Production of high octane gasoline by catalytic cracking of petroleum gasoil with palm’s triglyceride and oleic acid

Z Azis, B H Susanto and M Nasikin
Universitas Indonesia, Depok, West Java, Indonesia
zarkoni.azis@ui.ac.id, bambanghs@che.ui.ac.id, mnasikin@eng.ui.ac.id

Abstract. The use of gasoline with appropriate octane number will affect directly to meet superfine engine performance and avoiding from knocking effect. Improvement of gasoline quality in fluid catalytic cracking process usually is achieved by replacement of new catalyst which needs higher production cost. This research work aimed to describe the alternative method for improving gasoline octane in catalytic cracking by means of feedstock modification using mixture of vacuum gasoil and few of palm’s triglyceride and oleic acid. The experimental work of cracking reaction was performed in a fluid-bed reactor of ACE unit using REY zeolite catalysts at temperature of 530 °C and catalyst-oil ratio of 5.5 g/g. The liquid product was analyzed by a gas chromatograph of simulated distillation to determine yields of gasoline, light cycle oil and bottom product continued by a gas chromatograph of detailed hydrocarbon analysis to obtain hydrocarbon composition and calculated research octane number of gasoline. Analysis of gaseous product was performed using a gas chromatograph of refinery gas analyzer to detect yields of dry gas and LPG, whereas coke deposited on spent catalyst was analyzed using the infra-red method. From the research work, it was found that feedstock prepared from vacuum gasoil added with 5 % refined bleached deodorized palm oil and oleic acid (9:1) had increased gasoline RON from 91.8 to 98.2. The improvement of gasoline octane was contributed by the presence of double-bond fatty acid that triggered promoting effect to aromatisation and hydrogen transfer reactions in the formation of more iso-paraffins, olefins and aromatics in gasoline.

1. Introduction
The necessary of gasoline in general has exceeded the production unit capacity as reported by Agus et al. [1], so each effort to overcome the gap will be highly awaited. The selection of process technology to produce gasoline is specific to each refinery depending on availability of feedstock, process route chosen and supporting facilities. Upgrading gasoline can be achieved through several process like isomerization, alkylation, catalytic cracking, reforming, but the end-product of gasoline fuel is prepared by blending of lower octane gasoline and higher octane one or added with oxygenates to meet the quality requirements. Fluid catalytic cracking (FCC) is an important process that converts heavier feedstocks like vacuum gasoil (VGO) and residue into a lot of gasoline and other lighter products. The basic principle of catalytic cracking is molecular cleavage of longer chain hydrocarbons of oil feed to some shorter molecules of products involving acid-catalyzed reactions at elevated temperature. The standard cracking feeds usually contains combination of hydrocarbons with a broad range of different polarities such as paraffinics, naphthenics and aromatics having boiling point from 250 up to 550 °C.
The products yield distribution and quality is basically influenced by catalyst properties, process condition and hydrocarbons compound of feedstock. Cracking mechanism involves formation of carbocation intermediates from acid sites of catalysts triggering the multiple reactions such as cracking or beta-scission, isomerization and hydrogen transfer with some secondary reactions like cyclization, dehydrogenation and condensation [2]. The acidity level of catalyst also influences to gasoline resulted from cracking reaction [3]. Gasoline contains hydrocarbons group types including n-paraffins, i-paraffins, naphthenes, olefins and aromatics [4]. Catalytic cracking process can direct reaction to produce gasoline having more iso-paraffins, olefins and aromatics for increasing octane number [5]. Commercial gasoline fuel usually has met to the quality requirement for spark-ignition engine especially octane number. The use of gasoline with appropriate octane number is very important thing to meet superfine engine performance and preventing it from knocking effect.

