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Biogasoline synthesis via fluid catalytic cracking of waste cooking oil using treated eggshell

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Abstract. This paper reports on preparation and characterization of eggshell for fluid catalytic cracking (FCC) reaction of waste cooking oil (WCO) to produce biogasoline. Hydrocarbon from condensate of gas emitted from a spherical flask reactor was agitated at 350, 400 and 450 rpm under 350, 400 and 450 °C reaction temperature by the one-factor-at-a-time (OFAT) approach was analyzed by using a gas chromatography mass spectrometer (GC-MS). Acid compounds were also recorded. Earlier, the eggshell was ground, calcined at 900 °C for three hours and sieved into 250 – 425 µm range of particle size before being analyzed using Fourier-transform-infrared-spectroscopy (FTIR) for calcium oxide content. About 30 wt% of biogasoline ranged from C₄ to C₁₂ of alkanes and alkenes was obtained from the 350-°C hydrocarbon condensate after 30, 45 and 60 min of which aromatic compounds increased with the reaction temperature. However, the biogasoline compounds decreased with the reaction temperature. More than 20 wt% were esters and free fatty acids of carbon number greater than 20 were also formed, respectively. Stirring speeds generally increased condensate yield but the increment does not have pattern due to various volatility of the content. The highest biogasoline yield through the FCC reaction was 4.5 wt% at 350 °C at 400 rpm stirring speed, and the product was found comparable with previous research and commercial gasoline.

1. Introduction

Biogasoline usually refers to bioethanol in mixture with petrol-gasoline employed in existing combustion engine [1] to solve the problem diminishing and hazardous-emission fuel of petroleum [1]. It can also be petro-gasoline equivalent producible from triglycerides via cracking [2], hydrolysis-deoxygenation [3], hydrothermal and pyrolysis [4] reactions. Our study used this biogasoline terminology here.

The glyceride-derived gasoline, which is also called renewable or green gasoline, bio-hydrocarbon and drop-in biofuel, has the advantage of single use in the same engine, as its fuel property is identical to petrol-gasoline according to the API and ASTM analysis methods. However, the conversion of triglycerides involves issues of uncertainty due to more than 300 fatty acid at various combinations in triglyceride molecules and other contents besides feedstock availability and quality. Process viability and product selectivity are relatively complicated and seeking out active and high selective catalysts is therefore essential to produce fuel.



Consuming fresh vegetable oils will threaten food security and lead to costly production. WCOs and inedible oils are therefore favorable since catalysts in gasoline syntheses were usually not affected by free fatty acids like biodiesel production process. Although formation of soap may occur between metal oxides and free fatty acids, the reaction will be followed by other reactions that form esters or hydrocarbon and leave the metal catalyst in different activity due to coking. Additional decoking and calcination were unfortunately required to regenerate the catalyst [3] as is currently practiced in many fluid catalytic cracking industries [5]. This indicated that the catalysts could not be reused directly although they are heterogeneous and costly catalyst handling will definitely become a liability to an FCC process.

Catalysts of combination of metals and metal oxides such as nickel, silicon, aluminium and calcium oxides were tested in many biogasoline studies and the reaction were carried out either in gas or liquid phase. For some instances, nanoparticle zeolite-based catalyst prepared by Taufiqurrahmi et al. [6] for fluid cracking reaction of palm oil obtained 16 wt% gasoline. Sousa et al. [3] mixed hydrogen with palm oil and palm kernel oil to undergo simultaneous deoxygenation, cracking and isomerization reactions by using HBeta zeolite catalyst at 10 bars and produced short chain hydrocarbon. The yield of hydrocarbon was higher than 90 wt% but their catalysts still suffered from coking and required activation. Sani et al [7] used NiO/SiO₂ in pyrolysis reactions (inert condition) to crack WCO and they only obtained 7.78 wt% and 12.47 wt% of gasoline at 350 and 400 °C for 3 hrs. The hydrocarbon condensate contained kerosene and diesel as well. In the work by Wang et al [4], 29.87 wt% yield of gasoline was obtained by using HZSM-5 in a fixed bed micro-reactor at 450°C gaseous palm oil in nitrogen flow. An issue with acid value deterioration of fuel was raised by Chang et al. [8] where sodium and potassium that promoted bentonite were prepared and tested in the pyrolysis reaction of WCO. CaO was found to have reduced acidity of biogasoline.

