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Catalytic cracking of castor oil via microwave assisted method

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Abstract

Castor oil extracted from seeds of *Ricinus Communis* plant has an immense potential being used to yield valuable hydrocarbons with shorter chain length. Castor oil contains chemical structures of heavy hydrocarbons and long chains may undergo a cracking process which are similar to that as in petrochemical industries. However, cracking process requires extremely high temperature and energy input. This research came by with an attempt to reduce waste of energy using both microwave assisted method and modified metal catalyst, Zn/ZSM-5 to provide sufficient energy for cracking process to occur at comparatively low temperature. Wet impregnation method was used for Zn/ZSM-5 catalyst preparation and the experiments were carried out via microwave-assisted method. The microwave effect on the temperature and mass of condensate formed was investigated at three different output powers; 650, 700 and 750 W, under different Zn/ZSM-5 concentrations; 5, 8 and 10 wt% for 1 h. Results showed that cracking of castor oil is feasible at low temperature (<250 °C) using modified Zn/ZSM-5 via microwave assisted method. The highest yield of total mass of condensate (5.61%) was obtained from 750 W output power and 10 wt% Zn/ZSM-5 catalyst concentration. In addition, the highest cracking percentage (97.7%) was obtained from 750 W output power and 5 wt% Zn/ZSM-5 catalyst concentration. Valuable cracked compounds such as octane for fuel products and undecylenic acid for pharmaceutical uses were obtained.

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1. Introduction

Biomass, vegetation and crops contain bio-oils that are foreseen as the future source to replace the non-renewable fossil fuel oil and production of many other useful chemicals [1–4]. Bio-oils can be classified into inedible and edible which the latter bio-oils presently cover over 95% of worldwide uses. This high demand causes competition with the food market and has made the prices of edible bio-oils to increase rapidly. Thus, inedible bio-oils that

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are not part of humans' nutrition starts to gain attention [5]. Castor oil received considerable attention among all those bio-oils classified as inedible because the **oil content** of castor seeds is more than 50% which is relatively higher as compared with other inedible biomass source [6]. Ricinoleic acid, which is the major constituents of castor oil consists of long hydrocarbon chain and the presence of functional groups such as double bonds and hydroxyl groups made this bio-oil possesses excellent lubricity, emollience, non-comedogenicity and available for many reaction [7]. Furthermore, castor oil occurs naturally with elevated viscosity and **polarity** also renders it extremely valuable for the **industrial production** of coatings, plasticizers, cosmetics, polyurethane polymer, soap and fine chemical compounds [8,9].

One of the synthesis routes for industrial product from castor oil is through cracking process. ÁlvaroIbarra et al. reported that raw bio-oil is feasible to be cracked down under fluid catalytic cracking unit [10]. A.A. Mancio et al. successfully performed the thermal catalytic cracking of palm oleic oil at temperature of 450 °C under atmospheric pressure [11]. Introducing an appropriate catalyst to biomass catalytic cracking process can boost the **biomass conversion** efficiency, reduce tar formation, and increase the target product yield [12,13]. The research by Negm, Rabie, and Mohammed managed to obtain biofuels from the catalytic cracking process of castor and jatropha oil using the synthesized nano-structured γ -Al₂O₃ at temperature of 280-320 °C [14]. Zeolite is normally used as the base catalyst in catalytic cracking of vegetable oils such as *Swida wilsoniana* oil for hydrocarbon biofuel [15]. Electromagnetic waves cause the dielectric heating of zeolite catalyst particles, providing the energy required for cracking reactions [16]. Abdelrahman M. Rabie et al. tried on modification of base catalyst, bentonite and showed that it performs efficiently for catalytic cracking of oil to biofuels at relatively low temperature and showed that the nature of biofuel is controlled by reaction temperature and catalyst concentration [17]. Copper modified zeolite ZSM-5 performance was investigated by Vagif et al. in the catalytic cracking process of cotton seeds and sunflower oil under vacuum condition. They proved also catalytic cracking of castor oil is feasible using metal modified zeolite. In addition, the metal will increase the gasoline yield by 4% and decrease the coking rate by 10% due to more efficient cracking [18]. Hamed Abdelfattah & Saleh et al. also show that the combination of NaOH with zeolite will crack the castor raw oil at temperature range of 233-347 °C [19]. Zn/ZSM-5 catalyst is normally used in catalytic cracking process to obtain biofuel from inedible biomass such as camelina oil and carinata oil [20,21]. In short, the temperature for cracking process of vegetable oil can be further decreased with suitable catalyst or metal modified catalyst.