In general there are two testing methods for determining octane number of gasoline namely direct measurement and indirect measurement. The direct measurement of research octane number (RON) is tested using CFR engine according to ASTM D2699 at mild condition of normal road performance and for direct measurement of motor octane number (MON) based on ASTM D2700 indicated high-speed performance at severe conditions [6]. Indirect measurement of gasoline is intended for special case with few sample obtained from laboratory scale production using gas chromatography analyzer to determine and predict the octane number. Basically the level of octane number is direct function of molecular composition of gasoline hydrocarbons [7]. The major constituent of gasoline are hydrocarbon groups of paraffins, iso-paraffins, olefins, naphthenes and aromatics abbreviated as PIONA. The calculated octane number is determined using gas chromatograph of detail hydrocarbons analysis (GC DHA) [8]. In case of high-octane characteristics, model of gasoline mixture consists of four components namely n-alkanes, isoalkanes, cycloalkanes and aromatics [9]. Modification of grouping hydrocarbons for finding an optimal correlation with RON applied on FCC gasoline has been investigated using high resolution gas chromatography analyses [10]. The following equation is proposed to calculate RON of FCC gasoline based on GC DHA analysis:

\[
\text{RON}_{\text{cal}} = X_{\text{NP}} R\text{ON}_{\text{NP}} + X_{\text{IP}} R\text{ON}_{\text{IP}} + X_{\text{O}} R\text{ON}_{\text{O}} + X_{\text{N}} R\text{ON}_{\text{N}} + X_{\alpha} R\text{ON}_{\alpha} + \text{Offset}
\]

with : \( \text{RON}_{\text{cal}} \) is calculated research octane number 
\( X_{\text{NP}}, X_{\text{IP}}, X_{\text{O}}, X_{\text{N}}, X_{\alpha} \) is volume fraction of n-paraffin, iso-paraffin, olefins, naphthenes and aromatics.
Offset is constants for sample type due to unknown species

The research about gasoline improvement in catalytic cracking process had been studied previously by some researchers. Doronin et al. [11] and Dupain et al. [2] reported that vacuum gasoil added with sunflower oil and rapeseed oil containing double bonds of triglycerides over zeolite catalysts showing formation of higher aromatic hydrocarbons in gasoline product [11], [12]. The molecular structure of palm oil is beneficial to be treated over the shape-selective zeolite since the light aromatics of gasoline can be higher than that of hydrocarbon feedstocks [13]. Catalytic cracking reaction of vacuum gasoil added with RBDPO and PFAD had been investigated by Azis et.al [14] showing increase of gasoline yield.

The research work aimed to describe new alternative method for upgrading gasoline octane in fluid catalytic cracking process by means of feed modification using vacuum gasoil added with palm’s triglycerides and unsaturated fatty acid. The use of refined bleached deodorized palm oil containing major triglycerides and double-bond oleic acid together with vacuum gasoil feed was investigated the effects on hydrocarbons composition of gasoline and its contribution to octane number.

2. Materials and Methods

2.1. Materials

The standard oil feed used in the cracking reaction was vacuum gasoil (VGO) composed of medium to heavy oil fractions coming from the local oil refinery. Refined bleached deodorized palm oil (RBDPO) containing most of triglycerides and oleic acid having double-bond was obtained from
local palm oil industry. Three different combined feedstock was prepared for cracking reactions including VGO, VGO+5 % RBDPO and VGO+5 % (RBDPO-oleic acid) at ratio of RBDPO-oleic acid 9:1. The feed properties was evaluated their boiling points distributions, acid numbers and infra-red spectra. Boiling cut-point analysis of VGO and RBDPO was performed using GC of simulated distillation. Infra-red analysis was examined by a spectrophotometer (Shimadzu) to indentify the stretching vibration of molecular group based on fourier-transform of interferogram. Catalysts used for cracking reaction was typical catalysts of commercial FCC process containing zeolite REY coming from oil refinery as equilibrium catalysts (E-cats). The catalysts used for this laboratory scale process was calcined first at 600 °C for 1 h to remove any residual coke and other contaminants before loaded into reactor for cracking reaction.

