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Catalytic Hydrothermal Liquefaction of Penicillin Residue for the Production of Bio-Oil over Different Homogeneous/Heterogeneous Catalysts

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Abstract: In this study, penicillin residue (PR) was used to prepare bio-oil by hydrothermal liquefaction. The effects of homogeneous (organic acid and alkaline catalysts) and heterogeneous catalysts (zeolite molecular sieve) on the yield and properties of bio-oil were investigated. The results show that there are significant differences in the catalytic performance of the catalysts. The effect of homogeneous catalysts on the bio-oil yield was not significant, which only increased from 26.09 (no catalysts) to 31.44 wt.% (Na_2CO_3, 8 wt.%). In contrast, heterogeneous catalysts had a more obvious effect, and the oil yield reached 36.44 wt.% after adding 5 wt.% MCM-48. Increasing the amount of catalyst enhanced the yield of bio-oil, but excessive amounts of catalyst led to a secondary cracking reaction, resulting in a reduction in bio-oil. Catalytic hydrothermal liquefaction reduced the contents of heteroatoms (oxygen, mainly), slightly increased the contents of C and H in the bio-oil and increased the higher heating value (HHV) and energy recovery (ER) of bio-oil. FTIR and GC-MS analyses showed that the addition of catalysts was beneficial in increasing hydrocarbons and oxygen-containing hydrocarbons in bio-oil and reducing the proportion of nitrogen-containing substances. Comprehensive analyses of the distribution of aromatic, nitrogen-containing and oxygen-containing components in bio-oil were also performed. This work is beneficial for further research on the preparation of bio-oil by hydrothermal liquefaction of antibiotic fermentation residue.

Keywords: hydrothermal liquefaction; penicillin residue; homogeneous/heterogeneous catalyst; bio-oil; chemical characteristics

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1. Introduction

Energy is an important material basis for the survivability and development of a modern society. As the amount of fossil fuel on the earth is limited, scientists have made concerted efforts in the research and development of renewable energy to feed our ever-increasing energy demand [1]. Biomass is a very promising renewable energy source. It can be converted into energy by thermochemical conversion. Antibiotic residue (AR) is a muddy by-product generated during antibiotic production. It is mainly composed of residual culture media, unextracted antibiotics, microbial metabolites and fermentation mycelia. AR is rich in organic matter such as proteins, lipids and polysaccharides, and its higher

heating value (HHV) is similar to that of low-rank coal, making it an attractive biomass material with a great energy potential [2]. Thermochemical methods such as pyrolysis and hydrothermal liquefaction can be utilized to produce bio-oil from AR. Pyrolysis is a process of thermochemical decomposition of biomass at medium to high temperature (350–700 °C) without oxygen. In hydrothermal liquefaction, biomass undergoes decomposition and liquefaction at high temperature and pressure in the presence of water. As AR contains a high moisture content, pretreatment of raw materials by drying is needed before the pyrolysis process. However, this consumes a large amount of energy. It has been reported that when the moisture content is more than 30%, the energy required to dry raw materials exceeded the energy consumption of supercritical hydrothermal liquefaction [3].

Meanwhile, bio-oil produced by hydrothermal liquefaction has high O and N contents, which reduces the HHV and makes it unattractive for use as a fuel. Ma et al. [4] studied the N transfer behavior during hydrothermal treatment of AR and found that most of the nitrogen in the solid was transferred to the liquid phase and oil phase. The N content of bio-oil produced by hydrothermal liquefaction of AR is usually between (3 and 10) %, which is much higher than the < 1% found in petroleum crude oil [2]. Therefore, it is necessary to reduce the content of oxygen and nitrogen in bio-oil to improve its potential as a renewable energy source. In order to solve the problems discussed, researchers have carried out research on catalytic hydrothermal liquefaction [3,5–7]. Results show that both homogeneous and heterogeneous catalysts can reduce the activation energy of hydrothermal liquefaction, promote the hydrolysis and decomposition of organic matter in biomass and improve the liquefaction performance of biomass. Moreover, they can inhibit side reactions such as polycondensation and repolymerization during liquefaction, reduce the formation of macromolecular coke and improve the yield and quality of the bio-oil produced. Common homogeneous catalysts mainly consist of organic acids (HCOOH, CH_3COOH, etc.) and alkaline catalysts (Na_2CO_3, NaOH, K_2CO_3, KOH, etc.). In the presence of alkali (Na_2CO_3, KOH) or organic acid (HCOOH, CH_3COOH) catalysts, the N content in the bio-oil obtained by hydrothermal liquefaction of *Spirulina* and *Chlorella* at 350 °C decreased from 7.3% to 4.7% and 5.3%, respectively [8]. In addition, alkaline and organic acid catalysts can improve the yield and HHV of bio-oil [9]. Heterogeneous catalysts such as metal oxides, molecular sieves and supported catalysts have also been employed to catalyze hydrothermal liquefaction. Duan et al. [10] found that heterogeneous catalysts (molecular sieve and metal catalysts) reduced the N content in bio-oil from 5% to 1.5–2.5%. Heterogeneous catalysts also reduce the O/C atom ratio in bio-oil, which is helpful for the deoxidation process of bio-oil, and increase the content of hydrocarbon organic matter in bio-oil [7]. Saber et al. [11] utilized a nanocatalyst of Ni/SiO_2 to catalyze the hydrothermal liquefaction of microalgae. They obtained a 30% yield at a temperature of 250 °C, in addition to the reduction in the O and N contents in the produced bio-oil.

The catalytic performance of bio-oil shows great differences due to differences in various catalysts, hydrothermal conditions and biomass raw materials employed during the process [12]. Presently, there are few studies on the hydrothermal liquefaction of AR. Furthermore, the effects and mechanisms of homogeneous and heterogeneous catalysts for AR deoxidation and denitrification demand further investigation.

In the present study, the effects of homogeneous (organic acid and alkaline catalysts) and heterogeneous catalysts (molecular sieve) on the hydrothermal liquefaction of penicillin residue (PR) were studied. The effects of the catalyst type and amount on the distribution of hydrothermal liquefaction products of PR were also analyzed. The change trend of the elemental composition, higher heating value (HHV) and energy recovery (ER) of bio-oil were investigated, and the removal effect of catalysts on heteroatoms (N, O) was determined. The functional groups and composition of bio-oil were characterized by FTIR and GC-MS, and the alteration in the organic components of bio-oil was investigated. This study will be beneficial to further research on the resource and energy utilization of AR.

2. Results and Discussion

2.1. Effect of Catalyst Types on Product Distribution of Hydrothermal Liquefaction of PR

The added catalyst was 5 wt.% of PR dry weight. The product distribution after hydrothermal liquefaction is shown in Figure 1. When no catalyst was added, the bio-oil yield and solid residue yield were 26.09 wt.% and 14.07%, with a conversion rate of 85.93%. The catalysts significantly improved the efficiency of the hydrothermal liquefaction of PR and promoted the formation of bio-oil. After homogeneous catalysis, the yield of bio-oil increased to 28.17–31.29 wt.%, and the conversion rate increased to 86.99–88.25%. In the case of heterogeneous catalysts, the yield of bio-oil increased to 31.91–36.44 wt.%, and the conversion rate was in the range of 89.81–90.15%. When using MCM-48 (bio-oil yield 36.44%), there was a 39.67% increase compared to the situation without the use of catalysts (bio-oil yield 26.09%), a relatively obvious increase in the yield.

