecules.

The WHSV reflects the material flow rate. Within the operational range of the reactor, the WHSV has little effect on the yield of the products. As a result, the yields of dry gas, liquefied gas, gasoline and coke gradually decrease with the increased WHSV. This was because the WHSV decreased and the secondary reaction intensified, leading to the deepening of aromatization, and the olefin polymerized to form coke. When the WHSV was 15.80 h^{-1}, the total yield of gasoline and diesel was the highest, reaching 48.91%.

3.1.2. Gas Yields

The content of the FCC gas yield is listed in Figure 3. The FCC gases mainly consist of CO, CO_2, CH4 and C2–C5 alkanes and alkenes. Compared with other catalysts, the LDO-75 catalyst has a higher propylene yield [5,9]. With the rising temperature, C1–C3 components increase from 50.88% at 400 °C to 61.97% at 550 °C, while the C4–C5 components decrease obviously from 38.38% to 26.11%. This phenomenon also indicates that a high temperature can promote a cracking reaction and generate small-molecule components. Besides this, the content of alkenes in cracking gas is much higher than that in alkanes; this is because the waste cooking oil is mainly constituted of unsaturated acid. Moreover, H_2 almost cannot be detected in the cracked gas; the possible reason is H_2 generated by dehydrogenation during the reaction, and may also involve the hydrogenation reaction through catalytic means.

As the catalyst–oil ratio increases, the content of C1–C3 increases from 54.68% when the catalyst oil ratio is 3 to 59.57% when the catalyst–oil ratio is 6, while the relative content of C4–C5 components decreases from 34.18% to 29.20%. This is because as the catalyst–oil ratio increases, the number of active catalyst bits per unit of raw material molecules increases, leading to the deepening of the secondary cracking. On the one hand, the dehydrogenation reaction of macromolecular hydrocarbons produces more small molecular hydrocarbons. On the other hand, propylene will generate aromatic hydrocarbons through condensation and polymerization, resulting in a gradual decrease in the propylene content. With the deepening of the secondary cracking, isobutane, n-butane and other C4-and-above substances will gradually undergo a hydrogen transfer reaction to produce light olefins, and olefins will continue to carry out the above reaction.

As the WHSV decreases, the content of methane, ethane, ethylene and other cracked final products gradually increases, and the contents of butane and butene gradually decrease. The smaller WHSV can deepen the degree of the cracking reaction and promote secondary cracking. Accordingly, larger molecular hydrocarbons will be cracked into small molecules. The hydrocarbons, such as ethane, ethylene, butene, etc., as intermediate products, will be more retained when the residence time decreases. It can be seen from Figure 3 that as the WHSV decreases, the contents of CO and CO_2 gradually increase, because as the degree of secondary cracking deepens, the deoxidation reaction becomes intense. The oxygen-containing derivatives of macromolecules will undergo more cracking deoxygenation reactions, and more of the oxygen will exist in the form of CO, CO_2 and H_2O.