The use of microwaves offers considerable advantages over traditional thermal heat sources in industrial processing such as rapid heat transfer, volumetric and selective heating, compact equipment, rapid on-and-off action and pollution-free operation as no combustion is involved [22]. JingSun, KeWang, ZhanlongSong et al. proved that compared with conventional pyrolysis using heat energy, microwave assisted method converts more char to bio-oil and biogas [23]. Rozita Omar et al. showed that maximum pyrolysis of organic liquid oil and light bio-oil using microwave as energy source occur at temperature 550 °C [24]. Research from Shiyu Liu et al. found that maximum bio-oil yield when pyrolysis temperature reached 550 °C through sequential two-step fast microwave-assisted pyrolysis (fMAP) [25]. Alexandro Stonoga V. da Silva et al. performed catalytic cracking on light gas oil using microwave with power 2.5 GHz as the source of energy with zeolitic acid and managed to get condensate oil similar to diesel fuel [16]. In addition, YongNie et al. was able to obtain methyl undecenoate from castor oil by microwave-assisted pyrolysis at temperature range of 500 °C [26].

In this study, a pilot-scale microwave oven was used for the catalytic cracking of castor oil under continuous constant supply of output power. The main objective is to prove that microwave energy and metal modified catalyst provide sufficient energy for catalytic cracking process to occur even at low temperature. In addition, a simplified mechanism is also proposed to promote a better understanding of chemical reaction aimed at aiding future studies especially on the process up-scaling.

2. Experimental

2.1. Materials

Pure castor oil was provided by Green Herbology obtained through cold pressing extraction technology. Zeolite ZSM-5, Ammonium (SiO₂:Al₂O₃) came in the powder form with surface area 425 m²/g, 80:1 mole ratio supplied by Alfa Aesar, Haverhill, Massachusetts, United States. Zinc metal powder (<150 μm) with trace metal basis (99.995%) was purchased from Sigma-Aldrich.

2.2. Preparation of catalytic cracking Zn/ZSM-5 catalyst

100 g of Zeolite ZSM-5 was activated by mixing with 0.5M of hydrochloric acid. 10 g of zinc metal was poured in the aqueous solution, refluxed and stirred for 24 h at 80 °C using a wet impregnation method. Then, it was filtered and dried overnight in an oven at 100 °C followed by calcination at 500 °C for 3 h in a furnace.

2.3. Catalytic cracking experiment setup

The catalyst and metal additive used in this experiment were zeolite ZSM-5 and Zinc (Zn). At first, 100 ml of castor oil was mixed with 10 g of zeolite ZSM-5 and Zn (ratio 1:1) in the flat-bottomed flask. A microwave was connected to the reflux system using a Friedrichs-type condenser. The microwave extraction system was set up and started at 650 W. The temperature of the microwave extraction system was recorded every 10 min interval for 1 h. The inlet of condenser was flowed in with tap water as a cooling medium to condense the vapor. The formed condensate flowed into the reflux tube, collected in a beaker and the mass of the condensate was weighted. Nitrogen gas was flowed into the system as an inert medium for safety precaution. The experiment was repeated using different parameters-output power (650/700/750 W) and various ratios of metal additives (5,8,10 wt%). Each metal additive of catalysts was operated using three different output powers(5 wt%:650/700/750 W), (8 wt%:650/700/750 W), (10 wt%:650/700/750 W) with the total of nine experimental runs.