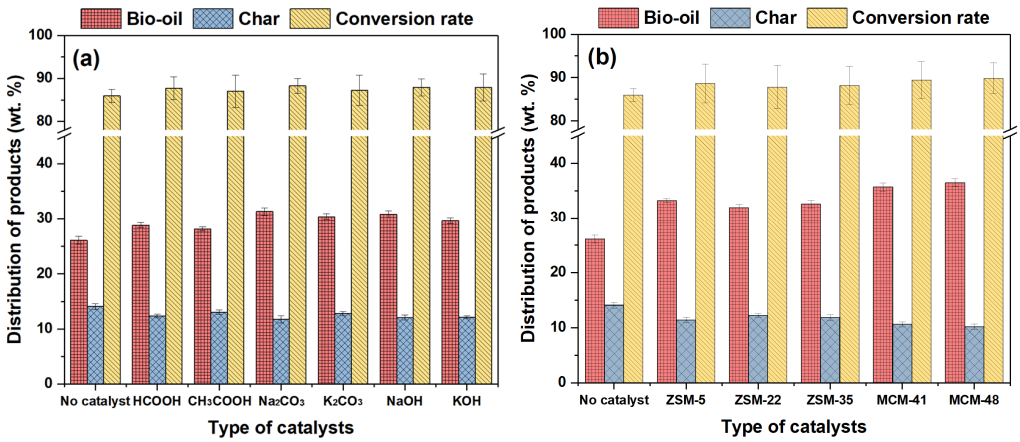

Figure 1. Influence of catalyst type on distribution of hydrothermal liquefaction products: (**a**) homogeneous catalysis, (**b**) heterogeneous catalysis.

Among the homogeneous catalysts tested in this work, the catalytic activity of the acid catalyst was significantly lower than that of the alkaline catalyst (Figure 1a). During the hydrothermal liquefaction reaction, precursors of bio-oil such as 5-hydroxymethylfurfural and levulinic acid, which are conducive to oil production, may be formed from carbohydrates under acidic conditions [13]. In contrast, organic acids may also promote protein decomposition into amino acids, which may then be further converted into ammonia and other water-soluble compounds, which are not conducive to the formation of bio-oil [14]. Therefore, the positive effect of organic acids on the increased yield of bio-oil may be partially offset by its adverse effect. Meanwhile, the alkaline catalyst can improve the gasification process, accelerate the water–gas conversion and boost the bio-oil yield [15]. Furthermore, the alkaline catalyst increases the pH value, thus inhibiting the dehydration of biomass monomers and coke formation. The highest yield (31.29 wt.%) and conversion (88.25%) and the lowest solid residue (11.75 wt.%) of bio-oil were obtained by using the Na_2CO_3 catalyst. The order of catalytic activity of the alkaline catalysts is Na_2CO_3 > NaOH > K_2CO_3 > KOH. The carbonates of alkali metals are more effective than the corresponding hydroxides. As the carbonate ions (CO_3^{2-}) react with water to form bicarbonate ions (HCO_3^-) and hydroxide ions (OH^-), the carbonate ions will be further decomposed into carbon dioxide (CO_2), as shown in Equations (1) and (2). Furthermore, CO_2 helps to extract part of the organic components of PR due to its low critical temperature (31.1 °C) and pressure (7.39 MPa), which accelerates the hydrothermal liquefaction reaction and promotes the more thorough decomposition of PR, resulting in the production of more bio-oil. A similar catalytic activity sequence has also been reported in other studies [9,16].

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \quad (1)$$

$$2HCO_3^- \rightarrow H_2O + CO_3^{2-} + CO_2 \quad (2)$$

Under heterogeneous catalysis, the yield and conversion of bio-oil during hydrothermal liquefaction of PR were higher than those of homogeneous catalysis (Figure 1b), which is consistent with earlier results from Saber et al. [11]. Their finding showed that the hydrothermal liquefaction of microalgae via zeolite molecular sieves was greater than that of Na_2CO_3, possibly because the heterogeneous catalyst increased the production rate and quantity of active hydrogen. The reaction of active hydrogen with fragments of unsaturated radicals produced by the decomposition of organic matter may result in the formation of stable components, increase the yield of bio-oil and inhibit the secondary polymerization of unsaturated substances into macromolecular coke. The amount of solid residue (9.85~10.36%) under heterogeneous catalysis was less than that under homogeneous catalysis (11.75~13.01%), which could explain our hypothesis. The type of molecular sieve has a profound effect on PR conversion. The MCM molecular sieve used in this study was much better than the ZSM molecular sieve in improving the bio-oil yield. By employing an MCM-48 molecular sieve, a 36.44% bio-oil yield and 89.81% conversion rate were obtained. As shown in Table 4, MCM molecular sieves had a larger surface area and average pore size than ZSM, which contributed to PR decomposition. The pore sizes of MCM-41 and MCM-48 were larger than ZSM-5, ZSM-22 and ZSM-35, making it possible for broken fragments to enter into the pores during hydrothermal liquefaction, thus allowing a continuous catalytic reaction to take place [17]. The acidity of zeolites increased with the decrease in the Si/Al ratio. More acidic sites could cause more C–O and C–C bonds of product fragments to cleave, resulting in dehydration, decarboxylation, dealkylation, cracking, etc., thus improving the yield of bio-oil [18].

2.2. Effect of Catalyst Addition Amount on Product Distribution of Hydrothermal Liquefaction of PR

Table 1 shows the effect of the amount of Na_2CO_3, NaOH, ZSM-5 and MCM-48 catalysts added to the hydrothermal liquefaction of PR. Experiments were performed at a reaction temperature of 280 °C, a residence time of 180 min and a total solid content of 18 wt.%.

The bio-oil yield increased with the increase in the Na_2CO_3 content. When the amount of Na_2CO_3 was 5 wt.% and 8 wt.%, the bio-oil yield increased to more than 31 wt.%. However, when Na_2CO_3 was increased to 10 wt.%, the bio-oil yield decreased to 30.35 wt.%. The catalytic effect observed on the NaOH catalyst was the same as that of Na_2CO_3. The bio-oil yield was the highest (30.83 wt.%) when the NaOH content was kept at 5 wt.%. A further increase in the NaOH amount resulted in a reduction in the bio-oil yield. Within a certain range, an increase in the amount of alkaline catalyst used will give rise to the yield of bio-oil. When the range is exceeded, the catalytic effect decreases. Similar results were obtained earlier by Yan et al. [19], when they used Na_2CO_3, NaOH and KOH to catalyze the hydrothermal liquefaction of *Ulva prolifera* macroalgae. In contrast, solid residue and bio-oil conversion tended to be stable with the increase in the amount of alkaline catalyst. Therefore, the reason for the decreased bio-oil yield could be due to the secondary cracking of bio-oil caused by an excessive amount of catalyst.

When compared with alkaline catalysts, the molecular sieve catalysts promoted more PR conversion, and more bio-oils were produced. In the presence of free radicals, more active fragments would be converted into products as more molecular sieves were added, resulting in a reduction in the solid residue and an increase in the bio-oil yield [18]. When the addition of ZSM-5 and MCM-48 was 8 wt.% and 5 wt.%, the bio-oil yield was the highest, i.e., 33.26 wt.% and 36.44 wt.%, respectively. Accordingly, the solid residue was 10.03% and 10.19%, and the conversion rate was 89.97% and 89.81%, respectively. An excessive amount of the molecular sieve catalyst had a negative effect on the preparation of bio-oil by the hydrothermal liquefaction of PR, possibly because the excessive molecular sieve catalyst provided more active surface for the reactants, thus increasing the cracking reaction frequency and gas production [20]. At a similar conversion rate, more bio-oil was

produced by MCM-48 than by ZSM-5. This may be due to the pore size, specific surface area and acidity of MCM-48 that allow more oil to be produced during hydrothermal liquefaction. Another reason may be that the free radical fragments produced by cracking are combined with each other during ZSM-5 catalysis to produce more gas products and water-soluble substances [18,21]. Alper et al. [22] also found that ZSM-5 promoted biomass gasification.

Table 1. Influence of the catalyst dosage on the distribution of hydrothermal liquefaction products.