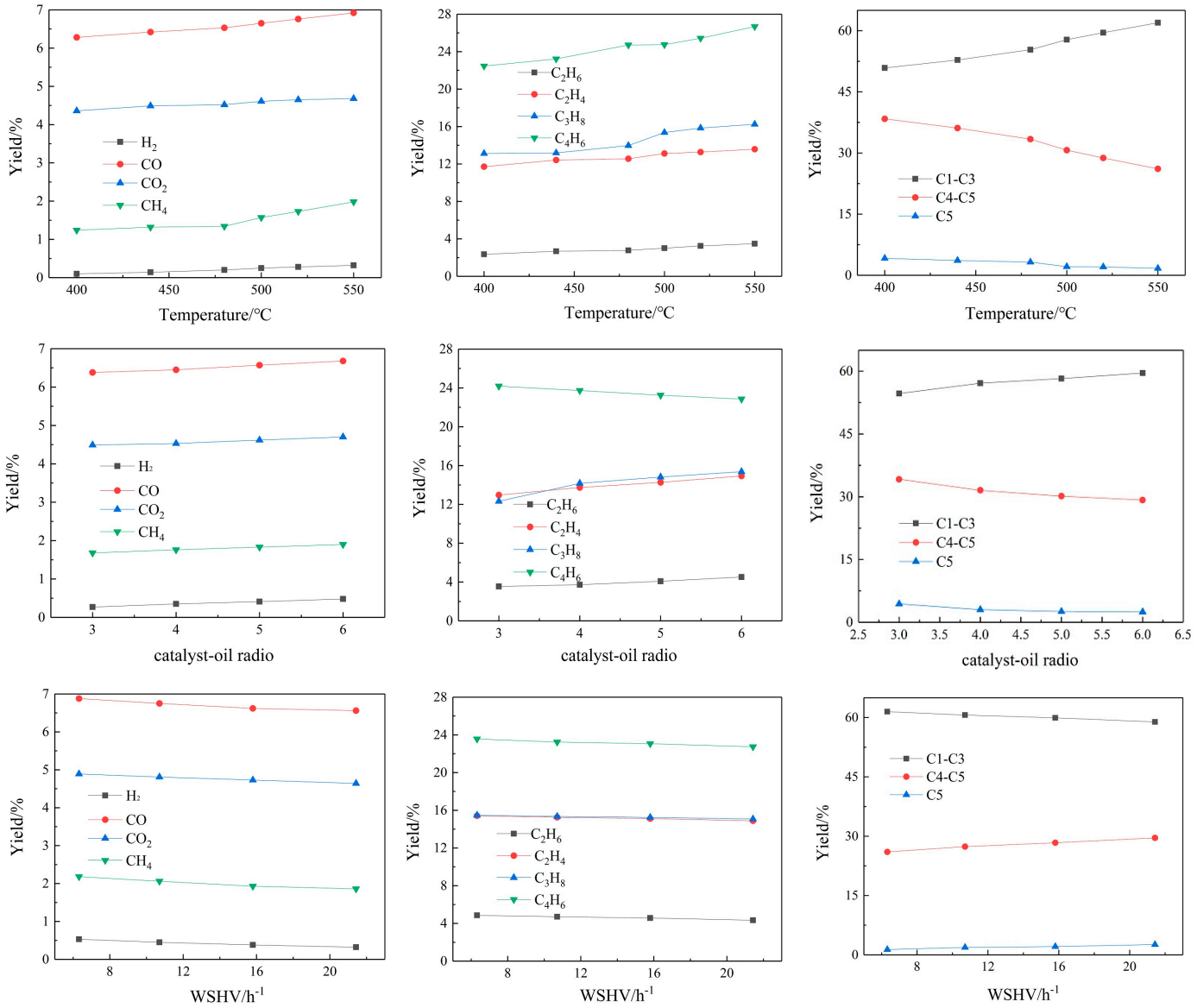


Figure 3. FCC gas yield of waste cooking oil in different process conditions.

3.1.3. GC-MS Analysis

GC-MS was used to qualitatively and quantitatively analyze the FCC gasoline fraction of waste cooking oil. According to the composition classification, the composition of the gasoline fraction was divided into alkanes, cycloalkanes, alkenes, aromatics and oxidized derivatives; the results are shown in Figure 4.

As shown in Figure 4, the reaction temperature and WHSV have a great influence on the group composition of the gasoline fraction. The greatest content of the gasoline fraction in the FCC products of the waste cooking oil is aromatic hydrocarbons; this is because there are many oxygen-containing compounds in waste cooking oil, which are easy to aromatize to aromatic compounds. With the increasing temperature, the content of aromatics increased and the contents of the other compounds decreased gradually. The fluid catalytic cracking of unsaturated aliphatic acid would form more alkenes, which can form more aromatics through a condensation reaction. It is generally considered that alkenes are the most active type of hydrocarbon in FCC. More alkenes may be produced due to secondary cracking at a higher temperature. Moreover, branched alkenes can react with naphthenic hydrocarbons to form aromatics by hydrogen transfer and condensation reactions. In addition, cyclic alkenes would be produced by side chain breaks of alkanes

and alkenes with side chains or conjugated dienes occurring in Diels–Alder reactions; then, aromatic hydrocarbons may be generated by the hydrogen transfer reaction of cyclic alkenes. Besides this, only a small amount of oxygen compounds are detected in the gasoline fraction, mainly composed of ethers and alcohols, which indicate that in the fluid catalytic cracking reaction of waste cooking oil, the oxygen compounds are decomposed to CO_2, CO and H_2O.