2.4. Characterization of condensate product

2.4.1. GC-MS chromatographic measurement

The condensate was analyzed using GC-chromatographic analysis. GC-7890 A instrument was equipped with DB-1MS column, which was 30 m length, 0.25 mm in diameter with 0.25 μm thickness film. The oven temperature was initially programmed at 40 °C for 2 min. raised to 100 °C at 3 °C/min for 1 min and retained at 270 °C at 4 °C/min for 1 min. The split ratio was set to 1:101 and helium (He) was used as a carrier gas at a flow rate of 0.9 mL/min.

2.4.2. ATR/FTIR analysis

Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (ATR/FTIR) measurement were acquired on a Nicolet™ iS50 FT-IR Spectrometer (Thermo Fisher, Scientific Inc., Waltham, US) equipped with built in iS50 ATR accessory. Spectra [4000–600 cm^{-1}] were collected with resolution of 0.09 cm^{-1} by co-adding 32 scans for each spectrum. Integrated software for Windows was used for spectra collection.

3. Results and discussions

3.1. Effect of output power on temperature

In Fig. 1, all three graphs of different Zn/ZSM-5 catalyst concentrations showed a similar trend that the temperature increased rapidly at the first 10 min before remaining constant throughout the experiment. In general, the temperature trends of 650,700 and 750 W were managed to sustain without having any significant drop of temperature through the reaction time of 60 min. Temperature increased when increasing the output power that generated stronger electromagnetic intensity causing the atoms within the castor oil molecules to vibrate more vigorously. The atoms collided with each other more frequently and produced much larger frictional force. As a result, great deal of heat energy was generated which causes elevation in temperature. Noticeably, there was a certain point of the experiment where the temperature started to drop. The slightly drop in temperature was possibly due to the cracking process which is an endothermic reaction that consumes part of the heat energy generated to break down the long chain into shorter chained hydrocarbons.

The highest Zn/ZSM-5 catalyst concentration of 10 wt% at the highest power of 750 W (gray solid line) tends to absorb more heat from the microwave system, and results in higher temperature increment. Although the highest catalyst concentration was expected to achieve the highest temperature, it was not sustained at the highest temperature during the experiment. The rate of evaporation of the castor oil was much higher at the highest catalyst concentration that possibly causes more cooling effects and a drop in the temperature trend.

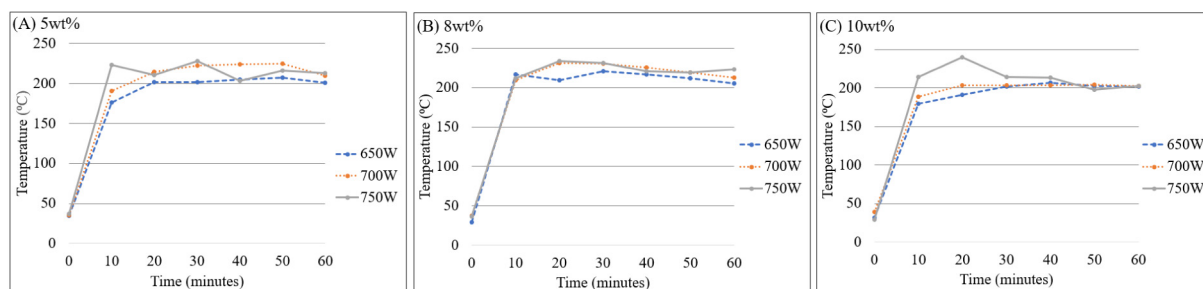


Fig. 1. Comparison of temperature versus time at different output powers for (A) 5 wt% (B) 8 wt% and (C) 10 wt% Zn/ZSM-5 catalyst.

3.2. Effect of output power on mass of condensate formed

Theoretically, higher output power will generate more mass of condensate formed as more castor oil molecules will attain enough energy to vaporize at high temperature. This theory only supported by graph C from Fig. 2 as higher output power (10 wt% of 750 W) generated relatively higher mass of condensate. However, the output power has no direct relationship on the mass of condensate formed. This is probably because the energy used was very random that some were used to break the bonds in the castor oil during cracking process while some energy was used for the latent heat in evaporation process. Thus, the masses of condensate formed were varied regardless of the output powers.

