Production of bio-oil via hydrothermal liquefaction of seafood waste--taking Zhoushan coastal anglerfish waste as an example

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Abstract: As an important part of renewable energy, the development and utilization of biomass hydrothermal liquefaction and oil production technology has become one of the important topics in the field of sustainable energy research in the new century. Based on China is rich in resources, low comprehensive utilization of seafood waste as raw materials, with low energy consumption, reaction conditions are relatively mild hydrothermal liquefaction process of the production of oil, to study the efficiency of oil in the process of hydrothermal liquefaction of biomass, and by comparing the experimental conditions (temperature, raw material and the water ratio, reaction time, catalyst and its concentration) the influence of the reaction. Through the analysis of the infrared spectrum, density and viscosity of the bio-oil, the bio-oil contains alcohols, phenols, acids, esters, ketones and amines. The product oil is heavy oil and can be used after certain processing.

1. Foreword

Due to the large consumption of fossil energy, resource shortage and serious environmental pollution, biomass energy is the only renewable energy that can be converted into liquid fuel. Its development and utilization have attracted the attention of researchers all over the world. Thermochemical conversion of biomass hydrothermal liquefaction, combustion, and gasification can convert lower grade biomass energy to high grade energy [2-6]. Of particular interest is the hydrothermal liquefaction process that produces bio-oil with the potential to replace fossil fuels. After hydrothermal liquefaction, the energy density of bio-oil is greatly increased (such as straw can be increased by about 10 times), renewable and easier to transport and store [7]. Bio-oil can be burned directly as fuel oil. It can be used alone, together with fossil fuels for internal combustion engines, or for the separation and extraction of chemicals for special purposes or high added value [8]. Wang Shurong and others from Zhejiang University [10] explored the law of hydrothermal liquefaction of agricultural wastes; Yang changyan et al., institute of process engineering, Chinese academy of sciences [11] studied the hydrothermal liquefaction of wheat straw. Although the hydrothermal liquefaction technology has been fully studied in recent years, the research objects of hydrothermal liquefaction are mostly agricultural wastes and other plant wastes. As a substitute for fossil energy, biomass hydrothermal liquefaction technology will play an important role in the future development of human society. The development of this technology is of great significance to environmental protection and sustainable development of society [12]. Therefore, the expansion of technical raw materials (such as anglerfish waste) is necessary for energy supplementation, the environment and society.

In addition, a lot now Anglerfish waste represented by anglerfish waste (viscera, etc.) is generally discarded or simply processed into fishmeal, which is not well treated [21]. The treatment method has the
problems of low utilization rate and environmental pollution. From the economic and environmental point of view, the comprehensive utilization rate of organic raw materials treated by hydrothermal liquefaction of bio-oil will be significantly increased. Moreover, Marine waste represented by anchovy fish waste contains a large amount of liquefied reaction materials (such as long-chain fatty acids and proteins) \[9\] with higher content than other raw materials.

This article the anglerfish waste represented by anglerfish waste is hydrothermal liquefaction raw material, and the oil yield and quality under different conditions are studied. By studying the oil yield and oil quality under different conditions, the mass and energy balance of the hydrothermal liquefaction process of anglerfish waste were analyzed. The optimal reaction conditions of the bio-oil yield were obtained and verified by experiments. The research results show that the liquid fuel can be used for combustion and heating of boilers and industrial furnaces, and it is expected to be used in motor vehicles after further refining. There is a certain development prospect.

2. Experimental materials, experimental devices, and experimental methods

2.1. Experimental materials

In this experiment, anglerfish waste was selected as raw material and nitrogen as protective gas. The dichloromethane is a colorless, transparent, volatile liquid heavier than water and slightly soluble in water \[13\]. It is mutually soluble with most common organic solvents, facilitating extraction and separation in the later stage of the experiment. In addition, dichloromethane is the least toxic of methane chloride, so dichloromethane is selected as the extraction agent. The main drugs and reagents are shown in Table 1.

| Reagent name          | Specification | Manufacturer                                      |
|-----------------------|---------------|---------------------------------------------------|
| Anhydrous sodium carbonate | AR            | Sinopharm Chemical Reagent Co., Ltd.              |
| Potassium hydroxide   | AR            | Sinopharm Chemical Reagent Co., Ltd.              |
| CH₃COOH               | AR            | Sinopharm Chemical Reagent Co., Ltd.              |
| Dichloromethane       | AR            | Sinopharm Chemical Reagent Co., Ltd.              |
| Deionized water       | /             | Zhejiang Ocean University Laboratory              |