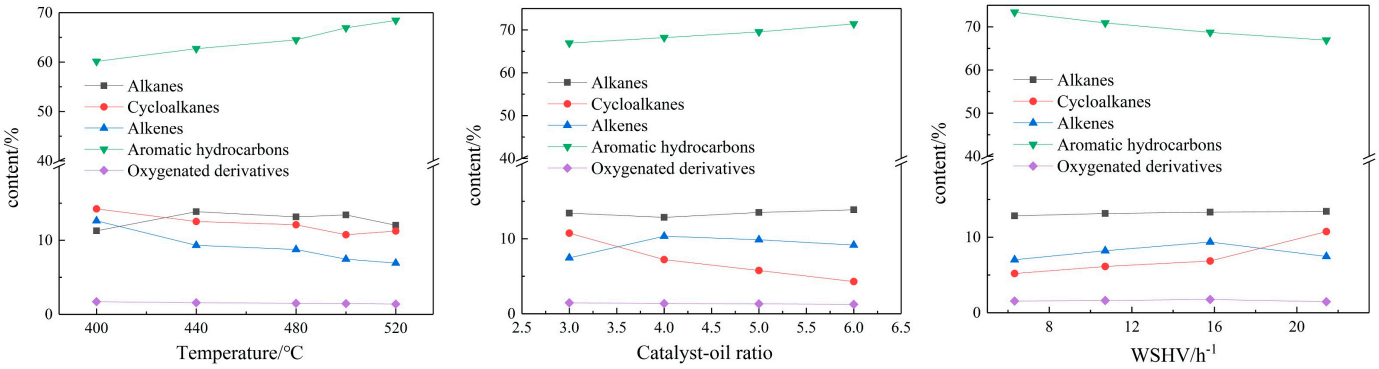


Figure 4. Relative contents of each compound of the gasoline fraction.

As the WHSV became smaller, the content of aromatics gradually increased, and the content of alkanes, cycloalkanes, alkenes and oxygen-containing derivatives gradually decreased. The smaller the WHSV, the longer the contact time between the raw material molecules and the catalyst, and the deeper the cracking reaction. The degree of reaction and secondary cracking deepened. The rings of cycloalkanes will be broken to produce olefins, and olefins will produce more aromatics through polymerization.

3.1.4. NMR Analysis

In order to obtain the composition and structure information of the diesel fraction and heavy oil fraction, the samples at different temperatures were analyzed by NMR. The ^{13}C NMR curves of the diesel and heavy oil fractions obtained at different temperatures were similar, indicating that the compounds of the samples demonstrate an overall similar distribution. Thus, the ^{13}C NMR technique is only employed for the samples at 400 °C, 440 °C, 500 °C and 550 °C. The ^{13}C NMR curves are shown in Figure 5.

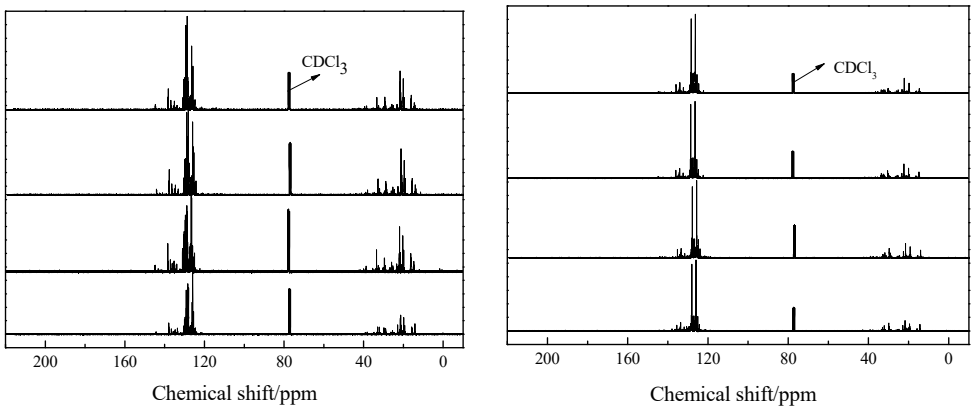
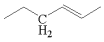
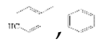
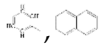


Figure 5. ^{13}C NMR curves of the liquid samples at different temperatures. (**a**) Diesel fraction; (**b**) heavy oil fraction.