Catalyst	Dosage (wt.%)	Yield of Bio-Oil (wt.%)	Solid Residue (wt.%)	Conversion (wt.%)
No catalyst	-	26.09 ± 0.73	14.07 ± 0.53	85.93 ± 1.52
Na_2CO_3	1	27.21 ± 0.51	13.85 ± 0.38	86.15 ± 2.66
	3	29.86 ± 0.49	13.04 ± 0.44	86.96 ± 2.33
	5	31.29 ± 0.68	11.75 ± 0.63	88.25 ± 1.77
	8	31.44 ± 0.35	11.99 ± 0.57	88.01 ± 2.27
	10	30.35 ± 0.62	11.64 ± 0.27	88.36 ± 1.48
NaOH	1	28.40 ± 0.27	13.16 ± 0.35	86.84 ± 1.41
	3	30.91 ± 0.38	12.32 ± 0.26	87.68 ± 3.31
	5	30.83 ± 0.61	12.09 ± 0.44	87.91 ± 1.99
	8	29.33 ± 0.45	12.25 ± 0.31	87.75 ± 2.16
	10	27.65 ± 0.51	12.73 ± 0.42	87.27 ± 1.31
ZSM-5	1	28.54 ± 0.57	14.07 ± 0.36	85.93 ± 3.14
	3	33.26 ± 0.75	13.33 ± 0.47	86.67 ± 1.97
	5	33.18 ± 0.34	11.37 ± 0.51	88.63 ± 4.43
	8	34.53 ± 0.48	10.03 ± 0.23	89.97 ± 3.74
	10	33.89 ± 0.51	10.42 ± 0.64	89.58 ± 2.52
MCM-48	1	29.76 ± 0.34	12.34 ± 0.39	87.66 ± 2.53
	3	35.23 ± 0.61	10.33 ± 0.52	89.67 ± 2.36
	5	36.44 ± 0.56	10.19 ± 0.17	89.81 ± 3.60
	8	36.15 ± 0.47	10.15 ± 0.35	89.85 ± 2.98
	10	34.69 ± 0.75	9.75 ± 0.47	90.25 ± 4.00

2.3. Analysis of Element Composition and HHV of Bio-Oil

Table 2 shows the elemental composition, superior HHV and ER of bio-oil with different catalyst dosages. Compared with non-catalytic conditions, the carbon and hydrogen contents of bio-oil under catalytic conditions were increased significantly, while the O and N contents were significantly decreased. This suggests that catalytic hydrothermal liquefaction can remove oxygen and nitrogen from PR bio-oil. In catalytic hydrothermal liquefaction, the dehydration or decarbonylation of organic compounds of PR was promoted, more intermediate products with a low oxygen content were generated and CO, CO_2 and H_2O were released [20]. Thus, the oxygen content in the bio-oil was reduced, and, finally, a bio-oil with a higher HHV was obtained [23]. For homogeneous catalysts, a hydrothermal reaction took place under alkaline conditions due to the addition of Na_2CO_3 and NaOH. The NH_4^+ generated by the deamination reaction of amino acids was easily converted into NH_3, which was released into the gas phase, thus reducing the nitrogen content of the bio-oil. This agrees with earlier results from Biler et al. [24]. The nitrogen removal efficiency for heterogeneous catalysts was better than that of homogeneous catalysts, and the nitrogen content in bio-oil decreased more substantially. When ZSM-5 and MCM-48 were added at 5 wt.% and 10 wt.%, the nitrogen content in bio-oil decreased to 4.25 wt.% and 5.01 wt.%, respectively.

Table 2. The influence of the catalyst dosage on the elemental composition, HHV and ER of bio-oil.

Catalyst	Dosage (wt.%)	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	H/C	O/C	HHV (MJ/kg)	ER (%)
No catalyst	-	73.07 ± 0.72	9.69 ± 0.33	6.39 ± 0.22	0.85 ± 0.02	10.01	1.59	0.10	36.72	53.14
Na_2CO_3	1	75.85 ± 0.96	10.65 ± 0.38	6.06 ± 0.25	0.60 ± 0.00	6.84	1.68	0.07	39.59	59.75
	3	76.78 ±1.73	10.01 ± 0.40	6.28 ± 0.27	0.54 ± 0.01	6.39	1.56	0.06	39.07	64.70
	5	77.29 ± 1.24	10.42 ± 0.29	6.38 ± 0.31	0.66 ± 0.01	5.25	1.62	0.05	40.03	69.47
	8	78.17 ± 2.11	9.92 ± 0.17	6.18 ± 0.12	0.49 ± 0.01	5.24	1.52	0.05	39.62	69.09
	10	77.89 ±1.86	9.81 ± 0.31	6.11 ± 0.34	0.63 ± 0.00	5.56	1.51	0.05	39.31	66.17
NaOH	1	74.72 ± 1.77	9.78 ± 0.43	5.94 ± 0.25	0.57 ± 0.01	8.99	1.57	0.09	37.59	59.21
	3	74.36 ± 1.38	10.12 ± 0.36	5.72 ± 0.42	0.74 ± 0.01	9.06	1.63	0.09	37.94	65.04
	5	76.42 ± 1.19	9.42 ± 0.36	6.26 ± 0.25	0.51 ± 0.00	7.39	1.48	0.07	37.93	64.86
	8	77.38 ± 1.22	9.86 ± 0.25	6.04 ± 0.18	0.73 ± 0.02	5.99	1.53	0.06	39.13	63.65
	10	76.61 ± 2.07	9.85 ± 0.49	6.12 ± 0.29	0.46 ± 0.01	6.96	1.54	0.07	38.69	59.33
ZSM-5	1	76.33 ± 0.83	10.48 ± 0.48	6.45 ± 0.26	0.52 ± 0.01	6.22	1.65	0.06	39.62	62.72
	3	75.76 ± 1.96	11.53 ± 0.29	6.17 ± 0.30	0.72 ± 0.00	5.82	1.83	0.06	40.99	75.61
	5	78.59 ± 1.35	10.41 ± 0.38	4.25 ± 0.19	0.66 ± 0.00	6.09	1.59	0.06	40.31	74.18
	8	78.65 ± 1.78	9.87 ± 0.31	5.32 ± 0.17	0.78 ± 0.01	5.38	1.51	0.05	39.69	76.01
	10	77.49 ± 1.24	10.12 ± 0.35	5.76 ± 0.18	0.81 ± 0.02	5.82	1.57	0.06	39.57	74.38
MCM-48	1	75.26 ± 0.94	10.78 ± 0.52	5.25 ± 0.23	0.92 ± 0.02	7.79	1.72	0.08	39.40	65.03
	3	74.74 ± 1.65	11.02 ± 0.46	6.16 ± 0.42	0.85 ± 0.01	7.23	1.77	0.07	39.67	77.51
	5	76.58 ± 1.79	10.06 ± 0.43	5.71 ± 0.37	0.63 ± 0.01	7.02	1.58	0.07	38.96	78.74
	8	77.53 ± 1.26	9.92 ± 0.22	5.83 ± 0.34	0.59 ± 0.01	6.13	1.54	0.06	39.25	78.70
	10	78.59 ± 2.09	11.49 ± 0.34	4.96 ± 0.25	0.47 ± 0.01	4.49	1.75	0.04	42.13	81.06

In addition, the bio-oil produced by the catalytic hydrothermal process had a higher HHV and ER. After the addition of the catalysts, the HHV of bio-oil was in the range of 37.59–42.13 MJ/kg, and the ER was between 59.21 and 81.06%, which were higher than those of bio-oil produced under non-catalytic conditions (HHV: 36.72 MJ/kg, ER: 53.14%). The O/C atom ratio of catalytic bio-oil was between 0.05 and 0.09, which was lower than that of non-catalytic bio-oil (0.10). The effect of heterogeneous catalysis was more obvious than that of homogeneous catalysis. In homogeneous catalysis, the HHV and ER of bio-oil were the highest when the Na_2CO_3 dosage was 5 wt.%, i.e., 40.03 MJ/kg and 69.47%, respectively. In heterogeneous catalysis, when MCM-48 was added at 10 wt.%, the HHV and ER of bio-oil were the highest, i.e., 42.13 MJ/kg and 81.06%, respectively. For the bio-oil prepared by Na_2CO_3, NaOH and ZSM-5, the ER increased first and then decreased with the increase in the catalyst dosage, which was related to the decrease in the bio-oil yield by the excessive addition of the catalyst. The catalyst promoted the decomposition of organic molecules in PR, reduced the content of heteroatoms (O, N) in bio-oil and improved the yield and quality of the bio-oil. However, compared to crude oil (O: 1.0%, N: 0.3%, HHV: 42 MJ/kg), the bio-oil still needs to be upgraded.