2.2. Preparation for experiment

The main instruments used in the experiment are as follows. As shown in Figuer 1, it is easy to operate, resistant to high temperature and high pressure, and solves the sealing leakage problem of traditional reactor. This experiment mainly uses this reactor for hydrothermal liquefaction reaction. As shown in Figuer 2, the instrument is mainly used in this experiment to separate dichloromethane extract from the product and obtain bio-oil.
2.3. Experimental method

2.3.1. Preparation of experimental materials. In this experiment, anglerfish waste was used as raw material to produce bio-oil. For the true reliability of the experiment, the collection of raw materials was carried out at random. The raw materials mainly contain fins, fish guts, fish scales, fish gills and minced fish. The collected waste is treated simply and then dried and frozen for later use.

2.3.2. Standard experimental procedure. The raw material was pulverized into a paste sample by a high speed universal pulverizer. A 30g sample was mixed with 200 ml of deionized water and placed in a reaction kettle. Purge the reactor with nitrogen (99.98%) for 1 minute, close the exhaust valve, continue to pass nitrogen for 1.5 minutes, then close the inlet valve and nitrogen valve of the microreactor in turn. The reaction temperature was set and the magnetic stirrer rotation speed was 500 r/min. The heating rate of the reactor was 2.5℃/min, the reaction time was 60 min. After the temperature had dropped to room temperature, the product in the reactor was flushed out with 100 ml of dichloromethane. The obtained mixed product was suction filtered, and the residue was weighted after drying at 60℃ for 24 hours, and the filtrate was subjected to liquid separation treatment. The lower layer liquid (dichloromethane phase) was subjected to rotary distillation under reduced pressure to obtain a dark brown viscous oily product, which is defined herein as a bio-oil, in a round bottom flask. The final product was characterized and analyzed; the supernatant (aqueous phase) was poured into a waste tank. Figure 3 below shows the experimental preparation process:

![Figure 3. The process of producing bio-oil by hydrothermal liquefaction.]

2.3.3. The comparative experiment. In order to explore the effects of different temperatures, different raw material ratios, and different catalysts and their concentrations on the yield of bio-oil. The control experiments were conducted in groups. In the comparative experiment, the experimental conditions and operation steps remain unchanged, and the variables are set as the ingredient ratio which is the ratio of the amount of raw material and the ratio of deionized water is 1:10, 1:6.67 and 1:5. Temperature makes 200℃, 225℃, 250℃, 275℃, 295℃; The catalysts are Na2CO3 and CH3COOH. The catalyst concentration was 0.3mol/L, 0.6mol/L and 0.9mol/L, and four parallel experiments were conducted.

3. Experimental data and analysis and discussion

3.1. Effect of different reaction conditions on hydrothermal liquefaction
In order to observe the conversion rate of dry weight and oil yield more intuitively, the proportion of dry weight of raw materials from gourd fish waste was calculated. The wet weight of the anglerfish waste was 10g, 20g and 30g respectively. After 72 hours of complete drying, the quality and final dry weight of the waste were as follows. The dry weight ratios were 37.48%, 39.56% and 38.00%. The dry weight ratio after the average was 38.34%. The experimental results are shown in Table 2 below:
Table 2. Dry weight ratio of Anglerfish Waste.

| Wet weight / g | Dry weight / g | Dry weight ratio | Dry weight average |
|----------------|----------------|------------------|--------------------|
| 21.0256        | 7.8811         | 37.48%           |                    |
| 9.9378         | 3.9312         | 39.56%           | 38.34%             |
| 30.5576        | 11.6123        | 38.00%           |                    |

3.1.1. Effect of different reaction temperatures on hydrothermal liquefaction. To investigate the effect of reaction temperature on hydrothermal liquefaction experiments, we set up a temperature comparison experiment with 1: 1.67 ratio of ingredient. The experimental results are shown in Figure 4.

![Quality of filter residue and biomass oil at different reaction temperatures](image1)

![Liquefaction rate and oil yield at different reaction temperatures](image2)

Figure 4. Reaction results at different reaction temperatures.