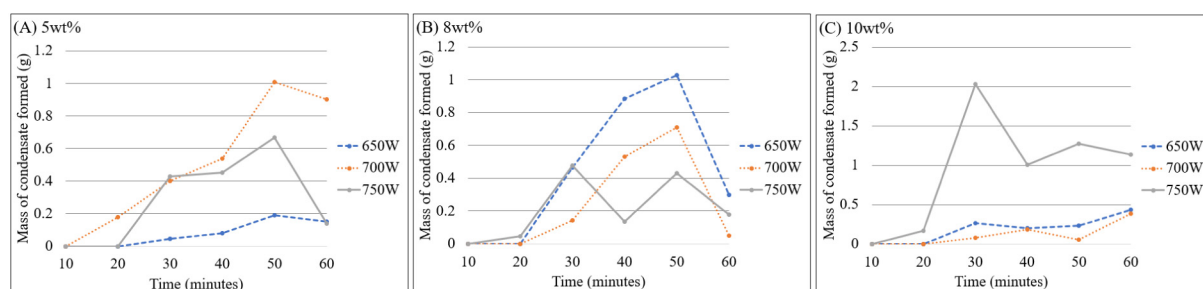


Fig. 2. Comparison of mass of condensate formed versus time at different output power for (A) 5 wt% (B) 8 wt% and (C) 10 wt% Zn/ZSM-5 catalyst.

3.3. Effect of catalyst concentration on mass of condensate formed

The theory was also supported by graph C from Fig. 3 as higher catalyst concentration generated relatively higher mass of condensate. However, catalyst concentration also has no direct relationship on the mass of condensate formed. The random energy was utilized to break the bonds during cracking process and some energy was consumed for the latent heat in evaporation. Thus, the masses of condensate were random regardless of the catalyst concentrations.

3.4. Parameter with the highest total mass of condensate formed

In Fig. 4, the output power of 750 W and catalyst concentration of 10 wt% gave the highest 5.62% yield with the total mass condensate of 5.61 g from 100 g of castor oil. Both higher output power and catalyst concentration gave higher temperature and generated more heated vapor and collected as condensate. On the contrary, the output power of 650 W and catalyst concentration of 5 wt% provided the lowest yield of 0.47%. Lower temperature which was due to both lower output power and catalyst concentration only enable some of the castor oil molecules to attain enough energy to rise up as heated vapor and then condensate. As a result, the total mass of condensate formed was the lowest among all the parameters.

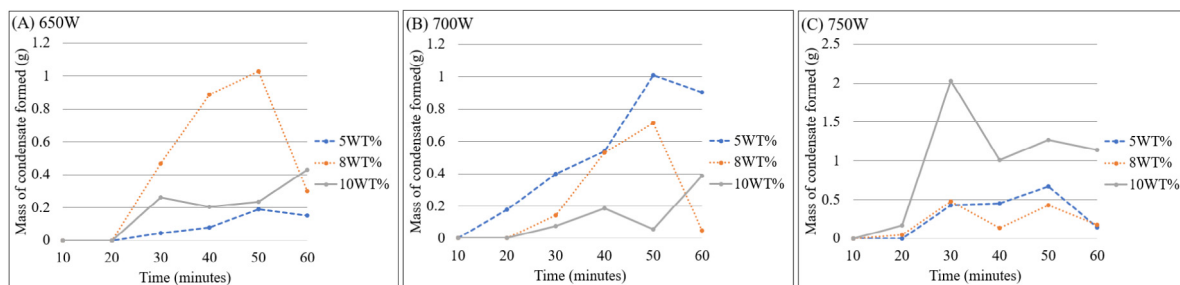


Fig. 3. Comparison of mass of condensate formed versus time at different Zn/ZSM-5 catalyst concentration for (A) 650 W (B) 700 W and (C) 750 W output power.

