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Green-Fuel Production Through Co-Processing Biomass Derived Oil with Standard Gasoil Feedstock

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ABSTRACT. To enhance refinery revenue through the use of new and renewable materials, lab-scale research on green-fuel production has been conducted. This involved co-processing biomass-derived oil with standard gasoil feedstock and existing E-cat to assess its feasibility for commercial fluidized catalytic cracking (FCC) units. The catalytic cracking process varied the type of biomass-derived oil (Crude Palm Oil (CPO) and Refined Bleached Deodorized Palm Oil (RBDPO)) against standard gasoil, using typical operating parameters: cracking temperature of 510 °C, C/O ratio of ~6, and regenerator temperature of 715 °C. The Advanced Cracking Evaluation (ACE) reactor modeled one cycle of reaction and regeneration. Product yields were calculated using mass balance of liquid and gas products, modeled with GC Simdist, GC RGA, and CO₂ Analyzer, while gasoline octane number was based on PONA composition using GC DHA. Results showed conversion rates of 85-86%, Research Octane Number (RON) of 91.2 - 93.55, and product yields for coke, dry gas, propylene, LPG, gasoline, LCO, and bottom fraction in the ranges of 6.9 - 7.1%, 1.26 - 3%, 6.79 - 8.5%, 19.52 - 23.1%, 44.8 - 51.63%, 10.21 -11.4%, and 3 - 3.68%, respectively. Both CPO and RBDPO can be used as co-processing feedstock in FCC units, but adjustments in operating conditions, catalyst formulation, or optimization of the wet gas compressor may be needed due to higher light fraction (Propylene and LPG) and lower gasoline production.

INTRODUCTION

Keywords:

green fuel;

co-processing;

fluidized catalytic

cracking (FCC).

Indonesia's energy demand is projected to grow by 2.1% per year until 2040, and while the proportion of new and renewable energy (NRE) is increasing, its energy mix still depends on fossil fuels. Indonesia has abundant Palm plantations with Crude Palm Oil (CPO) production as a food feedstock material reaching 42 – 46 million MT annually, equivalent to 800-900 MBSD (Pertamina's BOD, 2020). The molecular similarity of the triglyceride content in CPO to the hydrocarbons that constitute fuel makes CPO a potential feedstock for biofuel production (Rupilius and Ahmad, 2007). Three of several pathways in the production of biofuel from CPO are transesterification, hydrotreating (HDT)/hydrodeoxygenation (HDO), and fluidized catalytic cracking (FCC) (Hidayat, 2022).

The first process is transesterification using methanol and KOH/NaOH as a catalyst to produce Fatty Acid Methyl Ester (FAME) biodiesel. This biofuel product is often called first-generation or conventional biodiesel. It cannot be used directly and must be blended with petroleum diesel to become B5, B10, or maximum B20 because its high oxygenate content can cause engine corrosion. Meanwhile, the second and third processes can be implemented in refineries, which include the HDT/HDO process for saturating chains and removing oxygen, as well as the FCC process for cutting hydrocarbon chains in the triglyceride carbon chain. This type of biofuel product produced from the second and third processes is often called drop-in biofuels or green fuels (Dyk *et al.*, 2019). Regarding product selectivity, because most CPO/Refined Bleached, Deodorized Palm Oil (RBDPO) feedstocks have a diesel carbon chain range, the HDT/HDO process used will produce green diesel. In contrast, the FCC process mainly produces green gasoline (Adiatma and Prasojo, 2021).

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As the leading domestic energy supplier (70% of national energy demand), Pertamina has introduced several initiatives to move towards cleaner energy by developing green fuels using green processing technology in refineries. This initiative also aligns with government programs related to the emission reduction target, which is cleaner fuels in the transportation sector. Co-processing bio-derived oil helps reduce greenhouse gas emissions by incorporating renewable feedstocks into refining. It also supports the transition to more sustainable energy sources, as co-processing enables the integration of renewable and recyclable feedstocks with fossil fuels, contributing to decarbonization efforts.

As is well known, the presence of free fatty acids and other acidic compounds in bio-derived oils can cause corrosion in the FCC unit's equipment, leading to material damage to the reactor internals, piping, and other components, which increases maintenance costs and the risk of operational downtime. Contaminants, such as various metals and oxygen, can damage the catalyst and affect the stability and performance of the FCC process. Therefore, a preliminary lab-scale trial is necessary before implementation. This research trial of green-fuel production research has been carried out on a lab scale through co-processing biomass-derived oil with standard gasoil feedstock and an existing FCC equilibrium catalyst (E-Cat) to determine its effect on the feasibility projection of processing it at the commercial FCC unit.