Catalyst from solid waste has benefit of low cost disposition. None of the studies, however, tested eggshell although the catalytic activity of its CaO content after calcination was reported in many studies on other biofuel productions [9]. This scenario might be attributed to the emphasis given more to industrial scale of production. Therefore, this study tested calcined eggshell onto FCC reaction of WCO to observe the potential of its catalysis.

2. Materials and Methods

Both WCO and eggshell waste were obtained from household kitchens and local restaurants. HPLC-grade pentane and CaCO₃ was purchased from Sigma Aldrich for analysis sample preparation and characterization reference, respectively. Eggshell catalyst was prepared through 4 steps: firstly grinded using mortar; secondly overnight-dried at 110 °C; thirdly calcined at 900 °C for 3 hours and finally sieved into 250 – 425 µm range of particle size. The calcined eggshell and calcined CaCO₃ were analysed by using FTIR. WCO was filtered to remove solid and semi-solid particles. Then, 100 g filtered oil and 4 g calcined eggshell were mixed in a spherical flask. The flask was heated by using a heating mantle and was connected to dean stark apparatus as FCC rig set-up. The flask's mixture content was vigorously agitated to ensure that the mixture was homogeneous and free mass transfer limitation. These steps were repeated for other 8 runs.

Fluid cracking reaction tests were carried out at 350 °C for 350, 400 and 450 rpm stirring speed at atmospheric pressure for 30, 45 and 60 min of reaction time. Similarly, the tests were repeated for 350, 400 and 450 °C of reaction temperatures at constantly 400 rpm stirring speed. Replication was carried out for each set accordingly. The vapour released from the reaction inside FCC rig was condensed by using cooling water at 5 °C.

After the reaction being stopped, the condensate samples were collected inside 5-ml bottles. Then, the clear yellow liquid at top layer of condensate was withdrawn by using a micropipette into 2-ml sampling vials, and mixed together with pentane solvent for analysis using GC-MS equipped with ZB-FFAP column. The analysis was started at 30 °C and the oven temperature was then raised at 20 °C/min to 150 for 30 seconds completing 9 min of run while the injection port and detector were set 280 and 180 °C respectively.

Besides GC-MS analysis run, the condensate samples were also tested by Brookfield DV-III Ultra Rheometer using a spindle size 18 with a stirring speed of 20 rpm for checking their viscosities. Their boiling points and densities were also determined by using Buchi Melting Point M-565 and micrometric AccuPyc II 1340 Pycnometer, respectively.

3. Results and discussion

Calcined eggshell had identical functional groups to the calcined CaCO_3 in the FTIR result. As shown in Figure 1, 3 bands were registered by the spectroscopy. 3642 cm^{-1} corresponded to $-\text{OH}$ group, probably from traces of $\text{Ca}(\text{OH})_2$ content in both samples. C-O bond transmitted infrared beam at 1432 cm^{-1} wavelength reflected from traces of unconverted carbonyl of carbonate. The big band of 401.6 cm^{-1} corresponds to CaO for both samples the main active metal oxide for the FCC reaction [9]