2.2. Catalytic Cracking Reaction

The experimental work of cracking reaction was performed in a fluid-bed reactor using advanced cracking evaluation (ACE) test unit. The process flow scheme of catalytic cracking in fluid-bed reactor of ACE unit is shown in Figure 1.

![Figure 1. Simplified process flow scheme of catalytic cracking in ACE unit.](image)

The process condition for cracking reaction was set at temperature of 530 °C and catalyst-oil ratio 5.5 g/g. The cracking product of gaseous phase was analyzed by online gas chromatography of refinery gas analyzer to obtain dry gas component (C\textsubscript{1}, C\textsubscript{2} & H\textsubscript{2}) and LPG (C\textsubscript{3}, C\textsubscript{4}). Liquid product was analyzed using gas chromatography of simulated distillation analyzer to obtain yields of gasoline (36 - 215 °C), light cycle oil or LCO (216 - 370 °C) and bottoms (> 370 °C). Carbon deposited on catalyst was burnt by in-situ air calcination at 715 °C and CO\textsubscript{2} formed flowing into catalytic converter, then analyzed by infrared analyzer to obtain coke yield.

Yield of each product fraction (Y\textsubscript{i}) was calculated according to the following equation:

\[ Y_i = \frac{\text{mass of fraction} / \text{total mass of feed} \times 100\%}{2} \]

Conversion of reaction was calculated from the sum of dry gas, LPG, gasoline and coke yields plus water content. The water resulted from deoxygenation of vegetable oil component in feedstock accumulated together with liquid products was analyzed using Karl Fischer method.

Hydrocarbon groups in gasoline was analyzed using gas chromatography of detailed hydrocarbon analysis using PAC DHA D 6730 Combo System ON 8890 GC to obtain composition of individual hydrocarbons and hydrocarbons by group type in gasoline and its octane rating as calculated RON. The detail hydrocarbon analysis (DHA) technique is based on the separation of individual hydrocarbon components by utilizing ultra-high resolution capillary gas chromatography and reference component databases based on retention time.
3. **Results and Discussions**

3.1. **Feed Characteristics**

Some important properties of feedstock were analyzed as shown in Figure 2, 3 and 4.

![Figure 2. Boiling points of VGO and RBDPO.](image)

![Figure 3. Feed acidity.](image)

Boiling cut-points of VGO as shown in Figure 2 was distributed from initial boiling point of 251 °C to final boiling point of 558 °C indicating a broad range of hydrocarbon compounds from medium to heavy vacuum gasoil. This VGO feed contained major heavy oil fraction about 70 % and LCO diesel fraction around 30 %. RBD palm oil had narrow range of boiling cut-points from 334 to 339 °C, but it is still higher than that of gasoline having boiling point of 36 to 215 °C, so these palm oil along with gasoil molecules can be cracked into gasoline and other lighter products.

The mixture of VGO+5 % RBDPO-oleic acid (9:1) as shown in Figure 3 showed higher acidity than that of VGO and VGO+5 % RBDPO coming from oleic acid contribution. The acidity level for process feedstock around 1.18 mgKOH/g may be in tolerance and safe to feed lines and process unit materials from corrosion effects.

![Figure 4. IR spectra of VGO (red) and VGO+5%RBDPO (blue).](image)

Figure 4 showed infra-red spectrums of VGO and mixture of VGO with 5 % RBDPO plotted in percentage of transmittance versus wave number in range of 600 to 4000 cm\(^{-1}\). The absorption of infra-red radiation cause each molecule in feeds to vibrate. However, only those vibrations that are accompanied by a change in electric dipole moment cause absorption of infra-red light [15]. The IR spectrum of feed showed dominant spectral features associated with VGO absorption regions of the CH stretching vibration appeared in wave number regions from 3050–2800 cm\(^{-1}\) and 1500–1350 cm\(^{-1}\), whereas on the IR spectra of VGO+5 % RBDPO there is new spectrums coming from carboxylate
compounds namely $C=O$ stretching absorption of triglycerides and double-bond fatty acid appeared at region 1800–1700 cm$^{-1}$, as well as C-O stretching absorption at 1200–1100 cm$^{-1}$.