2.4. Analysis of Main Functional Groups of Bio-Oil

The functional group characteristics of bio-oil obtained under different catalytic conditions were analyzed by FTIR, as shown in Figure 2. The characteristic absorption peaks within the 3000–3700 cm^{-1} region represent O–H and N–H stretching vibrations, which are caused by alcohols, phenols, carboxylic acids and amides in bio-oil [19]. The characteristic absorption peaks within 2800 to 3000 cm^{-1} are related to the C–H stretching vibration in methyl (–CH_3) and methylene (–CH_2), indicating that the bio-oil may contain alkyl, aliphatic and methoxy groups [20]. The absorption peak at 1640 cm^{-1} is the bending vibration of the N–H bond, which is related to the amine and amide groups. The peaks around 1360 cm^{-1} and 1440 cm^{-1} are due to the bending vibrations of C–H functional groups on aliphatic compounds and alkylated aromatic derivatives [14]. The characteristic absorption peaks in the 1200–1300 cm^{-1} region represent C–O or C–N stretching vibrations,

which are caused by acids, alcohols, esters and N-containing compounds in bio-oil [25]. The absorption peaks within 1100 to 1200 cm^{-1} are mainly related to the stretching vibration of C–O in alcohols. In the fingerprint region, the characteristic absorption peak at 680–880 cm^{-1} represents the bending vibration of hydrocarbons on the benzene ring, suggesting the existence of aromatic groups [20]. It should be noted that the FTIR spectra of different bio-oils are similar due to the similarity of compounds found in bio-oils. However, it could still be seen that the absorption peaks of FTIR spectra change with the increase in the catalyst dosage added under the catalytic hydrothermal condition.

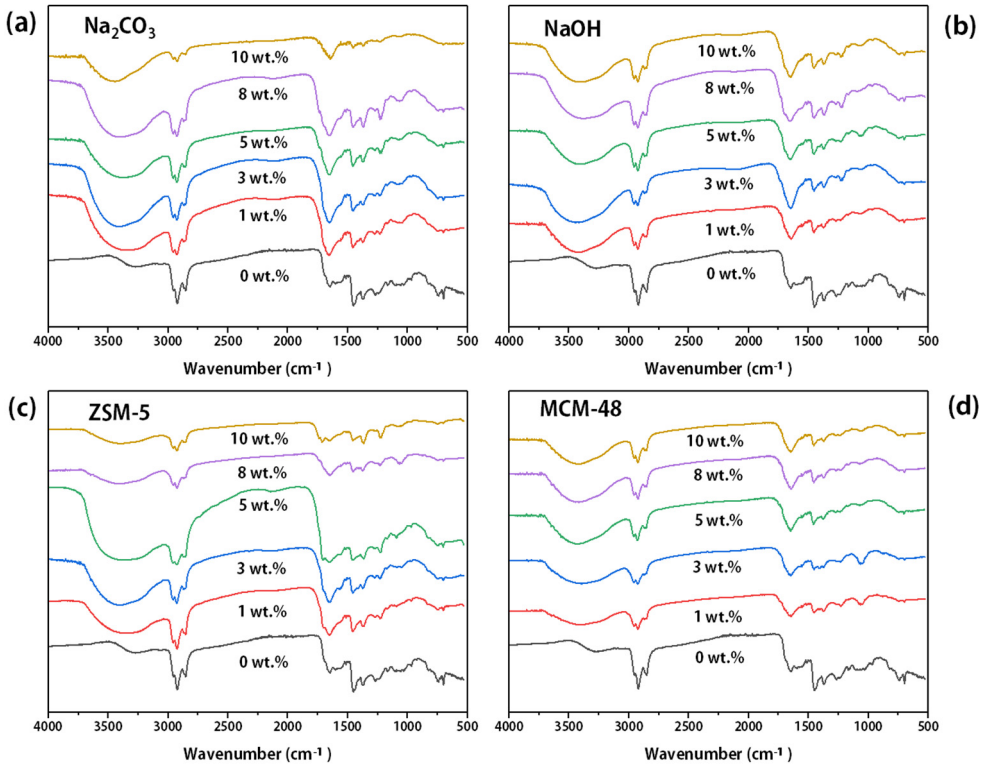

Figure 2. Effect of the catalyst dosage on the functional groups in bio-oil: (**a**) Na_2CO_3, (**b**) NaOH, (**c**) ZSM-5, (**d**) MCM-48.

The absorbance of catalytic liquefaction bio-oil was higher than that of non-catalytic liquefaction bio-oil within 3000 to 3700 cm^{-1}, which indicates that a large number of alcohols, phenols, carboxylic acids and amides were produced from PR decomposition after catalytic liquefaction. With the increase in the catalyst dosage, the peak intensity of catalytic bio-oil in this range first increased and then decreased. This might be due to the fact that the cracking reaction of the PR component increased with the increase in the catalyst dosage, and the repolymerization of cracking fragments occurred at higher catalyst dosages [18]. In the range of 2800–3000 cm^{-1} and at 1640 cm^{-1}, the infrared spectra of bio-oil showed strong absorption peaks, which indicates that the catalytic bio-oil contained more alkyl, aliphatic and amide groups. At 1640 cm^{-1}, the peak intensity of homogeneous catalysts was slightly stronger than that of heterogeneous catalysts, indicating that more amines and amides were present in the homogeneous catalytic bio-oil. This is consistent with the results of elemental analysis, and the content of nitrogen in the homogeneous catalytic bio-oil was higher than that of heterogeneous catalysis. The absorption peaks of the C–H bond on the benzene ring in the fingerprint region weakened after the addition of the catalysts, possibly because the catalysts promoted a polycondensation reaction and benzene compounds with higher aromaticity were produced, meaning that the H atom on the C–H bond was substituted.

2.5. Alteration of Main Organic Components in Bio-Oil

The main organic components in bio-oil were determined by gas chromatography-mass spectrometry (GC-MS). The percentage of the peak area for each component was calculated by the area normalization method. The composition of bio-oil is very complex, and the component distribution thus varies. Tables S1–S3 detail the composition and percentage of compounds in bio-oil found in this work. It should be noted that the area percentage values presented in this study only indicate the relative concentrations of compounds in the bio-oil that can evaporate and pass through the GC column.

2.5.1. Distribution of Main Components in Bio-Oil

After catalytic hydrothermal treatment, the main components of bio-oil were oxygen-containing hydrocarbons and nitrogen-containing compounds, as well as a small amount of hydrocarbons, as shown in Figure 3. Compared with non-catalytic conditions, catalytic hydrothermal liquefaction significantly increased the content of hydrocarbons and oxygen-containing hydrocarbons whilst reducing the content of nitrogen-containing compounds.