RESEARCH METHODS

Materials

The blended co-processing feedstock of Medium Heavy Vacuum Gasoil (MHVGO), Crude Palm Oil (CPO), Refined Bleached Deodorized Palm Oil (RBDPO), and Bio-Oil were used with properties shown in Table 1. FCC equilibrium catalyst (E-Cat) was supplied with properties shown in Table 2.

Parameter	Unit	Methods	MHVGO	VC_8515	VB_8515	VRW_8515
SG at 60/60 °F		ASTM D-1298	0.8869			
Distillation						
IBP	°C	ASTM D-7500	290.0	222.2	216.0	245.2
10%-vol	°C		350.0	334.2	331.6	334.8
30%-vol	°C		400.0	385.0	382.0	384.8
50%-vol	°C		428.0	424.0	418.4	424.2
70%-vol	°C		449.0	459.0	451.8	459.6
90%-vol	°C		480.0	589.2	554.4	591.6
FBP	°C		518.0	628.0	614.6	613.8
Kin. Viscosity						
140 °F	Cst	ASTM D-445	10.33			
210 °F	Cst		4.127			
212 °F	Cst			1.185	11.62	4.626
Pour Point	°F	ASTM D-97	110	42	39	42
CCR	%-wt	ASTM D-189	2.63			
Sulfur Content	%-wt	ASTM D-4294	0.19	0.359	0.28	0.248
Metal Content						
V	ppm	UOP-391/ICP		< 0,01	< 0,01	<0,01
Fe	ppm	METHOD		3.070	2.825	0.310
Ni	ppm			0.200	0.190	0.200
Na	ppm			0.715	1.015	0.455
Si	ppm			11.900	12.895	10.995
TAN	mg KOH/g	ASTM 664		0.7774	1.1289	0.0318
MCRT	%wt	ASTM 4530		0.2338	0.2114	0.1815

Table 1. Properties of raw materials in this experiment.

Notes:

MHVGO: Standard Gasoil Feedstock

VC_8515: Feedstock MHVGO:CPO with blending ratio of 85:15.

VB 8515: Feedstock MHVGO:Bio Oil with blending ratio of 85:15.

VR_8515: Feedstock MHVGO:RBDPO with blending ratio ratio of 85:15.

Table 2. Properties of E-Cat in this experiment.

Properties	E-Cat	
Zeolite Surface Area (m^2/g)	49.62	
Matrix Surface Area (m ² /g)	123.83	
Total Surface Area (m ² /g)	173.45	
Z/M	0.40	
Average Pore Diameter (Å)	58.2	
Total Pore Volume (cc/g)	0.25	
PSD		
0–20 Micron	0	
0–40 Micron	0.695	
0–150 Micron	90.976	
APS	87.95	
UCS	24.3	

Methods

Green-fuel production through co-processing biomass-derived oil was carried out using Advanced Cracking Evaluation (ACE) pilot reactor units: Model R+ and R+ Multi-Mode, from Kayser Technology Inc, Houston, USA, as shown in Figure 1.



Figure 1. (a) Advanced cracking evaluation reactor (Kayser, 2000) and (b) simplified data analysis methods.

Before adding the E-Cat, the cracking reactor tube is placed in the furnace and heated to a set-point temperature of about 510 °C for cracking. About 9 g of E-Cat is prepared into the catalyst feed hoppers, and then the reactor is added to it by the ACE control software. The co-processing feedstock ratio of Medium Heavy Vacuum Gasoil (MHVGO) to Biomass-derived oil at 85:15 was prepared. The cracking feedstock is drawn from the oil feed vessel and supplied by a syringe pump. The pump is calibrated to supply the oil at a preset volumetric or mass rate by Catalyst to Oil ratio (C/O) ~6. The Gas product was analyzed using Gas Chromatography-Real Gas Analysis (GC-RGA) type Fusion by Inficon, while the liquid product of catalytic cracking was collected and analyzed using Gas Chromatography-Simulation Distillation (GC-Simdist/ASTM D7500) and Gas Chromatography-Detailed Hydrocarbon Analysis (GC-DHA/ASTM D7169) both using type Agilent 7890B Analytical Control by PAC.

