



Effect of unsaturation degree on microwave-assisted pyrolysis of fatty acid salts



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ABSTRACT

This work is aimed to study the effect of unsaturation degree on microwave-assisted pyrolysis (MAP) of fatty acid salts. Sodium stearate, sodium oleate, and sodium linoleate were selected as model compounds. MAP of sodium oleate obtained the highest yield of liquid product. GC–MS analysis of liquid product revealed that MAP of unsaturated fatty acid salt could produce alkadienes, cycloalkanes, cycloalkenes, alkynes and aromatics, which could not appear in liquid product obtained from MAP of saturated fatty acid salt, and unsaturation degree had a great influence on liquid product composition. Analysis of the gas product indicated that MAP of sodium oleate produced more CO₂ and CO, while the MAP of sodium linoleate produced more gaseous hydrocarbons and H₂. Analysis of the solid char showed that MAP of unsaturated fatty acid salts favors the cyclization and aromatization of pyrolysis vapours. The properties of liquid product were measured and analyzed, which confirmed that MAP of fatty acid salts is a feasible technology to produce high-quality renewable hydrocarbon fuels.

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1. Introduction

With dwindling petroleum reserves and increasing environmental concerns, biomass conversion for the production of biofuels as an alternative source of energy has been considered to be a promising approach [1–3]. To convert biomass into renewable fuels and chemicals, effective and promising conversion and processing technologies are needed. Pyrolysis is a well-recognized process for the production of liquid fuel [4]. Recently, microwave-assisted pyrolysis (MAP) is widely applied in biomass conversion due to its advantages over traditional heating routes including: (1) Simple microwave heating system is in favour of large-scale industrial technologies; (2) Microwave heating is rapid, highly efficient, and selective, in which only polar components or materials can be heated; (3) Microwave heating can be instantly turned on or off; (4) Microwave devices are inexpensive and easy to operate compared with other heating modes [5–7].

Fats and oils are primarily composed of triglycerides and free fatty acids. Moreover, triglyceride is made of one mole of glycerol

and three moles of fatty acids. These materials can be pyrolyzed to fuel-grade hydrocarbons under proper reaction conditions. Many literatures have reported the pyrolysis of triglycerides [8–10], while the pyrolysis of free fatty acids recovered from hydrolysis of fats and oils were reported rarely. Bressler and his co-workers investigated the pyrolytic conversion of stearic acid, oleic acid and linoleic acid to hydrocarbon products for use as renewable chemicals and fuels [11–13]. They uncovered the dominant reaction pathways in the pyrolysis of these free fatty acids and demonstrated the feasibility of producing liquid hydrocarbons through this pyrolysis. To the best of our knowledge, the effect of unsaturation degree on MAP of fatty acid salt has not been studied.

In our previous studies, MAP of fatty acid salt for renewable hydrocarbon fuel production was carried out [14,15]. Experimental results indicated that the carboxyl terminal of fatty acid salt has a stronger polarity than that of fatty acid and this terminal is more likely to be dipole polarized and ionically conductive in a microwave field. The surface of glycerol formed a “High-Temperature Locus” in microwave radiation reaction system, which played a role as the hydrogen donor of reaction intermediates and facilitated the decarboxylation processes. C₈–C₂₀ *n*-alkanes and *n*-alkenes were arranged regularly in liquid prod-

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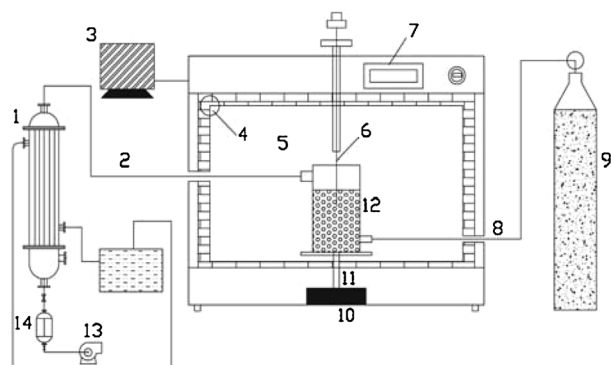


Fig. 1. Schematic diagram of MAP experimental setup.

ucts. It was demonstrated that it was feasible to obtain renewable hydrocarbon fuel from MAP of fatty acid sodium salt.

The purpose of our work was to investigate the effect of unsaturation degree on MAP of fatty acid salts. In addition, the properties of pyrolysis oil were measured and compared with biodiesel and 0# diesel.