3.2. Catalytic Cracking Products

The product yield distribution obtained from cracking reactions of three different feeds were shown in Figure 5 including dry gas, LPG, gasoline, LCO, bottoms and coke. Yield of gasoline obtained from cracking of VGO+5 % RBDPO was increased, but LPG, LCO and bottom product were decreased, whereas dry gas almost constant and coke was increased slightly. Cracking of VGO+5 % (RBDPO_oleic acid) increased gasoline yield, but it was slightly lower than that of VGO+5 % RBDPO due to unsaturation index of RBDPO is lower than that of oleic acid causing the long chain of saturated fatty acid was cracked easier to form iso-paraffins in gasoline. LPG and LCO yields appeared constant, bottom slightly were increased, while dry gas and coke were decreased. The increase of gasoline yield from this co-process was linked with the promoting effect of olefins through hydrogen transfer reactions activated by acid sites of catalysts enhancing conversion of VGO feed as proton donor. Furthermore, contribution of secondary transformations of gasoline fraction into LPG and dry gas decreased due to competitive sorption with olefins formed [2, 11]. The formation of coke was contributed by shortly thermal cracking at initial step of reaction where not all of catalyst surface contacted with oils vapour, in addition to polymerization and condensation reactions of polycyclic aromatic compounds during process [16]. In the cracking of VGO+5 % RBDPO_oleic acid, yield of coke was decreased slightly, whereas dry gas and LCO was almost constant, but bottom product was increased slightly. There was no water found in liquid product from cracking of VGO, but small amount of 0.2 %wt water was detected in liquid products from cracking of VGO+5 % RBDPO, and VGO+5 % RBDPO_oleic acid.

Gasoline product from cracking of each feed was composed of several groups and types of hydrocarbons as shown in Figure 6 which was detected from a gas chromatograph of detailed hydrocarbon analysis. Hydrocarbon components in gasoline consisted of n-paraffins, iso-paraffins, olefins, naphthenes and aromatics.

![Figure 5. Product yields from each feed.](image1)

![Figure 6. Composition of gasoline hydrocarbon.](image2)

Compared to gasoline composition from cracking of VGO as base line, cracking of VGO+5 % RBDPO produced more iso-paraffins, olefins and aromatics, slightly higher n-paraffin and lower naphthenes. The cracking of VGO+5 % (RBDPO_oleic acid) produced more iso-paraffins and highest olefins, but aromatics and naphthenes seem unchanged.

The increase of olefins in gasoline was contributed by cracking reaction of paraffins, olefins and naphthenes in feedstock, also isomerization of normal paraffins to iso-olefins. Olefins is very reactive over brønsted acid sites of catalyst that can initiate aromatics formation through dehydrogenation. The number of double-bonds fatty acids in feedstock played role to enhance VGO conversion through alkylation, cyclization and dehydrogenation reactions [17]. Octane contribution from each hydrocarbon group and type in gasoline was shown in figure 7.

---

5
Figure 7. RON contribution of gasoline hydrocarbon.

Figure 8. RON of gasoline.

Gasoline produced from cracking of VGO with 5% RBDPO, also 5% RBDPO_oleic respectively showed higher octane number from contribution of more iso-paraffins, olefins and aromatics. The increase of iso-paraffins came from aromatisation of olefins with naphthenes to paraffins and aromatics, then isomerisation from n-paraffins to iso-paraffins. The higher increase of olefins in gasoline from cracking of VGO+5 % RBDPO_oleic acid caused by cracking olefins to smaller olefins and isomerization n-olefin to form iso-olefins and olefin bond shift [18]. The increase of aromatics in gasoline was caused by hydrogen transfer reaction that promotes interaction olefin with naphthene to form more paraffin and aromatics. The research octane number (RON) of gasoline calculated from GC-DHA analysis showed increase significantly from 91.8 to 96.2 after cracking of VGO+5 % RBDPO as shown in Figure 8. The highest RON of gasoline at 98.2 was obtained from cracking of VGO + 5% (RBDPO_oleic acid) contributed by formation more iso-paraffins, olefins and aromatics.