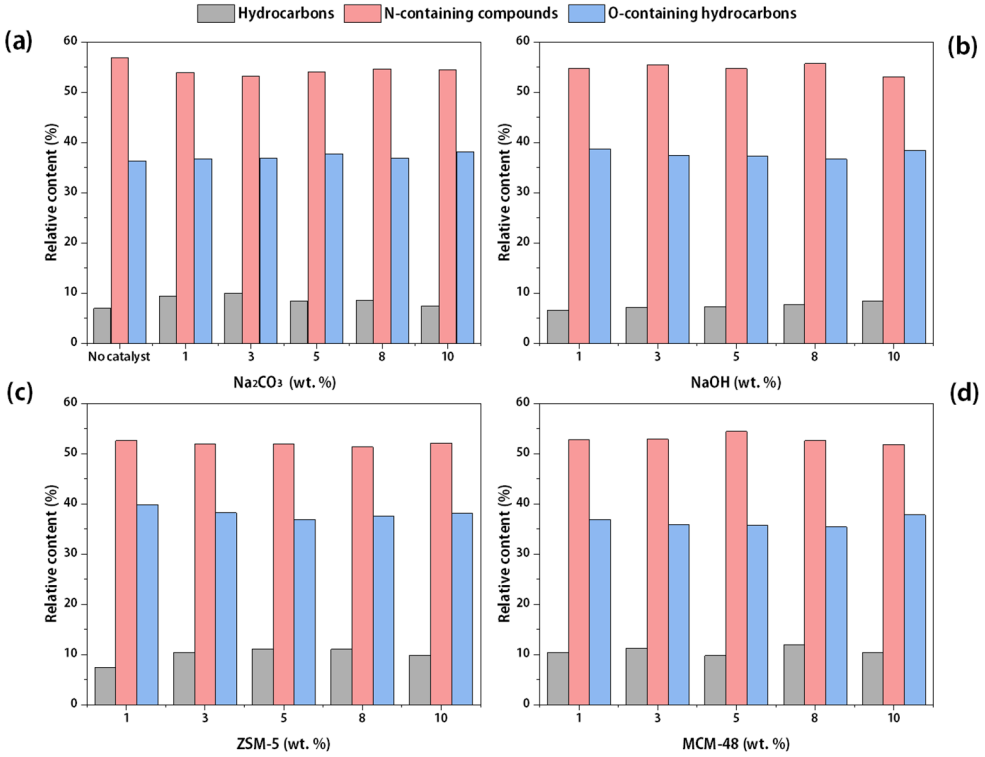

Figure 3. Distribution of hydrocarbons, N-containing compounds and O-containing compounds in bio-oil: (**a**) Na_2CO_3, (**b**) NaOH, (**c**) ZSM-5, (**d**) MCM-48.

The contents of hydrocarbons, nitrogen-containing compounds and oxygen-containing hydrocarbons in the bio-oil from non-catalytic hydrothermal liquefaction were 6.92%, 56.76% and 36.21%, respectively. With the addition of homogeneous catalysts of Na_2CO_3 and NaOH, the hydrocarbon content in bio-oil increased to 7.41–9.96% and 6.62–8.46%, respectively. The content of oxygen-containing hydrocarbons after the addition of Na_2CO_3 and NaOH also increased to 36.7–38.15% and 36.62–38.66%, while the content of nitrogen-containing compounds decreased to 53.18–54.61% and 53.09–55.66%, respectively. Compared with homogeneous catalysts, heterogeneous catalysts promoted the production of hydrocarbons and further reduced the proportion of nitrogen-containing compounds. When ZSM-5 and MCM-48 were added, the contents of hydrocarbons and nitrogen-containing compounds in the bio-oil were 7.52–11.07% and 51.36–52.63%, and 9.79–11.92% and 51.84–54.42%, respectively. Meanwhile, the oxygen-containing hydrocarbons were in

the range of 36.89–39.86% and 35.45–37.80%, respectively. The introduction of a catalyst enhances the decarboxylation of organic acids (produced by lipid hydrolysis or amino acid deamination), resulting in a decrease in the organic acid content and an increase in the hydrocarbon content. The main chemical reaction pathways for the formation of nitrogen-containing compounds are polycondensation between amino acids, and Maillard reactions between a reducing sugar and amino acids. The catalysts might promote the deamination of amino acids from protein hydrolysis to produce other compounds [26], thus inhibiting the formation of nitrogen-containing compounds. The amount of catalysts, especially NaOH, ZSM-5 and MCM-48, had a significant effect on the component distribution of bio-oil. Increasing the amount of catalysts gave rise to hydrocarbons at the expense of oxygen-containing compounds. When the addition of MCM-48 was 8%, the highest hydrocarbon content of 11.92% and the lowest oxygen-containing hydrocarbon content of 35.45% were obtained, and the content of the corresponding nitrogen-containing compounds was 52.63%.

2.5.2. Length Distribution of Carbon Chain of Components in Bio-Oil

The carbon chain distribution of compounds in bio-oil under catalytic and non-catalytic conditions is shown in Figure 4. The content of C1-4 components in non-catalytic bio-oil was 1.94%. Homogeneous catalysts increased the content of C1-4. When the addition of Na_2CO_3 and NaOH was 5% and 1%, the C1-4 content increased to 4.15% and 4.46%, respectively. When heterogeneous catalysts were employed, the content of C1-4 remained at a low level. C5-13 and C14-C22 accounted for the majority of total compounds in bio-oil, which also represented the length range of the carbon chain for gasoline and diesel. The content of C5-13 increased with the increase in the catalyst dosage, which could be mainly caused by the decomposition of the C14-C22 and >C22 components.

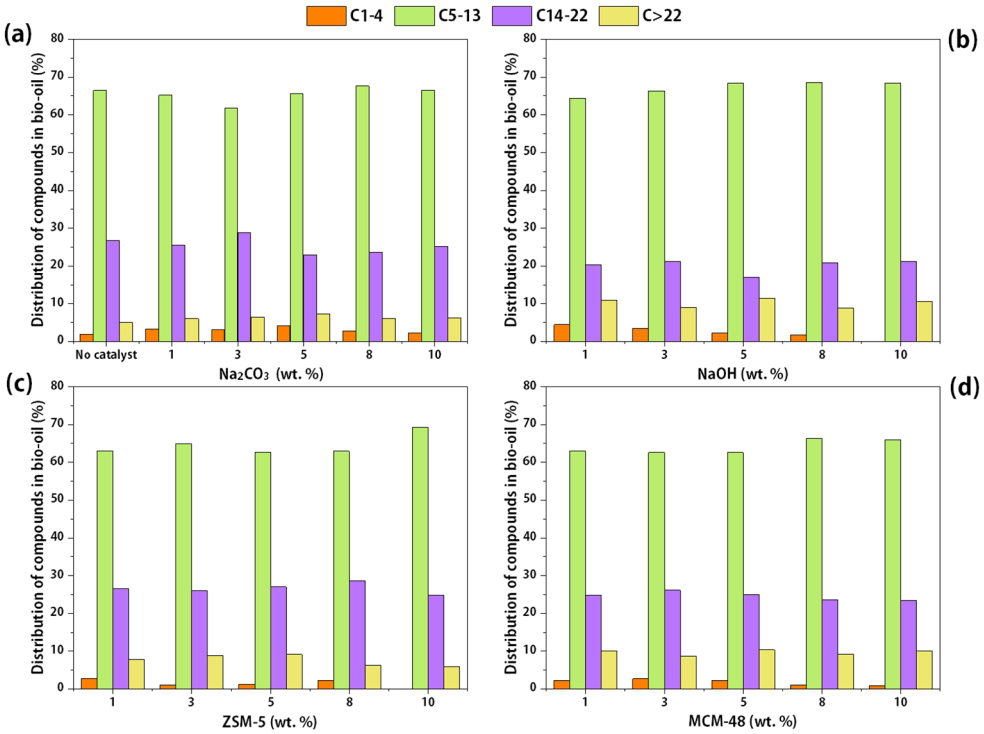

Figure 4. Carbon chain length distribution in the bio-oil: (**a**) Na_2CO_3, (**b**) NaOH, (**c**) ZSM-5, (**d**) MCM-48.

It should be noted that compared with the 4.92% of non-catalytic bio-oil, the content of >C22 in catalytic bio-oil significantly increased, i.e., 6.04–7.35% (Na_2CO_3), 8.86–11.52% (NaOH), 6.22–9.12% (ZSM-5) and 8.63–10.29% (MCM-48). The main >C22 components

were neoergosterol, ergosterol, cholest-5-ene and 3,5-cyclo-6,8(14),22- ergostatriene [27]. These substances were derived from the macromolecular cereal compounds which were important components of the culture media during the penicillin fermentation process. This indicates that the addition of catalysts can promote the decomposition of macromolecular compounds during hydrothermal liquefaction [28].

