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Production of Bio-hydrocarbon from Refined-Bleach-Deodorized Palm Oil using Micro Activity Test Reactor

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Abstract

Catalytic cracking of vegetable oil for the production of bio-hydrocarbons had been developed. In this study, the catalytic cracking of Refined-Bleach-Deodorized Palm Oil (RBDPO) had carried out over Fluid Catalytic Cracking Unit (FCCU) equilibrium catalyst in a micro activity test reactor at 510° C under various catalyst to oil (CTO) ratio of 1.20 - 2.01 g/g. The catalytic cracking of RBDPO had produced the organic liquid product (OLP) containing bio-hydrocarbon, water, gas, and coke on the catalyst converted to CO_2 during the catalyst regeneration process. The increase in CTO ratio from 1.20 to 2.01, OLP yield decreased from 80.48% to 70.12%. The OLP was separated into gasoline, light cycle oil (LCO), and heavy cycle oil (HCO) based on boiling point difference by a simulated distillation gas chromatography (SimDis GC). High gasoline fraction as 31.56% was produced at CTO of 2.01 g/g. The gasoline fraction influenced the research octane number (RON) of the fuel.

Keyword: bio-hydrocarbon; catalytic cracking; micro activity test reactor; RBDPO

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INTRODUCTION

Various process technologies have been developed to improve the quality of biofuels so that they can be mixed with fossil oils in a larger composition, including technology, to convert vegetable oils into bio-hydrocarbons. Ng *et al.* (2019) used heavy gas oil (HGO) mixed with 15 v% canola oil and processed in fluid catalytic cracking (FCC) over equilibrium catalyst to lower heat requirement

because the canola oil contains oxygen that caused an exothermic reaction in the formation of water. The addition of 10% non-refined sunflower oil and cottonseed oil to FCC of vacuum gas oil (VGO) reaction by using halloysite nanotubes (HNT) catalyst can significantly increase gasoline yield. It triggers isomerization reactions in-branch hydrocarbons formation compared to commercial high alumina zeolite FCC catalyst (Abbasov *et al.*, 2016).

Studies on catalytic cracking of vegetable oil into green gasoline are widely studied and generally focus on developing catalysts that can increase gasoline yields and suppress coke formation (Ong and Bhatia, 2010). The first catalytic cracking of vegetable oils was carried out in 1979 using a ZSM-5 catalyst, producing paraffinic, olefin, and aromatic hydrocarbons (Luque, Campelo, and Clark, 2011). Furthermore, much research was carried out to develop cracking of vegetable oils with various acid catalysts. Luque et al. (2011) published the general route of the triglyceride catalytic cracking reaction, which is also accompanied by thermal cracking. Triglyceride molecules decomposed into heavy oxygenated hydrocarbons such as fatty acids, esters, aldehydes, ketones, alcohols, and ether. Then, the reaction is followed by the formation of heavy hydrocarbons by breaking the C-O and C-C bonds through competing routes, namely de-carboxylation and de-carbonylation. Cyclization of the heavy oxygenated hydrocarbons produced aromatics with coke as a by-product. The elimination of functional groups of the heavy oxygenated hydrocarbons (i.e., carbonyl, carboxyl, and hydrate) produced heavy hydrocarbons. Then, it produced olefins and paraffin after radical scission, cyclic isomerization, and Helimination reactions. Feed oil saturation level affects the route of reactions (Luque et al., 2011).

Various types of vegetable oils and catalysts used to produce biogasoline. Catalytic cracking of *Swida wilsoniana* oil by adding 10% Cu to ZSM-5 catalyst can increase yield hydrocarbon biofuel production from 38% to 68% (Li *et al.*, 2018). Catalytic cracking of Castor and Jatropha oils over nano γ -alumina also produce hydrocarbons biofuel with 94.5% of reaction efficiency (Negm, Rabie and Mohammed, 2018). These product hydrocarbon biofuels were analyzed by gas chromatography (GC) (Li *et al.*, 2018; Negm, Rabie, and Mohammed, 2018) but not yet separated into gasoline, kerosene, and diesel oil.