A proposed reaction pathway for catalytic cracking of vacuum gasoil mixed with triglycerides and fatty acid over zeolite REY based catalysts is shown in Figure 9.

Figure 9. Proposed reaction pathway for catalytic cracking of vacuum gasoil mixed with triglycerides fatty acid over zeolite REY catalysts.
The reaction pathway for cracking of vacuum gasoil added with triglycerides fatty acid over REY zeolite catalysts is proposed by adopting the earlier reaction mechanism for cracking of triglycerides [12] and taking into account the catalytic cracking data obtained in this research work. Based on reactions pathway scheme in Figure 9, the first step in short time involves thermal decomposition of gasoil hydrocarbon and triglycerides to form intermediates of free radicals containing olefins rich, heavy oil and fatty acid by means of radical mechanism forming few of coke and dry gas as by-products. Further transformation takes place catalytically cracking of heavy oil and fatty acids occurring in the pores surface of catalysts involving intermediates of carbonium ion formation by acid sites of catalysts. This promotes multiple reaction including cracking reactions of beta-scission, isomerization and hydrogen transfer followed by some other reactions like aromatisation, dealkylation, deoxygenation and condensation. In primary reactions, heavy oil converts into LCO, gasoline, LPG and dry gas through cracking reaction. The main reaction of catalytic cracking followed by isomerisation and hydrogen transfer reactions play important roles in the formation of gasoline. In secondary reaction, LCO can undergone dealkylation of paraffinic fragments to form gasoline and LPG, whereas condentation of polyaromatics in LCO will form coke. In certain case of excessive reaction, further cracking of gasoline can take place to form addition of LPG and dry gas. Fatty acid content in the feedstock will react with hydrogen gas to form hydrocarbon compound and small amount of water through deoxygenation, whereby hydrogen gas was created by dehydrogenation reaction of n-paraffins to olefins and from naphthenes to aromatics [16].

4. Conclusions

Modified feedstock from vacuum gasoil added with few of RBD palm oil and oleic acid had been demonstrated to be potential catalytic cracking process to improve gasoline yield and octane grade. For a given catalyst type of REY zeolite, catalyst-oil ratio and reaction temperature, higher change of gasoline yield was obtained from cracking of vacuum gasoil added with 5% RBDPO, whereas higher increase of gasoline octane came from combined feed of VGO with 5% RBDPO-oleic acid. Yields of dry gas and LCO diesel seemed unchanged, LPG and coke were slightly decreased, and bottom product was slightly increased. The interesting process route gave beneficial gain for gasoline octane improvement from 91.8 to 98.2. The increase of gasoline RON came from the formation of more iso-paraffins, olefins and aromatics influenced by the presence of double-bond fatty acid and triglyceride in gasoil feed promoting aromatisation and hydrogen transfer reactions. The reaction pathway for catalytic cracking of vacuum gasoil mixed with triglycerides and fatty acid over REY catalysts was proposed to describe some of reasonable reaction routes to produce overall of cracking products.

Acknowledgments

This research work was supported by PUTI 2020 Fund of Universitas Indonesia.

References

[1] Agus, C.A., Farida, L., Anton, B.P., Vony, M.S., *Handbook of Energy & Economic Statistics of Indonesia 2018*, E.a.M.R.o. Indonesia, Editor 2019, Ministry of Energy and Mineral Resources of Indonesia Jakarta.

[2] Dupain, X., *Fluid Catalytic Cracking: Feedstock and Reaction Mechanism*, in Chemical Engineering 2006, Technische Universiteit Delft: Netherlands. p. 311.

[3] Merdrignac, I., Espinat, D., *Physicochemical Characterization of Petroleum Fractions: the State of the Art. Oil & Gas Science and Technology*, 2007. 62(1): p. 7-32.