During catalyst regeneration at 715 °C, reactor effluent gases pass through a catalytic converter, which oxidizes any CO and hydrocarbons to CO₂ and H₂O. The H₂O is adsorbed in a dryer, and the CO₂-containing gases are diverted through a mass flow meter and an Infrared CO₂ Analyzer, type Servopro 4900 Multigas Analyzer, by Servomex. These online measurements are used to calculate the amount of carbon deposited on the catalyst during the catalytic cracking step of the cycle. Leak checks are performed each time the product receivers are removed and replaced. The pilot laboratory operation of catalytic cracking was conducted by the following steps: (1) injection of oil over the catalyst (simulates a riser reactor), (2) catalyst stripping for a specified duration (simulates the catalyst stripper), (3) catalyst regeneration with air at elevated temperatures (simulates the regenerator), and (4) an optional reaction of the catalyst (simulates fuel gas lift and partial burn operation) (Kayser, 2000). The collection and analysis of the products from the cracking cycle make it possible to calculate the mass balance and yield of the products (Mansur *et al.*, 2020).

RESULTS AND DISCUSSION

CPO mainly consists of mono-, di-, triglycerides, free fatty acids, and minor impurities such as moisture and unsaponifiable matter (Japir *et al.*, 2017). RBDPO is a derivative product obtained from the purification of CPO through degumming, bleaching, and deodorization processes to improve the quality and stability of the resulting oil (Azis *et al.*, 2020). Compared with standard MHVGO feedstock, CPO and RBDPO have the potential to be used as co-processing feedstock, with the main advantages are associated with the low content of impurities such as total acid number (TAN), sulfur, metal, and it is part of bioenergy (Green-fuels feedstock).

Co-processing Product Yields

The comparison results of catalyst performance and selectivity are summarized in Figure 2 and Table 3, while the detailed breakdown of product yields is shown in Table 4. The base product yields of standard MHVGO are Dry gas: 1.2%-wt; Propylene: 6.79%-wt; Liquid Petroleum Gas (LPG): 19.52%-wt; Gasoline: 51.63%-wt; Light Cycle Oil (LCO): 10.21%-wt; Bottom: 3.68%-wt; and Coke: 6.9%-wt.





When the product yields from standard MHVGO were compared with those from bio-derived oil coprocessing feedstock for catalytic cracking, an increase in dry gas yield of approximately +1.6 - 1.7 wt% and light petrochemicals fraction, including propylene and LPG, by around +1.3 - 1.7 wt% and +2.1 - 3.6 wt%, respectively, was observed. An increase in LCO yield was observed, while a lower yield for the bottom product was obtained.

Product/Yields	MHVGO	VC_8515	VB_8515	VR_8515
Coke (wt-%)	6.90	+0.2	0.0	+0.2
Drygas (wt-%)	1.26	+1.7	+1.7	+1.8
Propylene (wt-%)	6.79	+1.4	+1.3	+1.7
LPG (wt-%)	19.52	+3.6	+2.1	+3.2
Gasoline (wt-%)	51.63	-6.6	-5.9	-6.8
LCO (wt-%)	10.21	+0.3	+1.2	+0.7
Bottom (wt-%)	3.68	-0.7	-0.3	-0.7
RON	93.55	-0.3	-1.6	-2.3

Table 3. The results summary of coprocessing performance and selectivity using a base catalyst.

This trend was expected because LCO could be used as a blending feedstock for Industrial fuel oil (Juarsa *et al.*, 2021). However, a decrease in gasoline product yields and the Research Octane Number (RON) quality of gasoline were also observed. Considering that gasoline is the main product of the FCC unit, this tendency to decrease yield and RON quality of gasoline is not expected because it could reduce refinery profitability. It can also be observed that the C^{5+} fraction in the gas phase obtained is quite high; this might cause the decrease in yield and RON of gasoline. Meanwhile, the coke yield remained relatively constant at around +0–0.2 wt%, and the E-Cat generated enough coke to provide heat as a source of catalyst regeneration. When the effects of different biomass-derived oil co-processing feedstock were compared, there was no significant difference between CPO, Bio-Oil, and RBDPO. A slightly higher RON was observed for MHVGO-CPO blending feedstock. The composition is also expected to play a role in this process, but further studies regarding the composition of biomass-derived oil feedstock, operating conditions, catalyst formulation, and optimization of subsequent support units must be carried out.