It can be seen from the experimental data that in the experiment using 30g of raw materials, the liquefaction rate of each group does not change much, and the oil yield decreases first with temperature, and the yield is the highest at 250℃, and the quality of the filter residue is the least. It can be determined that 250℃ is the optimum reaction temperature.

3.1.2. Effect of different reaction materials ratio on hydrothermal liquefaction. In the comparative experiment, we set up a comparison test of 20g and 40g, and the comparison was carried out at a reaction temperature of 250℃ and 275℃. The operation and steps of the experiment remain unchanged. The experimental results are shown in Figure 5.
The figure shows that within the temperature range of 250 °C, the oil quality as anglerfish waste biomass increases with increasing the quality of raw materials, and is proportional to the quality of raw materials, but in the temperature range of 275°C of oil quality and the quality of raw materials have no obvious linear relationship. This result also shows the temperature range of 250°C is from the side anglerfish waste hydrothermal liquefaction oil yield of the maximum temperature.

3.1.3. The effect of different reaction time on hydrothermal liquefaction. The reaction time is another important parameter affecting the hydrothermal liquefaction yield, liquefaction rate and product distribution. Usually, the reaction time of hydrothermal liquefaction is 20~90min [19]. In order to study the effect of reaction time on the hydrothermal liquefaction process and oil yield, we set up a comparative test at different reaction time. The experimental results are shown in Figure 6 below.

According to the graph, the liquefaction rate has little change with time, the liquefaction rate and bio-oil yield are both higher. The yield is still greatly improved in 60 minutes under the reaction condition of 250°C. It shows that the optimal reaction time is about 60 minutes.

3.2. Effect of different catalysts and concentrations on bio-oil
In order to study the influence of different catalyst types and different catalyst concentrations on the experiment, this experiment took Na₂CO₃, CH₃COOH, catalyst-free and their different concentrations as variables for comparison test, and obtained the yield of bio-oil and solid residue for analysis and discussion. The experimental results are shown in Figure 7, Figure 8 and Figure 9 below:
Figure 7. Oil yield under different catalysts.

Figure 8. Liquefaction rate under different catalysts and concentrations.

Figure 9. Pressure variation of catalysts and their concentrations.

The experimental results show that adding CH₃COOH can minimize the residue yield of hydrothermal liquefaction products and maximize the oil yield at the same time. The yield of bio-crude oil is high with organic acid as catalyst, which is closely related to the higher lipid content of raw materials[20]. Therefore, in hydrothermal liquefaction, organic acids play an important role in increasing bio-oil yield and reducing solid residue.

The bio-oil prepared by adding the catalyst changed significantly with the increase of catalyst dosage. When the hydrothermal liquefaction reaction was catalyzed by 1mol/L catalyst, the addition of
CH$_2$COOH effectively promoted the increase of bio-oil yield and inhibited the generation of solid residues in the reaction process.

At the same time as the yield of bio-oil is higher, the lower the solid residue yield, the more complete the reaction of the material, the lower the pressure change, the less gas generated by the reaction, and the safer the reaction environment. As the amount of catalyst increases, the yield of bio-oil and the yield of solid residue generally increase, while the pressure change during the hydrothermal liquefaction reaction decreases.

4. Detection and analysis of experimental products

4.1. FT-IR.

We use infrared spectroscopy characterization of 250℃ respectively, residence time of 60 min under the conditions of different catalysts of biomass of oil. The characterization results are shown in figure 10 below:
Bio-oil is a complex mixture system. It can be observed that the bio-oil contains a large amount of alkane compounds, aldehydes, ketones, carboxylic acids, esters, amides, phenols, acids, alcohols substance, olefinic substances and more benzene ring structure. In addition, the carboxylic acid is present in the bio-oil catalyzed by Na$_2$CO$_3$ without catalyst and catalyst; catalyzed by CH$_3$COOH bio-oils are found in alcohols, phenols, and amines.