[4] Albahri, T.A., *Structural Group Contribution Method for Predicting the Octane Number of Pure Hydrocarbon Liquids*. Industrial & Engineering Chemistry Research, 2003. 42(2003): p. 657-662.

[5] Nee, J.R.D., Harding, R.H., Yaluris, G., Cheng, W.C., Zhao, X., Dougan, T.J., Riley, J.R., *Fluid Catalytic Cracking (FCC): Catalysts and Additives*, in *Kirk-Othmer Encyclopedia of Chemical Technology* 2004, John Wiley & Sons, Inc.: USA. p. 1-37.
[6] Demirbas, A., Balubaid, M.A., Basahel, A.M., Ahmad, W., Sheikh, M.H., Octane Rating of Gasoline and Octane Booster Additives. Petroleum Science and Technology, 2015. 33(2015): p. 1190-1197.

[7] Ghosh, P., Hickey, K.J., Jaffe, S.B., Development of a Detailed Gasoline Composition-Based Octane Model. Industrial & Engineering Chemistry Research, 2006. 45(2006): p. 337-345.

[8] Ali, N.S., Aboul-Fotouh, T.M., The Effect of Compositions (PIONA) on the Octane Numbers of Environmental Gasolines of Reformate, Isomerate and Hydrocracked Naphtha Blends by Using GC. Oil, Gas and Coal Engineering, 2017. 5(6): p. 167-174.

[9] Maylin, M.V., Kirgina, M.V., Sviridova, E.V., Sakhnevitch, B.V., Ivanchina, E.D., Calculation of gasoline octane numbers taking into account the reaction interaction of blend components. Procedia Chemistry, 2014. 10(2014): p. 477-484.

[10] Telen, S., Jambrec, N., Beer Romac, I.S., FCC Gasoline Research Octane Number Determination By Gas Chromatography goriva i maziva., 2003. 42(2): p. 92-115.

[11] Doronin, V.P., Potapenko, O.V., Lipin, P.V., Sorokina, T.P., Catalytic cracking of vegetable oils and vacuum gas oil. Fuel, 2013. 106(2013): p. 757-765.

[12] Dupain, X., Costa, D.J., Schaverien, C.J., Makkee, M., Moulijn, J.A., Cracking of a rapeseed vegetable oil under realistic FCC conditions. Applied Catalysis B: Environmental, 2007. 72(1-2): p. 44-61.

[13] Xiaojie, C., Catalytic Cracking Characteristics of Plant Oil for Producing Light Olefins and Light Aromatics. Petroleum Processing and Petrochemical Technology, 2019. 21(1): p. 55-61.

[14] Azis, Z., Susanto, B.H., Nasíkin, M., Upgrading Gasoline Yield and Octane Quality in Fluid Catalytic Cracking by Coprocessing of Vacuum Gasoil with Palm's Triglyceride Fatty Acids Using REY-type Zeolite Catalysts. Engineering Research and Technology, 2019. 12(12): p. 2676-2682.

[15] Man, Y.B.C., Setiowaty, G., Van de Voort, F. R., Determination of iodine value of palm oil by fourier transform infrared spectroscopy. Journal of the American Oil Chemists' Society, 1999. 76(6): p. 693-699.

[16] Gueudré, L., Thegarid, N., Burel, L., Jouguet, B., Meunier, F., Schuurman, Y., Mirodatos, C., Coke chemistry under vacuum gasoil/bio-oil FCC co-processing conditions. Catalysis Today, 2015. 257, Part 2: p. 200-212.

[17] Bielansky, P., Weinert, A., Schönberger, C., Reichhold, A., Catalytic conversion of vegetable oils in a continuous FCC pilot plant. Fuel Processing Technology, 2011. 92(12): p. 2305-2311.

[18] Sadeghbeigi, R., Fluid Catalytic Cracking Handbook. Design, Operation and Troubleshooting of FCC Facilities. 2000, Texas: Gulf Publishing Company. 369.