2.5.3. Distribution of Aromatic Hydrocarbons in Bio-Oil

In the PR bio-oil, the main aromatic components are hydrocarbons, amides, amines, alcohols, phenols and other aromatic nitrogen-containing heterocyclic compounds that only appear in the non-catalytic bio-oil, as shown in Figure 5. The content of aromatic components in bio-oil with a catalyst was lower than that of bio-oil without a catalyst. This could be due to the formation of organic compounds with higher aromaticity through condensation and polymerization of aromatic compounds during catalysis [26], which reduced the proportion of aromatic components. Polycyclic aromatic hydrocarbons, such as 2,3-dihydro-1,1,4-trimethyl-1H-indene and 1,2,3,4-tetrahydrochrysene (Tables S2 and S3), were found in the bio-oil after catalysis, which supports our hypothesis. In addition, the catalytic hydrothermal reaction led to the formation of a large number of non-aromatic components, which was also one of the reasons for the reduction in aromatic components. For both homogeneous and heterogeneous catalytic processes, increasing the amount of catalyst led to an increase in the content of aromatic compounds to a certain range. When the amount of MCM-48 was 5%, the content of aromatic components was 11.89%, which was higher than that of homogeneous catalysis (11.21% in 8% NaOH). This is due to the fact that zeolites are more effective in the production of aromatic compounds [10]. Moreover, the content of aromatic amides and phenolic compounds in bio-oil decreased after catalytic hydrothermal treatment, while the content of aromatic alcohols increased significantly as compared to the non-catalytic process conditions.

2.5.4. Distribution of Nitrogen-Containing Compounds in Bio-Oil

Nitrogen-containing compounds in bio-oil mainly consist of amine, amide, pyrrole, pyridine, indole, pyrazine, piperidine and other nitrogen-containing heterocyclic compounds (diketopiperazine and nitriles), as shown in Figure 6 and Tables S1–S3. After catalytic hydrothermal treatment, the content of nitrogen-containing compounds decreased. In this study, we found that the content of nitrogen-containing components in heterogeneous catalytic bio-oil (51.36–54.42%) was lower than that in homogeneous catalytic bio-oil (53.09–55.66%), which is consistent with the results of elemental analysis. For the same type of catalyst, the content of nitrogen-containing compounds did not change significantly with the increase in the catalyst dosage. This suggests that catalysts used in this study, whether homogeneous or heterogeneous, had little effect on the total proportion of nitrogen-containing components in the bio-oil but mainly changed the proportion of different nitrogen-containing components.

The formation of nitrogen-containing compounds in bio-oil might be related to the decomposition of protein N (protein and amino acid) in PR. The hydrolysis of proteins produced nitrogen-containing components such as amides, amines and nitrogen-containing heterocyclic compounds. Fatty acids produced by lipid decomposition react with NH_2/NH_3 to form aliphatic amides [29] such as dodecanamide, hexadecanamide and stearic amide (as (Z)-9-octadecenamide, N-methyl-1-octadecanamine and N-butyl octadecanamide). The addition of catalysts could reduce the content of amides and amines. In homogeneous and heterogeneous catalysts, when NaOH and MCM-48 were added at 10% and 8%, the amide content decreased to 5.29% and 5.19%, respectively; when the addition of Na_2CO_3 and MCM-48 was at 3% and 10%, the amine content decreased to 2.17% and 1.83%, respectively.

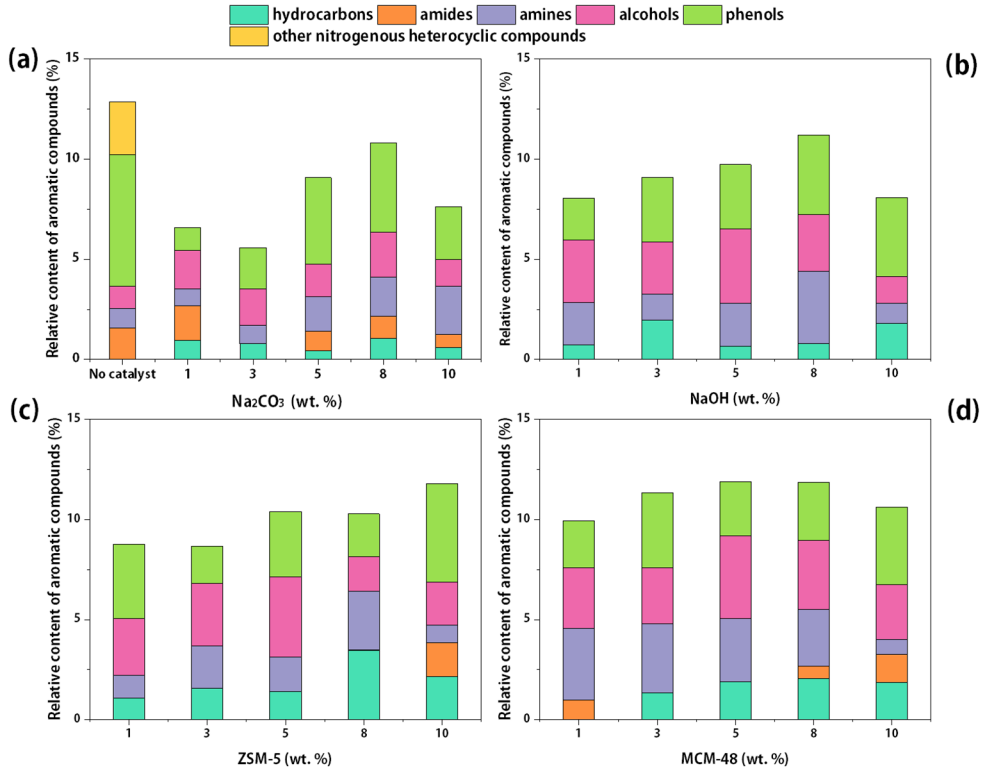

Figure 5. Aromatic compound distribution in PR bio-oil: (**a**) Na_2CO_3, (**b**) NaOH, (**c**) ZSM-5, (**d**) MCM-48.

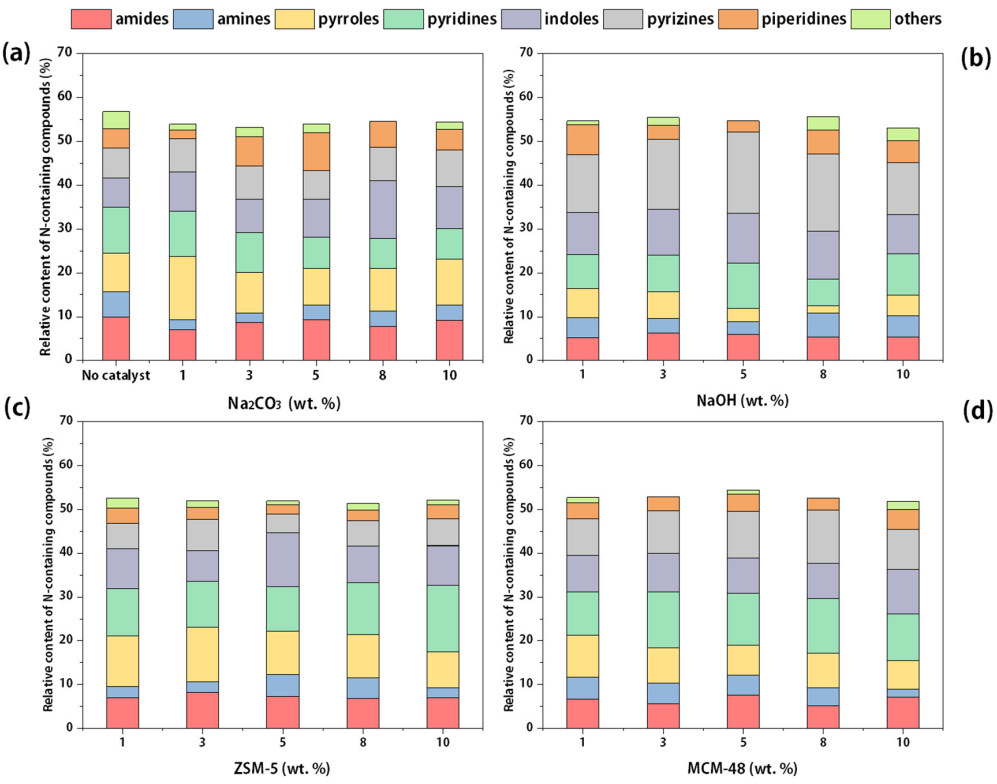

Figure 6. Nitrogen-containing compound distribution of PR bio-oil: (**a**) Na_2CO_3, (**b**) NaOH, (**c**) ZSM-5, (**d**) MCM-48.