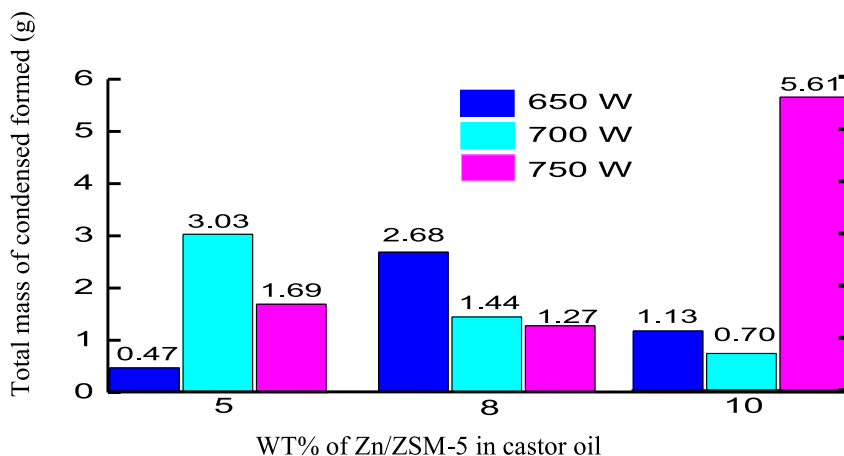


Fig. 4. Comparison of total mass of condensate formed at different output power for 5 wt%, 8 wt% and 10 wt% Zn/ZSM-5 catalyst.

3.5. Parameter with the highest cracking percentage

Fig. 5 shows that the output power of 750 W and catalyst concentration of 5 wt% has the highest percentage of cracking in condensate product (97.7%). Higher output power will contribute more energy to the chemical bonds within castor oil molecule to vibrate more vigorously. Hence, the chemical bonds are easily broken when the supplied energy exceeds the forces of attraction between atoms and this is where cracking happens. However, small

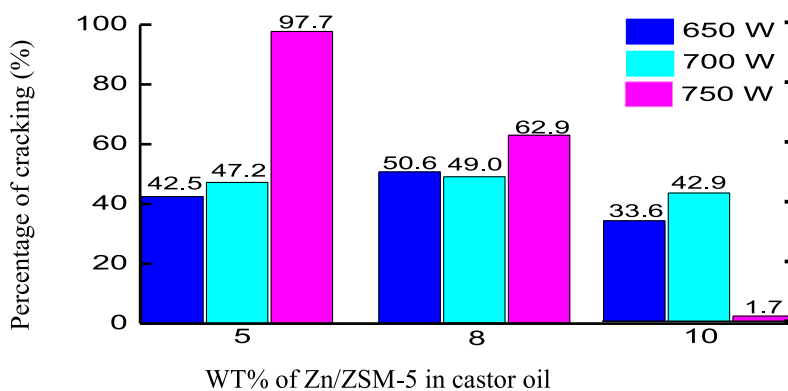


Fig. 5. Comparison of percentage of cracking for 9 parameters with different output power and Zn/ZSM-5 catalyst concentration.

amount of catalyst (5 wt%) was sufficiently needed for the cracking process to occur. On the contrary, catalyst in excess amount will absorb more heat energy generated from the microwave and thus only small portion of energy is available for the cracking process. Thus, high concentration catalyst is not favored for the cracking process.

3.6. Characterization of condensate from parameter with the highest cracking percentage

Three main peaks of GC–MS indicated three major constituents of 9,17-octadecadienal, (Z)- $C_{18}H_{32}O$, octane (C_8H_{18}), and undecylenic acid ($C_{11}H_{20}O_2$). The first, second and third highest peaks have the percentage area of 47.58, 24.16 and 20.85, respectively. ATR/FTIR shows the presence of functional groups such as $C=O$ stretch at 1708.2 cm^{-1} , $=C-H$ bend at 966.59 cm^{-1} and further discussion is performed in the proposed catalytic cracking reaction.