Feed name	VC_8515	VB_8515	VR_8515
Cracking Temperature (°C)	530.0	530.0	530.0
Catalyst-to-Oil (wt/wt)	6.0	6.0	6.0
Conv. (wt%)	86.6	85.2	86.1
Yields (wt%)			
Coke	7.1	6.9	7.1
Dry Gas	3.0	2.9	3.0
Hydrogen	0.1	0.1	0.1
Methane	1.0	0.9	1.0
Ethane	0.6	0.6	0.6
Ethylene	1.3	1.3	1.4
Propane	3.6	3.5	3.6
Propylene	8.2	8.1	8.5
n-Butane	2.2	2.1	2.2
Isobutane	9.6	9.1	9.5
C4 Olefins	7.7	6.9	7.5
1-Butene	1.4	1.3	1.4
Isobutylene	2.0	1.9	2.0
c-2-Butene	1.5	1.4	1.5
t-2-Butene	2.1	1.9	2.0
Butadiene	0.6	0.4	0.6
Gasolie	45.1	45.7	44.8
LCO	10.5	11.4	10.9
Bottoms	3.0	3.4	3.0
LPG	31.4	29.7	31.2
C ⁵⁺ in the Gas	17.5	15.8	16.1
RON-GC (FCC NAPHTA)	93 3	91 9	91.2

Table 4. The detailed breakdown of product yields of coprocessing feedstock.

E-Cat Analysis

The physical properties of E-Cat were characterized using X-Ray Diffraction-Unit Cell Size (XRD-UCS), Brunauer-Emmett Teller Surface Area (BET), and Particle size diameter (PSD), as shown in Table 2. The Surface and morphology characterization of E-Cat catalyst particle was performed using Scanning Electron Microscope (SEM) and summarized in Table 5 and Figure 3.



Figure 3. SEM Analysis of E-Cat with: (a) 100× magnitude; (b) 500× magnitude; (c) SEM-EDX of E-Cat.

BET analysis showed that the E-Cat has a surface area and pore volume diameter are about 173.45 m^2/g (Zeolite surface area: 49.6 m^2/g ; Matrix surface area: 123.8 m^2/g) and 0.25 Å. The E-Cat still has enough surface area and pore volume diameter for a cracking reaction to convert the large feedstock molecules to the desired molecules (Afife *et al.*, 2012). XRD-UCS analysis showed that E-Cat has a unit cell size (UCS) of around 24.3 Å. The catalytic activity of Y-zeolite is mainly controlled by its UCS, which controls its acidity (in terms of concentration and strength). This high UCS and high porosity are expected to provide high catalytic activity and greater coke selectivity (Stratiev *et al.*, 2021).

Spectrum label	Spectrum 16	Spectrum 17	Spectrum 18	Spectrum 19	Spectrum 20
0	52.38	46.04	54.73	48.67	53.74
Na	0.26			0.25	
Al	30.97	34.13	18.58	30.18	28.62
Si	16.13	18.57	23.02	18.6	15.42
Р		0.87			
Ti			0.56	0.28	0.36
Fe	0.25	0.38	0.35	0.32	0.27
La	0	0	2.76	1.7	1.59
Total	100	100	100	100	100

|--|

Based on PSD and SEM analysis, the E-Cat showed an average particle size of around 87.95 microns and still had a good microsphere morphology, which is suitable for fluidization (Sadeghbeigi, 2000). However,

Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) analysis indicated the possible presence of FeO/Fe₂O₃ impurities. These impurities can react with SiO₂-based matrix and binder to form low melting temperature phases (eutectic phase), which close the catalyst pore, inhibit the primary cracking reaction, and direct product selectivity toward less desirable products (Liu *et al.*, 2015).

CONCLUSION

Lab-scale green-fuel production through co-processing biomass-derived oil with standard gasoil feedstock has been successfully performed using base refinery E-Cat in an ACE reactor, which provided a preliminary projection on the feasibility of processing it at a commercial FCC unit. However, compared to standard MHVGO feedstock, these co-processing feedstocks (CPO, Bio-Oil, and RBDPO) have caused a shift in product yield, increasing dry gas, light petrochemical bases such as LPG and propylene, and LCO, while decreasing gasoline yield and RON quality. A slightly higher RON was observed for the MHVGO-CPO blending feedstock. Gasoil yield and RON play an important role in economic feasibility. While co-processing feedstocks contribute to cleaner and greener fuel, intensive studies on the nature of E-Cat and process conditions must be carried out to maintain gasoline yield and RON.

CONFLICT OF INTEREST

There is no conflict of interest in this article.

AUTHOR CONTRIBUTION

All authors have read, reviewed, and approved the final version of the manuscript and are engaging in the following activities: RE (conceptualization, methodology, reviewer); ZAF (conceptualization, data analysis, manuscript drafting, review, & editing); RR (lab supervising, equipment preparation), and WYP: (lab resources, data collecting & acquisition).

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