2. Materials and methods

2.1. Materials

Sodium stearate ($\geq 99\%$), sodium oleate ($\geq 99\%$), sodium linoleate ($\geq 99\%$) were purchased from Sigma-Aldrich (China). Their characteristics are shown in Table 1. Glycerol ($\geq 99\%$) was purchased from Aladdin (China). H_2 , CO_2 , CO , CH_4 and C_1 – C_4 alkanes and alkenes standards were purchased from Dalian Special Gases Co. Ltd. (China). All chemicals were used as received.

2.2. Microwave-assisted pyrolysis

The MAP experiments were carried out in a self-designed microwave apparatus with the power of 2 kW at 2.450 MHz, which was manufactured by SinEo in Shanghai, China. The schematic experimental setup was shown in Fig. 1. It was composed of: (1) condenser; (2) gas outlet; (3) computer-control system; (4) camera; (5) furnace chamber; (6) K-type thermocouple to measure the reaction temperatures; (7) control over LED display contact screen; (8) gas inlet; (9) gas bomb; (10) precision balance; (11) polytetrafluoroethylene mass sensor; (12) quartz reactor; (13) gas pump; (14) liquid fraction collector. For safety purpose, a microwave detector (MD-2000, Digital Readout) was used to monitor microwave leakage.

Firstly, 30 g samples mixed with 10 wt.% glycerol were prepared, which in turn was placed in the bottom of the quartz reactor. The reactor was specially made for the microwave apparatus used in the experiments. It was built with fused quartz, with 250 mL of volume. The opening at the top was used to insert the thermo-

couple to measure the reaction temperatures. The opening in the side of the quartz reactor were used to connect the outlet tube. After the quartz reactor was placed inside the furnace chamber, the outlet quartz tube was connected to the condenser and liquid fraction collector. In order to maintain an inert atmosphere within the quartz reactor during pyrolysis, the system was vacuumed at 170 mmHg for 5 min prior to the commencement of the microwave heating, with the vacuum being maintained during the entire heating process. The microwave apparatus was then turned on for heating process. The reaction temperatures were maintained by changing microwave power with the aid of control programs in the computer-control system. Samples of the gas product were collected during pyrolysis. All the liquid and solid fraction products were collected after pyrolysis, and were weighted. The liquid and solid fraction yields were calculated based on the actual weight, while the gas yield was calculated by difference based on the mass balance. The above experiments were repeated thrice to mitigate the effects of experimental error.

2.3. Products analysis

2.3.1. Liquid product analysis

After filtering using a 0.22- μm organic syringe membrane, the liquid fraction was analyzed by GC–MS equipped with the chromatographic column (HP-5 ms; 30 m \times 0.25 mm \times 0.25 μm). The following conditions were used: the column temperature was kept at 60 °C for 2 min and then raised to 280 °C at a rate of 10 °C/min; the vaporizer temperature was 250 °C; the sampling size was 0.2 μL ; the split ratio was 20:1; and the carrier gas was He which was introduced at a flow rate of 1.0 mL/min. For MS settings, the electron multiplier voltage was 1941 V; the ion source temperature was 230 °C; the interface temperature was 280 °C; and the analysis mode was the scan mode. Some complex components in the pyrolysis products could not be differentiated, although the determination of components was based on the retention time of certain internal standards (for example, adamantane). Therefore, the mass spectrograms of these pyrolysis products should be used for analysis. A mass ratio greater than 90% was required. The components in the pyrolysis products were identified by comparing their mass spectra with those from the National Institute of Standards and Technology mass spectral data library. A semi-quantitative method was used to determine the relative content of each component in the pyrolysis oil by calculating the chromatographic area percentage.

As for the fuel properties, they all were determined according to the ASTM methods. The density was measured on a K86200 automatic digital densitometer with ASTM D1250 standard. In order to determine the kinematic viscosity of hydrocarbon fuel, ASTM D445 method was applied on a Tanaka KV-5S viscometer. The cold filter plugging point of hydrocarbon fuel was analyzed on a CFPP-200 automatic petroleum cold filter plugging point meter according to ASTM D6371. In addition, the calorific value was measured using a IKA C-2000 calorimeter according to ASTM D240-02.

Table 1
Characteristics of sodium stearate, sodium oleate, and sodium linoleate.

| Name | Chemical structure | Molecular formula | C=C number |
|------------------|--------------------|---------------------|------------|
| Sodium stearate | | $C_{18}H_{35}O_2Na$ | 0 |
| Sodium oleate | | $C_{18}H_{35}O_2Na$ | 1 |
| Sodium linoleate | | $C_{18}H_{35}O_2Na$ | 2 |

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