Some research on catalytic cracking of vegetable oils into bio-hydrocarbons has stated the percentage of fuel fractions such as gasoline produced. Catalytic cracking of CPO in the transport riser reactor operated at 450°C and atmospheric pressure. The Rare earth-Y (REY) catalyst is used with a catalyst/palm oil ratio of 5 g/g and residence time of 20 s, which could convert 75.8 wt.% of CPO into the products. The yield of organic liquid products (OLP) was 53.3 wt.%, which contained 33.5 wt.% gasoline fraction, and the yield of gas was 14.2 wt.%. Determination of the gasoline fraction based on boiling point analysis of commercial gasoline injected gas into chromatography with a flame ionization detector (GC-FID) (Tamunaidu and Bhatia, 2007). A higher yield of gasoline fraction as 44.4 wt.% was produced from the catalytic reaction of palm oil-based fatty acid mixture residue at 440°C over HZSM-5 catalyst in a fixed-bed microreactor at atmospheric pressure with a weight hourly space velocity (WHSV) of 3.66 h⁻¹ and fatty acid mixture to catalyst ratio of 9.64 g/g. The reaction temperature and WHSV were the most important process variables in the production of gasoline fraction from vegetable oil. Gasoline fraction was determined based on the boiling point of the detected components by gas chromatography-mass spectrometry (GCMS) in the range temperature of 60-120°C (Ooi, Zakaria, Mohamed. and Bhatia. 2004). Yigezu and Muthukumar studied several types of catalysts to convert sunflower oil into biofuel include gasoline production. Reaction over the V₂O₅ catalyst at 320°C for 40 min, sunflower oil was converted into 33.62% of gasoline. The gasoline fraction is obtained through fractional distillation OLP at a temperature of 80-140°C (Yigezu and Muthukumar, 2014). Besides temperature and WHSV, the effect of catalyst to oil (CTO) ratio is likely also to affect OLP and the gasoline fraction in the product. One study that investigates the effect of the CTO ratio on catalytic cracking of rapeseed oil in a range of 2-12 using MAT reactor over the FCC equilibrium catalyst at 525°C found that gasoline fraction range from 30-34% by increasing CTO ratio (Lovás, Hudec and Hadvinová, 2015). Therefore, studying a lower CTO ratio needs to be done to find the sufficient amount of catalyst used for catalytic cracking to produce the same gasoline fraction.

In this study, the effect of CTO ratio (1 - 2 g/g)was studied using a micro activity test (MAT) reactor, and OLP was analyzed by simulated distillation gas chromatography (SimDis GC) and gas chromatography for detailed hydrocarbon analysis (GC-DHA). Both of these analysis results are still rarely discussed in various publications to describe the quality of OLP produced from catalytic cracking of vegetable oils. MAT reactor was a standard reactor that made based on ASTM D-3907-92 for analysis of fluid catalytic cracking (FCC) using petroleum oil or renewable sources as feedstocks. The MAT reactor was a fully automatic, controlled, and computerized laboratory reactor (PID-ENG&TECH, 2020). A (SimDis GC) can quickly and accurately determine the true boiling point distribution and shorten timeconsuming for physical distillation (Separation-System-Inc., 2020). A GC-DHA determines the bulk hydrocarbon group-type into paraffins, olefins, naphthenes, and aromatics (PONA) of gasoline fraction and other spark-ignition engine fuel such as research octane number (RON) and motor octane number (MON) (Shimadzu, 2018).

MATERIALS AND METHODS Materials

The raw material of vegetable oil was a commercial grade of Refined Bleached Deodorized Palm Oil (RBDPO). FCCU equilibrium catalyst was purchased from Badische Anilin und Soda Fabrik (BASF) The Chemical Company. n-Hexane (99.0%) and ethanol (96%) were purchased from Merck.

Methods

Before catalytic cracking, RBDPO was analyzed by thermogravimetric analysis (TGA) to understand its thermal characteristics. TGA is a technique to monitor changes in the mass of a material to changes in temperature and time (Groenewoud, 2001). Approximately 18 mg of RBDPO was put into TGA (STA PT 1600, Linseis), and then the sample was heated in the nitrogen stream from 30 °C to 1000 °C at a rate of 10 °C/min to obtain the weight loss profile.