Amino acids and carbohydrate derivatives in PR could form nitrogen-containing heterocyclic components such as pyrrole, pyridine and pyrazine through Maillard reactions [30]. Indole could be formed by dehydrogenation, decarboxylation or cyclization of aromatic amino acids (phenylalanine and tyrosine) in bacterial residue [31]. The total content of nitrogen-containing heterocyclic compounds (pyrrole, pyridine, indole, pyrazine and piperidine) in the catalytic bio-oil increased significantly in this study. Compared with non-catalytic bio-oil (41%), the proportion of nitrogen-containing heterocyclic compounds in catalytic bio-oil increased to 44.6% (Na_2CO_3, 1 wt.%), 45.9% (NaOH, 5 wt.%), 43.03% (ZSM-5, 1 wt.%) and 43.41% (MCM-48, 8 wt.%). There were some other nitrogen-containing compounds in bio-oil, including 3-benzyl-6-isopropyl-2,5-piperazinedione, 3,6-Diisopropyl-2,5-piperazinedione and 2,4,6-trimethyl-benzonitrile. The former two compounds belong to 2,5-piperazinedione compounds and could be produced by dehydration and condensation of amino acids [31], which were an important intermediate product of the hydrothermal liquefaction of PR. According to Chen et al. [32], the conversion of nitrogen-containing compounds such as protein N, amine and amide to nitrogen-containing heterocyclic compounds led to the removal of amino groups, which could be an important reason for the reduction in the N content in catalytic bio-oil. Based on this result, it is possible to further reduce the content of the N element in bio-oil by enhancing the amino removal through a catalytic reaction.

2.5.5. Distribution of Oxygen-Containing Components in Bio-Oil

The oxygen-containing hydrocarbons found in bio-oil are mainly carboxylic acid, alcohol, lipid, phenol and aldehyde, as shown in Figure 7 and Tables S1–S3. In general, catalytic hydrothermal treatment increased the proportion of oxygen-containing hydrocarbons. The content of oxygen-containing compounds was 36.21% under non-catalytic conditions. After the addition of catalysts, the proportion of oxygen-containing components in bio-oil increased to 36.7–38.15% (Na_2CO_3), 36.62–38.66% (NaOH), 36.89–39.86% (ZSM-5) and 35.45–37.80% (MCM-48).

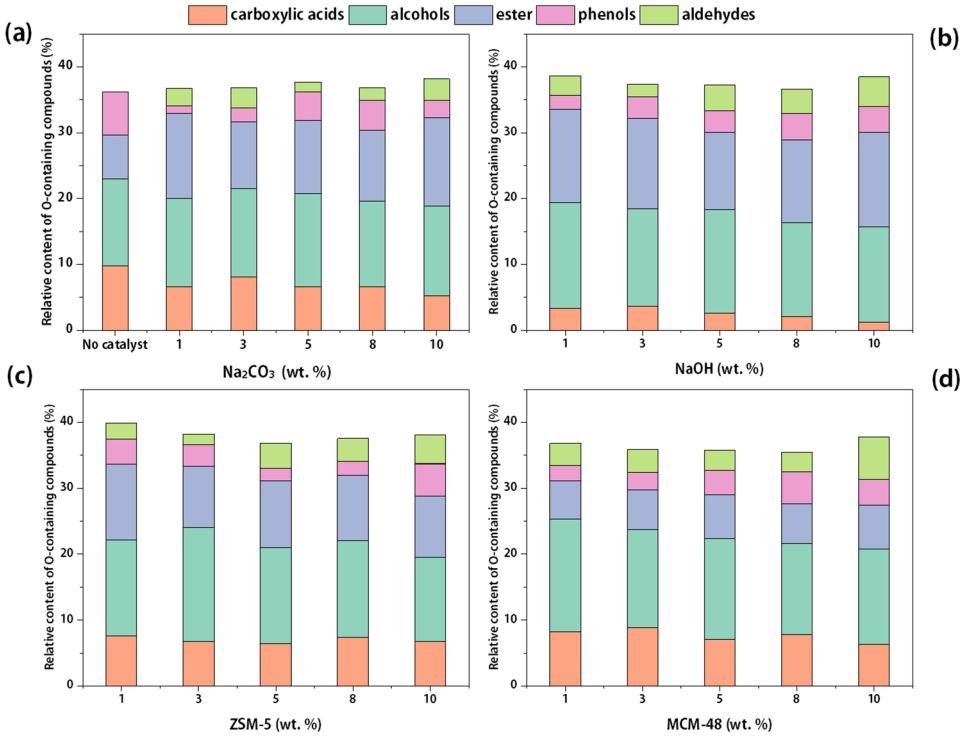

Figure 7. Oxygen-containing compound distribution of PR bio-oil: (**a**) Na_2CO_3, (**b**) NaOH, (**c**) ZSM-5, (**d**) MCM-48.

The main components of organic acids in bio-oil were n-hexadecanoic acid and (Z,Z)-9,12-octadecadienoic acid. The addition of catalysts promoted the decarboxylation of organic acids to produce alkanes and alkenes, which led to the decrease in the organic acid content. This might be the reason for the increase in hydrocarbons, i.e., heptadecane and 1-nonadecene, found in this work. Under homogeneous catalysis, the content of organic acids decreased more significantly. In particular, with the increase in the NaOH content, the content of organic acids decreased from 3.31% to 1.26%, possibly due to the neutralization of fatty acids by the alkaline catalyst [33]. The content of organic acids in the bio-oil production catalyzed by ZSM-5 and MCM-48 remained at a high level (6.4–8.9%). This could be attributed to the fact that ZSM-5 and MCM-48 are acidic catalysts, which expedited the extraction of esters in PR. The extracted esters could then be converted into carboxylic acids via hydrolysis [34]. The proportion of esters in heterogeneous catalytic bio-oil (9.28–11.6%, ZSM-5; 5.87–6.68%, MCM-48) was lower than that of homogeneous catalysis (10.85–13.42%, Na_2CO_3; 11.77–14.35%, NaOH). This might be due to the conversion of esters to organic acids. For example, hexadecanoic acid ethyl ester and (Z,Z)-9,12-octadecadienoic acid methyl ester in bio-oil might be converted to n-hexadecanoic acid and (Z,Z)-9,12-octadecadienoic acid, respectively.

The main alcohols in bio-oil were sorbitol, isosorbide, neoergosterol and ergosterol. The defoamer polyether polyol was used in the penicillin fermentation process, and sorbitol mainly came from the decomposition of polyether polyol [35]. Isosorbide was the dehydration product of sorbitol. Ergosterol and neoergosterol might come from the microbial cell membrane in bacterial residue [36]. After the addition of catalysts, the content of alcohol in bio-oil increased, which was mainly due to the increase in ergosterol and neoergosterol. In addition, the contents of hydrocarbons, such as 3,5-cyclo-6,8(14),22-ergostatriene and cholest-5-ene, increased in the catalytic hydrothermal process. This indicates that the catalysts led to an increase in macromolecular alcohols entering the bio-oil, and some of the macromolecular alcohols were dehydroxylated into hydrocarbons in the subsequent catalytic hydrothermal reaction. This is consistent with the increase in >C22 components in carbon chain analysis. The content of alcohols increased from 13.14% under non-catalytic conditions to 12.98–14.08% (Na_2CO_3), 14.23–16.12% (NaOH), 12.77–17.32% (ZSM-5) and 13.79–17.13% (MCM-48). It is evident that the heterogeneous catalyst is more conducive to the production of alcohol in bio-oil. Furthermore, the content of phenolic compounds in bio-oil decreased after catalytic hydrothermal treatment. This may be due to the substitution of carbonyl groups on phenolic components with amino or amide groups to produce aromatic amines such as N-(2-phenylethyl)-acetamide, 3-methoxy-benzenamine and 3,4-dimethoxy-benzenamine. The formation of aldehydes may be due to the secondary reactions of hydrocarbons and aliphatic amines such as decane to decanal and N-ethyl-dodecanamide to dodecanal.

3. Materials and Methods

3.1. Raw Materials

The antibiotic fermentation residue used in this study was penicillin fermentation residue (PR) which was dried by sludge dewatering and was taken from North China Pharmaceutical Group Corporation (NCPC). The PR sample was dried in an electric blast drying oven at 60 °C until constant weight. The main components of PR used in the experiment are shown in Table 3.