4.2. Density.
The oil density of the product to which catalyst-free was added was calculated to be 1095 kg/m$^3$ by a conventional method, and the product oil density of the catalyst CH$_3$COOH was 1,150 kg/m$^3$. The density of China's heavy crude oil and atmospheric vacuum residue is about 920–1000kg/m$^3$ (20°C)[11]. The density of motor gasoline is 790–840 kg/m$^3$ (20°C) (GB/T 1885). Therefore, the bio-oil produced by the experiment has a high density and cannot be directly used. It needs further modification before it can be used.

4.3. Viscosity.
In this experiment, the viscosity of the product oil was 2.6518mm$^2$/s and the dynamic viscosity was 2904cP. The viscosity of the product oil added with catalyst was 2.362.6518mm$^2$/s. The viscosity is 2711cP. The viscosity of bio-oil obtained in this experiment is higher than that measured by J L Zheng et al.[15] at 305 cP (20°C).

According to the corresponding national standards, the viscosity (20°C) of motor gasoline in China is 1.8–8.0mm$^2$/s (GB/T 265). Therefore, the oil viscosity of the bio-oil prepared in this experiment meets the standard. In addition, when the bio-oil was stored at low temperature (-1-7℃), some of the existing bio-oil was found to be solidified, which indicated that the bio-oil produced by the hydrothermal liquefaction of anglerfish was not suitable for storage and use at low temperature.

4.4. pH.
Bio-oil with high acid value can cause corrosion to storage and transportation equipment and damage to burners, resulting in its limited application. We use titration to determine the acidity and alkalinity of bio-oil. The principle is that the free acid in the sample is neutralized with potassium hydroxide, and the amount of free acid can be calculated from the consumption of the potassium hydroxide standard solution, and the equation is: RCOO$^+$+KOH→RCOOK+H$_2$O

100ml of a potassium hydroxide solution having a concentration of 0.1mol/L and a concentration of 2ml of a basic blue 6B solution having 95% ethanol as a solvent were placed. After diluting 1g biomass oil sample with 200ml 95% ethanol solution, add 10ml diluted solution and 2–3 drops of prepared basic blue solution (indicator) to the flask for titration. In the titration experiment, 50ml potassium hydroxide solution was added to the 50 ml burette tube. 0.1mol/L potassium hydroxide solution was slowly added to the conical bottle, and the conical bottle was shaken continuously until the liquid in the bottle turned pink and remained colourless for 30 seconds, that is, the titration end point. At this time, the volume of potassium hydroxide consumed in the burette was recorded. The Acid value of bio-oil at different temperatures is shown in the figure 11 and figure 12 below:
For crude oil, a total acid value of >5mgKOH/g is a very high acid value crude oil [16]. For bio-oils, the bio-oil acid values of Elliott [17] and the like and Bai [18] using microalgae as raw materials were 59-74mgKOH/g and 133.2mgKOH/g, respectively. The experimental results show that the acid value of the oil is too high, and the prepared bio-oil must be refined to reduce the acid value before it can be put into use.

5. Conclusion

(1) In this experiment, the common anglerfish waste in coastal areas was selected as the experimental raw material, and the material oil was produced by hydrothermal liquefaction method. The product oil contains alcohols, phenols, acids, esters, ketones and amines. Taking CH$_3$COOH as an example, the density and viscosity of the product oil are 1150kg/m$^3$ and 2711cP (20℃), which belong to heavy oil. The acid value of the product oil is higher than that of the fuel oil and biodiesel, and similar to that of the biomass oil produced by other raw materials. It needs further processing to reduce the acid value before it can be put into use.

(2) Temperature is one of the important factors affecting the liquefaction rate and oil yield of anglerfish waste water liquefaction. When other reaction conditions are determined, there is an optimum temperature for hydrothermal liquefaction, and a bio-oil having a high liquefaction rate and a high oil yield is obtained. From the perspective of oil ratio and liquid ratio analysis of experimental results of hydrothermal liquefaction, reaction temperature at 250℃ can be obtained the highest rate of oil production. The experimental results also show that the optimal temperature corresponding to the maximum liquefaction rate is not correlated with the temperature corresponding to the maximum oil yield.

(3) The addition of CH$_3$COOH can effectively increase the yield of bio-oil, and plays a big role in reducing the yield of solid residue.

(4) The catalytic action of organic acid CH$_3$COOH in hydrothermal liquefaction not only improves the yield of biomass oil, but also effectively reduces the yield of solid residue. It is a good hydrothermal liquefaction solvent.

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