Production of bio-hydrocarbon from RBDPO was carried out using a micro activity test (MAT) reactor (PID Engineering & Technology, Spain), according to ASTM D-3907-92 that operated by Lab viewTM software. RBDPO was inserted into the feeding bottle and heated up to 60 °C. A feeding pump was calibrated and determined the mass flowrate of RBDPO. The RBDPO was pumped from the feeding bottle with a flow rate of 2.731 g/min at 60°C into a fixed bed reactor. The reaction was carried out at 510 °C for 88 - 147 seconds with the catalyst to oil ratio of 1.20 - 2.01 g/g over the FCCU equilibrium catalyst. Weight hourly space velocity (WHSV) of the process was 20.3 h⁻¹. The residence time of reaction was 2.95 min. Before and during the reaction, nitrogen gas flowed with a rate of 100 mL/min as a carrier gas. The product of the reaction was captured in a condenser at -10°C that cooled using ethylene glycol and recovered as organic liquid product (OLP) and water. Uncondensable product was collected in a gas chamber to be mixed and then recovered by a gas pack. The gas pack was removed from the reactor before the regeneration process of the catalyst.

Moreover, the process was continued by the regeneration process of the used catalyst using the same apparatus. The regeneration proses were conducted at 550° C for around 120 min by flowing compressed air with a flow rate of 100 ml/min into the reactor. During the regeneration process, coke on the catalyst was oxidized in the cracking reactor into CO and CO₂. Then CO was converted into CO₂ using a shift CO-CO₂ (regeneration) reactor containing CuO catalyst at 600 °C, as shown in Figure 1. Total CO₂ was detected by a CO₂ detector Servomex (Servopro 4000 series analyzer) to give information to the system how much the formation of coke during the reaction.

Organic liquid products (OLP) were analyzed by a SimDis GC and a GC-DHA that operated based on ASTM D7169. Based on SimDis GC, the OLP was separated into gasoline (bp. IBP - 216°C), light cycle oil (bp. 216.1 - 343 °C), and heavy cycle oil (bp. 343.1 - FBP °C). IBP and FBP stand for the initial boiling point and final boiling point, respectively.

On the other hand, the gas product was analyzed by GC with packed columns of porapak-Q and molecular sieve (MS) for determining the composition and mass of the gas. Porapak-Q and MS columns were operated at 80 °C, an injection temperature of 110°C with a TCD detector.



Figure 1. Micro activity testing (MAT) reactor

Standard gas with the composition, as shown in Table 1, was injected for 0.1 - 1.0 mL into both columns to identify the area of each component for calibration curves. Air was also injected into the MS column for correction of oxygen and nitrogen that appeared in chromatograms of either standard gas and sample. A 1.0 mL of sample gas product was injected into both columns for determining the composition and mass based on the calibration curves of each component.

After the experiment, the condenser line of the MAT reactor was washed using n-hexane-ethanol (1:1 by volume).

RESULTS AND DISCUSSION Thermogravimetric analysis of **RBDPO**

The thermal characteristics of samples were measured using TGA/DTG (thermogravimetric analysis/the derivative thermogravimetric). The TGA and DTG curves of RBDPO are shown in Figure 2. At 37°C, the RBDPO raw material started to degrade due to the evaporation of water and light compounds containing. Then, in a temperature range of 150-300°C, a slow decomposition process occurs, which causes the mass of the RBDPO sample to decrease.

Table 1.	Composition	of mixed	gas	standard	for
	an	alvsis			

Name of gas	Composition		
Name of gas	(vol. %)		
CO	15		
CO_2	20		
CH_4	4.5		
C_2H_2	2		
C_2H_4	3		
C_2H_6	2		
C_3H_6	2		
C_3H_8	2		
H_2	14		
N_2	35.5 (Balance)		



Figure 2. Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of RBDPO

When it reaches a temperature of 300-500°C, the RBDPO mass decreases dramatically because the decomposition process takes place maximally. After 500°C, the mass change tends to be constant because almost all RBDPO has evaporated. Based on these results, the catalytic cracking of the RBDPO in the vapor phase can be carried out starting at 500°C because at that temperature almost all of the RBDPO component is in the vapor phase.