3.7. Proposed reaction of cracking

First highest peak indicates that 47.58% from 100% castor oil had been converted to unsaturated aldehyde by dehydration process of water removal to give 9,17-octadecadienal, (Z)- ($C_{18}H_{32}O$). This finding was suggested by the presence of $C=O$ stretch at 1708.2 cm^{-1} and $=C-H$ bend at 966.59 cm^{-1} in ATR/FTIR analysis. Two hydroxyl functional groups had been removed with hydrogen atoms at carbon terminal to produce terminal alkene of 9,17-octadecadienal, (Z). The second highest peak area of 24.16% indicates that 24.16% from 100% castor oil had been cracked down to a mixture of octane (C_8H_{18}) which was supported by $C-H$ bend at 1459.17 cm^{-1} . The third highest peak area of 20.85% indicates that 20.85% from 100% castor oil had been cracked down to undecylenic acid [27] ($C_{11}H_{20}O_2$), which is supported by the presence of $=C-H$ bend, $C=O$ stretch and $C-O$ stretch at 966.59 cm^{-1} , 1708.2 cm^{-1} and 1241.02 cm^{-1} , respectively. The schematic diagram of the proposed reaction is shown in Fig. 6.

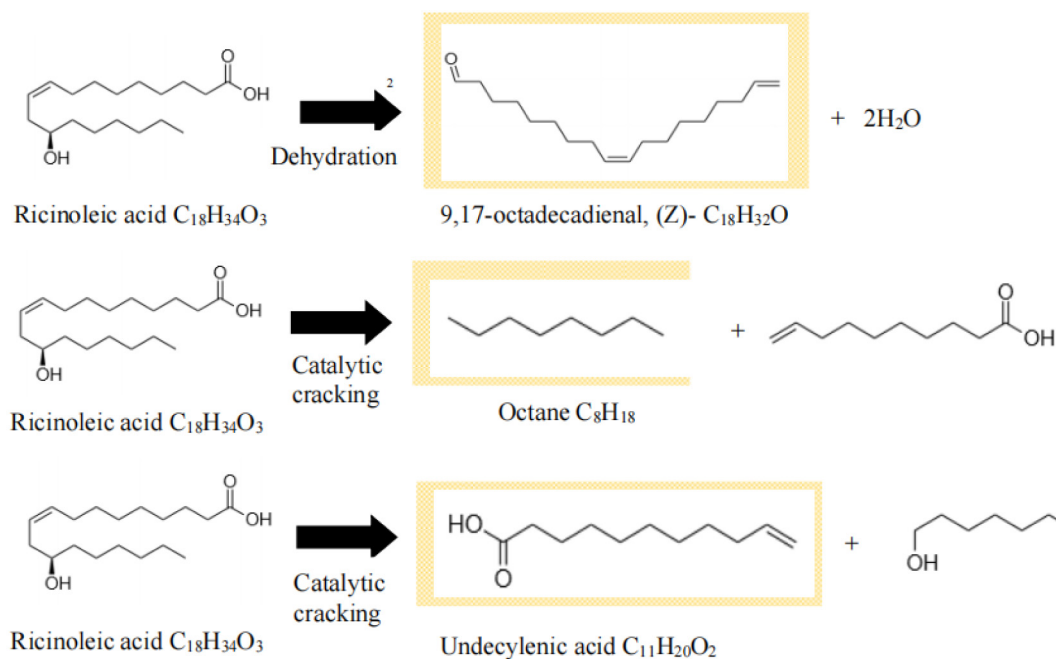


Fig. 6. Schematic diagram of the proposed catalytic cracking process.

4. Conclusions

Microwave assisted method with the modified metal catalyst, Zn/ZSM-5 provided sufficient energy for the cracking process to occur even at low temperature. The cracking process was observed at low temperature which was supported by the data analysis using GC–MS and ATR/FTIR. The schematic diagram of the propose catalytic

cracking process was proposed to produce octane and undecylenic. Fuel and pharmaceutical products of octane and undecylenic acid were obtained through catalytic cracking process via microwave assisted method.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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