The ^{13}C NMR spectra exhibit signals at 15–40 ppm, which are assigned to the carbons of alkane and alkene, whereas the signals at 120–160 ppm correspond to aromatic carbons

(Figure 3; the signal at 77 ppm is assigned to the solvent of the NMR measurement). The carbon skeleton structure information corresponding to different chemical shifts is listed in Table 1.

Table 1. ^{13}C NMR analysis results of different samples.

Chemical Shift	Location	Diesel Fraction				Heave Oil Fraction			
		400 °C	440 °C	500 °C	550 °C	400 °C	440 °C	500 °C	550 °C
12–15		2.82	2.70	2.45	2.02	1.90	1.76	2.81	2.33
15–18		3.03	3.06	2.50	2.37	1.56	1.24	1.54	0.96
18–20		4.91	5.73	5.75	5.43	4.25	4.92	4.54	4.10
20–22		9.93	9.68	9.46	9.16	4.94	5.37	4.67	4.95
22–24.5		2.38	1.23	1.81	1.10	1.43	0.55	1.12	1.89
24.5–26.5		0.99	1.72	1.76	1.23	1.73	1.91	1.73	1.07
28.5–31		4.21	3.68	3.35	5.70	4.12	3.31	3.76	4.76
31–33.5		2.53	2.70	2.13	2.54	4.27	4.07	4.19	2.11
33.5–36		0.10	0.25	0.64	0.26	0.00	0.58	0.26	0.19
36–40		0.64	0.61	0.75	0.96	0.00	0.52	0.30	0.79
120–127.5		27.26	25.86	23.26	22.83	29.71	30.47	30.24	31.25
127.5–134		36.39	36.52	39.12	40.53	40.35	41.62	41.86	42.60
134–137		1.98	2.21	2.50	1.84	3.05	2.52	1.90	2.21
137–143		2.43	3.19	3.67	3.24	1.54	0.49	0.48	0.35
143–160		0.40	0.86	0.85	0.79	1.15	0.67	0.60	0.44
>160		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

As shown in Figure 5 and Table 1, the main components of the diesel fraction and heavy oil fraction are aromatic compounds, which account for more than 68% of the diesel fraction and more than 75% of the heavy fraction. It should be noted that there are no aromatic hydrocarbons in waste cooking oil; the aromatic compounds detected in the products were formed by the aromatization of the unsaturated fatty acids in waste cooking oil. Besides this, with the increase of the fluid catalytic cracking temperature, the content of polycyclic aromatic hydrocarbons in the diesel and heavy oil fractions increases, which indicates that the degree of reaction will deepen with the increase of the fluid catalytic cracking temperature.

Waste cooking oil is mainly composed of C_{18} unsaturated fatty acids; with the fluid catalytic cracking reaction, aromatic compounds with hydrocarbyl substituted are mainly produced in the products. Among them, alkenyl groups are the main substitution. Because there is also a small amount of saturated fatty acids in waste cooking oil, there is a small quantity of alkyl-substituted aromatic compounds in the liquid products. Carboxyl groups were not detected in the liquid products at different temperatures; it has been reported that

the oxygen in the feedstock would be removed through the formation of water, CO_2 and CO though deoxygenation [28].

3.2. Reaction Pathway

Waste cooking oil contains a variety of fatty acids, including saturated fatty acids and unsaturated fatty acids, which are mainly unsaturated fatty acids. Undergoing a series of reactions, various hydrocarbons, gases and water are generated. The possible reaction pathway for the FCC of waste cooking oil over a LDO-75 catalyst is proposed in Figure 6.