Catalytic cracking in micro activity test (MAT) reactor

Catalytic cracking was carried out using a reactor MAT at a temperature of 510° C under various CTO ratio of 1.20 to 2.01. The reaction at 510° C occurred in the vapor phase because according to Figure 2, almost all of RBDPO component was in the vapor phase. The process was resulting in products that are grouped into the organic liquid product (OLP), water, gas, and coke on the catalyst that was converted to CO₂ during the catalyst regeneration process. The yield of the products can be seen in Table 2.

Based on Table 2, it can be seen that the increase in catalyst to oil (CTO) ratio from 1.20 to 2.01 g/g, OLP yield decreased from 80.48% to 70.12%, and gas yield increased from 5.35% to 14.08% and then relatively constant at CTO of 2.01 g/g. These results suggested that an increase in the value of the CTO ratio means that the more catalyst in the reactor, the catalytic activity to crack RBDPO into a lighter fraction will be higher so that gas production increases. However, yields of coke on the catalyst and water have no trend on various CTO ratio that has a range of 2.68 – 7.13% for water and 2.32 – 11.48% for coke. Compared to catalytic cracking of Swida wilsoniana oil using a 10% Cu-modified ZSM-5 catalyst, it produced about 0.16% water and 6% coke (Li et al., 2018). On the other hand, catalytic cracking of rapeseed oil produced higher water fraction as 9.6% and 6,3% of coke (Lovás, Hudec and Hadvinová, 2015).

Gas product of the catalytic cracking of RBDPO was analyzed by gas chromatography equipped by two types of packed columns of porapak-Q and molecular sieve (MS).

Table 2.	Yield of product	distribution	after catalytic
oracki	ng at 5100C with	2 713 a/min	

cracking at 510°C with 2.715 g/min of RBDPO						
CTO*	1.20	1.33	1.50	1.72	2.01	
OLP (wt.%)	80.48	79.78	79.45	71.88	70.12	
Coke (wt.%)	11.48	2.35	2.32	10.43	9.30	
Water (wt.%)	2.68	7.13	5.65	3.62	6.55	
Gas (wt.%)	5.35	10.73	12.59	14.08	14.03	
NOTO CIL		· (1)				

*) CTO = Catalyst-to-oil ratio (g/g)

The composition of detected gas based on the gas standard is shown in Figure 3.



Figure 3. Composition of the gas product after catalytic cracking of RBDPO

Based on Figure 3, detected gas was hydrogen, methane, acetylene (C_2H_2) , ethylene (C_2H_4) , ethane, carbon monoxide, and carbon dioxide. Under the CTO ratio of 1.20 g/g, mainly hydrogen, methane, and CO2 were produced. However, an increase in CTO ratio from 1.33 to 2.01 g/g, more types of gas were produced because of a higher amount of catalyst for cracking of RBDPO. These results indicate that at the CTO ratio of 1.02 g/g, the catalytic cracking has not yet proceeded completely. The incomplete cracking of triglyceride molecules accumulates on the surface of the catalyst to form a reasonably high coke (Li et al., 2018), as shown in Table 2. According to these results, a CTO ratio of 1.02 is considered less effective for catalytic cracking of RBDPO.

The organic liquid product (OLP) of catalytic cracking of RBDPO was analyzed by SimDis GC and separated into three fractions of gasoline, light cycle

Table 3. IBP, FBP, and amount of gasoline, LCO, and HCO fractions on various CTO ratio

СТО	IBP	FBP	Gasoline	LCO	HCO
ratio	[°C]	[°C]	[%]	[%]	[%]
[g/g]					
1.20	39.8	823.2	28.34	37.18	33.90
1.33	34.1	724.4	19.23	27.21	52.96
1.50	38.8	842.8	15.42	25.69	58.31
1.72	65.0	732.7	23.94	39.25	36.23
2.01	64.3	733.6	31.56	40.51	27.39

oil (LCO), and heavy cycle oil (HCO). IBP (initial boiling point), FBP (final boiling point), and amount of fractions of gasoline, LCO, and HCO are shown in Table 3.