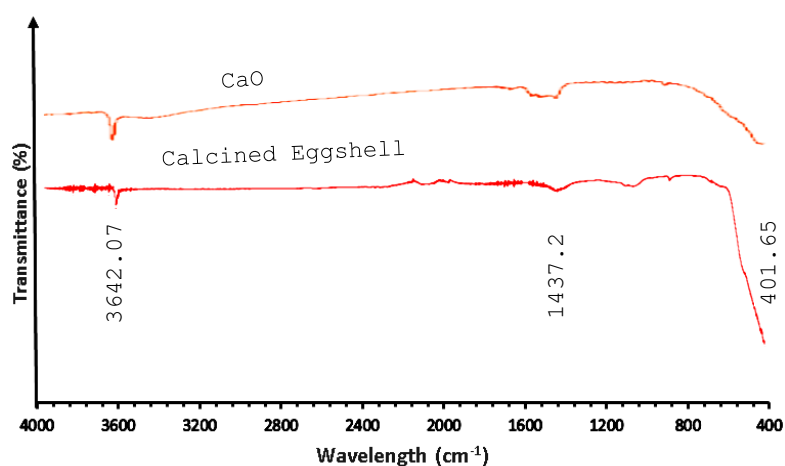


Figure 1. Spectrogram of FTIR

2 layers of liquid condensate were resulted in the collector. The top layer color was golden yellow probably condensate of evaporated oil. The bottom layer was the sample of interest and was analyzed. At $400\text{ }^\circ\text{C}$, 3rd layer of aqueous solution appeared at the bottom indicating that oxidation or dehydrogenation might have occurred at high temperature producing water dissolving polar compound. The yield of gasoline was computed as Equation (1).

$$Yield = \frac{\text{Gasoline mass (g)}}{\text{WCO mass (g)}} \times 100\% \quad (1)$$

Alkane and alkene with carbon numbers ranged from 5 to 12 were considered as biogasoline for all reaction temperatures and stirring speeds in this study [10]. As shown in Figure 2, using the same stirring speed of 400 rpm, the highest yield was obtained at $350\text{ }^\circ\text{C}$ i.e. 4.5% (or 31 wt% of total condensate). Interestingly, this is higher than what Twaiq et al. [11] obtained using MCM-41 commercial catalyst. Other reaction temperature had lower yield because products other than biogasoline i.e. kerosene and diesel were yielded more.

More than 20 wt% composition of esters of carbon number greater than 20 was measured as well indicating that esterification of free fatty acid with alcohol simultaneously formed during the reaction. The alcohol might have been synthesized from decomposition of glycerol [3]. Aromatic components such as ethyl benzene, xylene, propyl benzene, butyl benzene, benzofuranone, benzyl phenethylamine, pentyl benzene and hexyl benzene were also increased by 3% as the reaction temperature increased, similar to the result obtained by Bielansky et al. [12] using conventional FCC zeolite catalyst on palmitic and oleic acid. Free fatty acids were also present at the compositions greater than 20 wt%, which is similarly from carbon numbers of greater than 12. Ester fuel property is comparable to diesel while alcohols and aromatic compounds from C_5 to C_{12} can be considered as identical components of standard

gasoline [13] and are grouped as biogasoline components. Low biogasoline yield at temperature higher than 350 °C was likely due to more production of other components mentioned thereof as also reported by Tamunaidu and Bhatia [14] in crude palm oil cracking using Zeolite REY catalyst. This implies an optimum reaction temperature need to be determined so that more desired products will be formed.

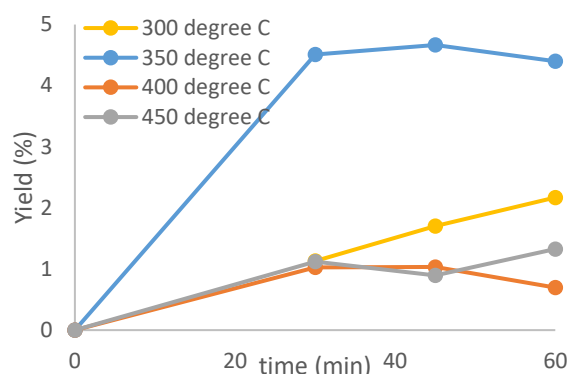


Figure 2. Effect of cracking temperatures on biogasoline yields at 400 rpm.