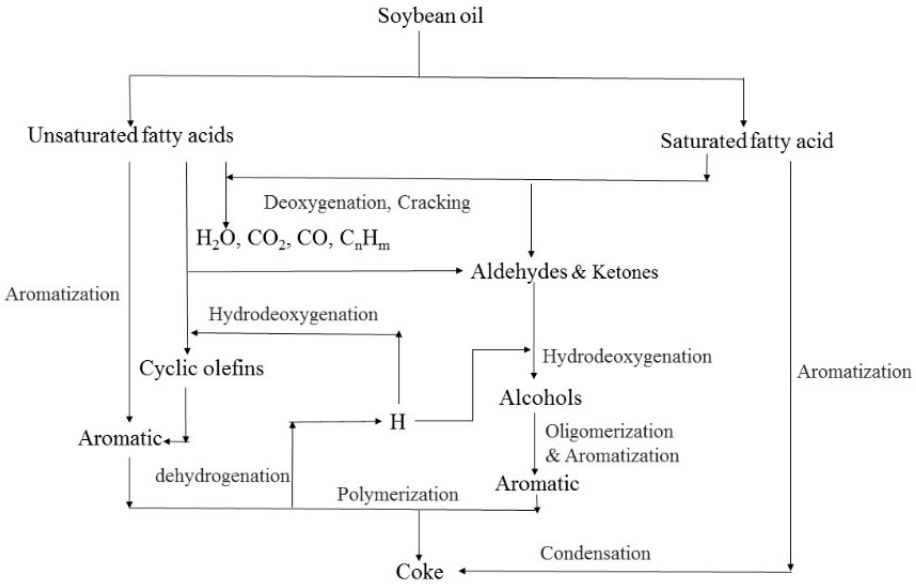


Figure 6. Main reaction pathway for the FCC of waste cooking oil over a LDO-75 catalyst.

The process of the fluid catalytic cracking of waste cooking oil is mainly composed of two simultaneous reactions: deoxygenation and cracking [29,30]. In the deoxygenation process, H_2O, CO, and CO_2 are generated, and then the oxygenated compounds produce saturated or unsaturated hydrocarbons, which are reacted with hydrogen generated from aromatization to form light alcohols [31]. The light alcohols will produce heavier aromatic hydrocarbons through oligomerization and aromatization. Unsaturated fatty acids will form cyclic olefin compounds through hydrodeoxygenation, and then undergo further dehydrogenation and hydrodeoxygenation to form aromatic compounds. At the same time, thermal and fluid catalytic cracking reactions occurred at the catalysts' surface to produce light olefins, light paraffins, light aldehydes, and ketones, which will further produce heavier alkane and aromatic hydrocarbons through oligomerization and aromatization [32,33]. The coke will be generated through the further polymerization of aromatic compounds. During this polymerization process, hydrogen was produced by dehydrogenation reactions. It can not only be used to stabilize unsaturated hydrocarbon compounds via a hydrogen transfer reaction but also participate in the deoxygenation of unsaturated oxygenated compounds. Besides this, due to the high temperature of the catalyst surface, some components will rapidly coke when it contacts the catalyst surface [34–36].

4. Conclusions

Bio-oil is an important sustainable energy source. In this paper, waste cooking oil was used as a raw material, and FCC treatment was carried out on LDO-75 through an FFB reactor. The effects of the reaction temperature, catalyst–oil ratio and WHSV on the yield of the product were studied. In addition, the GC, GC-MS and NMR analysis products were characterized. The results were as follows.

(1) As the reaction temperature increased, the yield of dry gas and liquefied gas gradually increased. In addition, the yield of the gasoline fractions gradually increased

from 19.73% at 400 °C to 24.30% at 550 °C. The GC-MS and NMR analysis results showed that the liquid product was mainly composed of aromatic compounds, accounting for more than 60%.

(2) As the catalyst–oil ratio increased, the yields of dry gas, liquefied gas, gasoline and diesel gradually increased, while the yields of the heavy oil fractions and coke gradually decreased. Similarly, the GC-MS and NMR analysis results showed that the liquid product is mainly composed of aromatic compounds, accounting for more than 65%.

(3) As the WHSV increases, the yield of dry gas, liquefied gas, gasoline, diesel, and coke slightly decreases, while the yield of heavy oil gradually increases. In general, the change of the WHSV has little effect on the distribution of the catalytic cracking products of waste cooking oil.

In addition, based on the characterization results, the reaction pathway of waste cooking oil FCC in the FFB reactor was proposed. This will provide encouraging research to further optimize the waste cooking oil FCC process and target product yield.

Author Contributions: J.S. analyzed and interpreted the experiment data regarding the yields of the products, GCMS, and NMR, and was a major contributor in writing the manuscript; H.A. performed the data analysis of GC and FTIR; C.W. and Y.C. provided technical support for the experiment. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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