Based on Table 3, the IBP value of CTO ratio from 1.20 - 1.50 g/g is lower than 1.72 - 2.01 g/g, which shows that a low CTO ratio can produce lighter compounds with lower boiling points. However, the IBP value does not determine the composition of the gasoline, LCO, and HCO fractions in OLP. Chemical compounds that have the same boiling point with the gasoline and LCO fractions produced higher at a CTO ratio of 2.01 g/g. Meanwhile, chemical compounds with a high boiling point (HCO) were produced more at a CTO ratio of 1.50 g/g. Compared to catalytic cracking of rapeseed oil at the CTO ratio of 2, the gasoline fraction produced from RBDPO is slightly higher at 31.6%, while rapeseed oil is 30.5% (Lovás, Hudec and Hadvinová, 2015).

Then, the organic liquid product (OLP) was also analyzed by GC-DHA for determination research octane number (RON) and the group of chemicals containing in the gasoline range boiling point, as shown in Table 3. Based on Table 3, the highest RON value produced from OLP at CTO of 1.20 g / g and the lowest was at CTO of 1.50 g/g. Calculated RON value is strongly influenced by the chemical compounds contained in the gasoline fraction. Based on the results of the analysis with GC-DHA, it is known that the sequence of chemicals that influences the high calculated RON value is oxygenated> aromatics > naphthenes > olefins > i-paraffins. Meanwhile, the presence of paraffin can reduce RON. Calculated RON on CTO of 1.20 and 1.33 g/g were higher than others because of the high content of oxygenates, naphthene, and i-paraffins. aromatics, The unidentified chemical in Table 4 did not contribute to the calculated RON value.

Table 4. Calculated RON values and group of chemicals in gasoline range boiling point

Domonwoton	Catalyst to oil (CTO) ratio (g/g)					
Parameter	1.20	1.33	1.50	1.72	2.01	
Calculated RON	140.93	131.99	59.85	80.52	77.29	
Paraffin	6.51	6.05	17.09	18.08	13.43	
i-Paraffins	12.10	16.73	11.47	8.51	4.05	
Aromatics:	50.59	48.29	18.87	20.83	38.09	
Mono-Aromatics	46.72	44.58	12.35	13.23	28.20	
Naphthalenes	0	0	3.51	4.64	7.95	
Indane	3.48	3.35	2.96	2.82	1.83	
Indenes	0.39	0.36	0.05	0.15	0.12	
Naphthenes:	3.76	3.64	1.87	2.37	1.20	
Mono-Naphthenes	3.74	3.60	1.87	2.37	1.20	
Di/Bicyclo-Naphthenes	0.02	0.04	0	0	0	
Olefins:	23.47	22.02	14.01	17.91	22.79	
n-Olefins	3.99	4.31	0.33	0.16	0.06	
Iso-olefins	9.62	9.03	2.22	1.27	1.26	
Naphtheno-Olefins	2.13	1.83	0.88	0.90	0.37	
Di-Olefins	7.73	6.85	10.58	15.58	21.09	
Oxygenates	1.79	1.56	0.17	0.11	0.02	
Unidentified	1.78	1.70	36.52	32.18	20.43	

CONCLUSIONS

Catalytic cracking of RBDPO was studied using a MAT reactor at 510 $^{\circ}$ C to find out an effective

CTO ratio to produce high OLP yields with high gasoline fraction. Based on the results, around 70 % of OLP was produced with a gasoline fraction of 31.6% at a CTO ratio of 2.01 g/g. The gasoline fraction has a RON of 77.3, with the main content being aromatic (38.1%), olefins (22.8%), and paraffin (13.4%). It also contains a small amount of i-paraffin, naphthene, and oxygenate. Based on the results of this study, the effectiveness of the use of catalyst and feed on catalytic cracking of RBDPO using the MAT reactor, and FCCU equilibrium catalyst is recommended to perform at a CTO ratio of 2.01 g/g.

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