Stirring speed was varied for the same mass WCO-eggshell ratio using the same rig set-up at 400 °C. Figure 3 exhibits the increment of the yield for 3 stirring speeds against reaction time. The yield for 350-rpm speed raised almost similar to 450-rpm one but they were differentiated with the datum at 45 min. 350 rpm shows gradual increment while 450-rpm trend is approaching steady state at 2 wt%. The yield of 400 rpm has different increment where it was 3.5 wt% after 60 minute of the run which is different than the result of the same stirring speed and reaction temperature in Figure 2. This random yield pattern was probably due to various volatility of compounds as indicated by various boiling points of the hydrocarbon condensate samples.

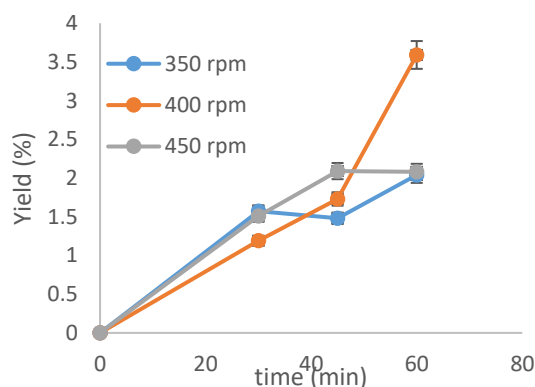


Figure 3. Effect of mixing speeds on biogasoline yields from FCC of waste oil at 400 °C.

Figure 4 shows distribution of carbon numbers for alkane and alkene in mass fraction on the hydrocarbon condensate basis. The highest fractions, C₉, C₁₀ and C₁₁, were obtained more than 7 wt% each, contributing 24 wt% in total, which is considered good and comparable with Wang et al. [4] result. No hydrocarbons below 8 were however detected in the condensate. The mass fractional conversions of WCO were 5, 5.5 and 6.2 % for 350, 400 and 450 °C, respectively. Residue of unconverted WCO after 60 min hardened and completely covered the eggshell catalysts at room temperature and recovering the catalyst was not possible. Thus, no longevity study was carried out.

Physical property of the hydrocarbon condensate was also determined. Average density and viscosity were 0.789 g/cm³ and 24.75 centipoise, respectively. Boiling point of the hydrocarbon condensate was

ranged from 81 °C to 169 °C without clear pattern, which justifies fluctuation in the yield of biogasoline due to different components. Complex methyl ester and ethyl ester compounds were also registered by GC-MS from 2 wt% to 6 wt% such as cyanoacetyl carbamic, methyl pentadecanoic and ethyl cyclohexyl esters. CaO of the calcined eggshell might have catalyzed esterification reaction. About 7-8 wt% of unconverted free fatty acid was still present in the hydrocarbon condensate.

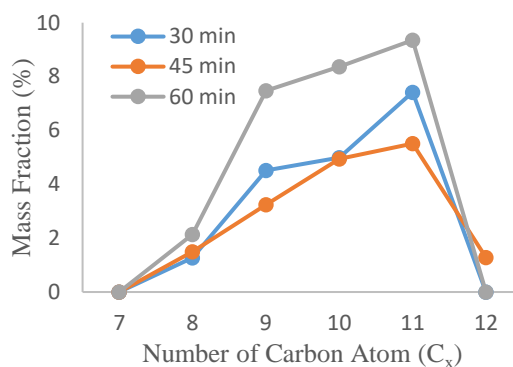


Figure 4. Alkane and alkene distribution based on carbon number at 3 reaction times for all settings of cracking temperatures and mixing speeds.

4. Conclusion

Synthesis of biogasoline from WCO by using calcined eggshell at 350 – 450 °C via the fluid catalytic cracking reaction was evidenced by chromatographic analysis using mass spectrometer detector. Identification of alkanes and alkenes inside the bottom layer of condensate revealed the biogasoline yields that were comparable with data reported in the literature. The highest yield through the FCC reaction was 4.5 wt% at 350 °C at 400 rpm stirring speed.

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