In addition, the higher heating value (HHV) was calculated using the Dulong formula (Equation (3)):

$$\mathrm{HHV} = 0.3383\mathrm{C} + 1.422\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) \quad (3)$$

C, H and O are the percentages of carbon, hydrogen and oxygen from the elemental analysis of the samples, respectively. The HHV of PR is 18.03 MJ/kg.

Table 3. Elemental analysis, industry analysis and composition analysis of PR (dry basis).

Elemental Analysis	wt.%	Industry Analysis	wt.%	Composition Analysis	wt.%
C	44.88	Volatile matter (VM)	83.62	Crude protein	45.4
H	6.27	Fixed carbon (FC)	9.34	Crude fat	3.85
N	5.93	Ash	8.04	Carbohydrate	1.66
S	0.77	-	-	Other	49.09
O [1]	34.12	-	-	-	-

[1] Calculated by difference (100%-C%-H%-N%-S%-Ash%).

The energy recovery rate (ER) is a comprehensive index used to evaluate the conversion efficiency of PR hydrothermal liquefaction. It can be discussed together with elemental analysis. The formula is shown in Equation (4).

$$\text{Energy recovery rate (ER)}(\%) = \frac{\text{HHV (Bio} - \text{oil)}}{\text{HHV (PR)}} \times 100\% \quad (4)$$

3.2. Experimental of Hydrothermal Liquefaction (HTL)

The reactor of HTL, sample collection and the detection system are shown in Figure 8. PR and water were mixed in a certain proportion, stirred evenly and then added to the subcritical reactor. The air in the reactor was replaced by argon. The reaction temperature was set to 280°C, and the residence time was counted after reaching the set temperature. Pressure that built up during the reaction process was generated by the solvent. In this experiment, the total solid content of PR was fixed at 18 wt.% (dry ash-free basis); 29.20 g PR and a certain proportion of the catalyst were put into 120 mL of water and stirred evenly; and the reaction temperature was 280 °C, and the residence time was 3 h. The solid and liquid phases of the hydrothermal products were first separated by vacuum filtration (SHB-III, Zhengzhou Great Wall Co., Zhengzhou, China) to obtain the aqueous products and solids. The solid substances were thoroughly cleaned with acetone. Bio-oil was obtained from the dissolved acetone phase by rotary evaporation (R1002VN, Zhengzhou Great Wall Co., Zhengzhou, China), leading to a solid residue.

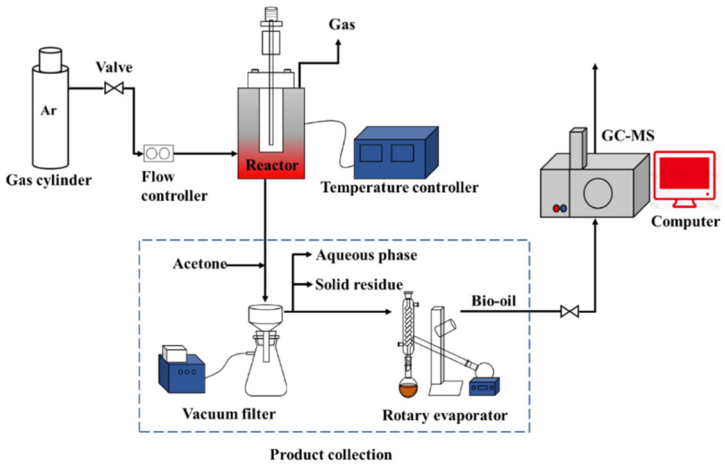

Figure 8. Experimental equipment for hydrothermal liquefaction.

The catalysts included homogeneous catalysts (HCOOH, CH_3COOH, Na_2CO_3, NaOH, K_2CO_3, KOH) and heterogeneous catalysts (zeolite molecular sieves: ZSM-5, ZSM-22, ZSM-35, MCM-41, MCM-48). The homogeneous catalysts were analytically pure and were purchased from China National Pharmaceutical Group, and the heterogeneous catalysts were purchased from JCNANO Tech. Co. (Nanjing, China). The physical properties of the five molecular sieve catalysts are shown in Table 4. The catalytic addition amount was 1 wt.%, 3 wt.%, 5 wt.%, 8 wt.% and 10 wt.% of the PR weight.

Table 4. Physical properties of heterogeneous catalysts.

Catalyst	Surface Area (m^2/g)	Average Pore Size (nm)	Si/Al Ratio
ZSM-5	385	0.55	40–50
ZSM-22	181	0.57	100–120
ZSM-35	302	0.55	70–90
MCM-41	705	2.5	30–35
MCM-48	782	3.5	20–30

The yields of bio-oils, the yields of solid residues and the conversion rate are expressed by Equation (4), Equation (5) and Equation (6), respectively:

$$\text{Yield of bio oil } (\%) = \frac{m_{bio-oil}}{m_{PR}} \times 100\% \quad (5)$$

$$\text{Yield of solid residue } (\%) = \frac{m_{Solid}}{m_{PR}} \times 100\% \quad (6)$$

$$\text{Conversion rate}(\%) = 100\% - \text{yield of solid residue} \quad (7)$$

where $m_{bio\text{-}oil}$ represents the quality of bio-oil, m_{Solid} represents the mass of the solid residue and m_{PR} represents the quality of PR raw materials. When testing the sample components, the sample needed to be pre-dried at 105 °C for 24 h to remove the moisture in PR. Values of these parameters for each sample were typically measured more than three times and then averaged.

3.3. GC-MS Analysis

The components of bio-oil were determined by a gas chromatograph-mass spectrometer (GC-MS, Shimadzu, Shimadzu, Japan). The solvent for bio-oil was acetone, which was chromatographically pure. The column was HP-5 dimethyl polysiloxane; the carrier gas was helium; and the flow rate was 1 mL/min. GC conditions: we maintained the initial temperature at 50 °C for 5 min and then increased it to 300 °C at a rate of 4 °C/min, and the shunt ratio was set as 1/30. The NIST program was employed for identifying the compounds in bio-oil.

3.4. FTIR Analysis

The Nicolet IS50 Fourier Transform Infrared Spectrometer (FTIR, Thermal Fisher Scientific, Madison, WI, USA) was employed to analyze the functional groups of the coke after hydrothermal liquefaction. The scanning range of the FTIR was 4000–400 cm^{-1}, and the spectral resolution was greater than 0.09 cm^{-1}.

4. Conclusions

(1) In hydrothermal liquefaction, the promoting effect of homogeneous catalysts on the bio-oil yield was obviously lower than that of heterogeneous catalysts. In heterogeneous catalysts, MCM molecular sieves presented good catalytic performance for oil production. When using MCM-48, the bio-oil yield reached 36.44%, which was increased 39.67% compared with the non-catalytic conditions.

(2) The catalysts slightly increased the C and H contents of bio-oil and reduced the contents of heteroatoms, especially oxygen, resulting in an increase in the HHV and ER. Thus, the quality of bio-oil was improved to some extent.

(3) The results of GC-MS show that the addition of catalysts was beneficial to increase hydrocarbons and oxygen-containing hydrocarbons in bio-oil and reduce the proportion of nitrogen-containing components. In comparison with homogeneous catalysis, the proportion of nitrogen-containing components in bio-oil produced by heterogeneous catalysis was lower. It is possible to further reduce the content of the N element in bio-oil by enhancing the amino removal through a catalytic reaction.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11070849/s1, Table S1: The main organic compound components of bio-oil (no catalyst), Table S2: The main organic compound components of bio-oil (Na_2CO_3, NaOH), Table S3: The main organic compound components of bio-oil (ZSM-5, MCM-48).

Author Contributions: Conceptualization, C.H. and Y.X.; Formal analysis, Z.W.; Writing—original draft, C.H., Z.W. and Y.S.; Software, J.Y.; Revising, L.F. and Y.W.; Writing—review & editing, J.H.; Investigation, Z.L.; Visualization, Y.L. All authors have read and agreed to the published version of the manuscript.

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