# Production of High Octane Gasoline by Catalytic Cracking of Petroleum Gasoil with Palm's Triglyceride and Oleic Acid

Zarkoni Azis, Bambang Heru Susanto and Mohammad Nasikin

August 10, 2020

# 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. G**asoline is primary liquid fuel needed for internal combustion of spark-ignition engines. The necessary of gasoline fuel currently has exceeded the existing production unit capacity. Most of gasoline coming from petroleum industry was produced by fluid catalytic cracking process that utilized heavy oil fractions like vacuum gasoil and residue using zeolitic catalysts. Alongside product yield, the quality of gasoline especially octane number is an important factor that determining and controlling the ignition quality and indicating the resistance of fuel to knock. The usual method to upgrade gasoline is done through catalyst selection and process optimization. This research work was aimed to describe new process for improving gasoline octane quality by means of feedstock modification using vacuum gasoil mixed with palm's triglyceride and oleic acid. The cracking reaction was performed in fluid-bed reactor of ACE unit using REY zeolite catalysts at temperature of 530°C and catalyst-oil ratio of 5.5 g/g. Gasoline fraction was separated from liquid product by gas chromatograph of simulated distillation and examined further using gas chromatogragh of detailed hydrocarbon analysis to detail hydrocarbon group and type, as well as calculated research octane number. From the research, it was found that combined feed from vacuum gasoil added with 5% of refined bleached deodorized palm oil and oleic acid (9:1) was able to raise gasoline octane quality of RON from 91.8 to 98.2. The octane quality improvement 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

Gasoline is petroleum-derived liquid containing $C_5$-$C_{12}$ hydrocarbons used primarily as fuel for internal combustion engines of spark-ignition types. Currently the necessary of gasoline in this country has exceeded to production capacity of existing refinery units as rep orted by *Agus et al*. [1], so each effort to overcome the gap will be highly awaited. The process technology for gasoline production is specific to each refinery depending on the process route, availability of feedstock and unit facility. Improvement of gasoline octane quality normally is done by several process routes such as isomerization, alkylation, catalytic cracking, reforming and at the end-product through blending with other higher octane hydrocarbons or with oxygenates. Fluid catalytic cracking (FCC) is an important refinery process that converts feedstocks of middle and heavy oil fractions of petroleum like vacuum gasoil (VGO) and residue becoming a lot of gasoline and other lighter and valuable products. Catalytic cracking is basically process of hydrocarbon molecular cleavage in oil feeds involving acid-catalyzed reactions at elevated temperature. Gasoils generally contains combination of hydrocarbons with a broad range of different polarities such as paraffinics, naphthenics and aromatics having boiling point range from 250 up to 550°C.

The change in process condition, feed type and catalyst used can alter product yield distribution. Cracking reaction 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, and others like cyclization, dehydrogenation and condensation [2]. The quality of gasoline resulted from catalytic cracking is influenced by formed hydrocarbons composition, feed properties, process condition and acidity level of catalyst used [3]. Gasoline is a mixture of hydrocarbon compounds composed of $C_5$ to $C_{12}$ having group types of *n*-paraffins, *i*-paraffins, naphthenes, olefins and aromatics [4]. Catalytic cracking reaction produces a lot of gasoline with more iso-paraffins, olefins and aromatics that gains its octane number [5]. Several important properties of gasoline include density, vapor pressure, distillation range, octane number and chemicals composition.

Gasoline fuel launched on the market must meet engine technical specification as shown by level of octane number. The direct measurement of research octane number (RON) at mild condition of normal road performance is normally tested on CFR engine based on ASTM D2699 method, whereas motor octane number (MON) indicated high-speed performance at severe conditions is tested according to ASTMD D2700 [6]. Because of little sample obtained from cracking reaction at laboratory scale, it is compulsory to use indirect method using gas chromatography to determine octane number of gasoline. In general, level of octane number is direct function of molecular composition of gasoline [7]. The major constituent of gasoline hydrocarbon groups are paraffins, iso-paraffins, olefins, naphthenes and aromatics abbreviated by PIONA. The octane number of gasoline can be calculated according to group type of PIONA obtained from gas chromatograph of detail hydrocarbons analysis at different physicochemical and structural properties of hydrocarbons [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 the purpose of finding an optimal correlation with RON applied on FCC gasoline has been investigated using high resolution gas chromatography analyses [10]. The following modified equation was used for calculating RON of FCC gasoline based on GC DHA analysis:

$$\mathrm{RON} = X_{NP}\mathrm{RON}_{NP} + X_{IP}\mathrm{RON}_{IP} + X_{O}\mathrm{RON}_{O} + X_{N}\mathrm{RON}_{N} + X_{A}\mathrm{RON}_{A} + \mathrm{Offset} \qquad (1)$$

where: $X_{NP}$, $X_{IP}$, $X_{O,}$ $X_N$, $X_A$ *is* volume fraction of n-paraffin, iso-paraffin, olefins, naphthenes and aromatics, and offset is constants for sample type due to unknown species

*Doronin et al*. and *Dupain et al.* reported that vacuum gasoil added with vegetable oil containing double bonds of triglyceride over zeolite catalysts showed formation of high concentration of aromatic hydrocarbons in gasoline product [11], [12]. *Xiaojie* reported the molecular structure of palm oil is beneficial to be treated over the shape-selective zeolite, since the light aromatics in gasoline is higher than that of hydrocarbon feedstocks [13]. Research about co-catalytic cracking of vacuum gasoil with RBDPO and PFAD showed increase of gasoline yield and octane quality [14]. Most of research works regarding coprocess in catalytic cracking has not described in detail the effect of saturated and unsaturated fatty acids in oil feed to hydrocarbons composition influencing octane number of gasoline.

This research work was aimed to describe new process pathway in fluid catalytic cracking for upgrading gasoline octane quality 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 along with vacuum gasoil feedstock was eximined their effects to hydrocarbons composition and octane contribution of gasoline product.

## 2. Materials and Methods

### *2.1. Materials*

The standard oil feed used for cracking reaction was vacuum gasoil (VGO) containing medium to heavy oil fractions supplied from oil refinery. Refined bleached deodorized palm oil (RBDPO) composed of major triglycerides and oleic acid as double-bond fatty acid were obtained from local palm oil industry. Three different combined feedstock prepared for cracking reactions included VGO, VGO+5%RBDPO and VGO+5%(RBDPO-oleic acid) at ratio of RBDPO-oleic acid 9:1. The testing of feed properties included boiling points distribution, acid number and infra-red spectra. Boiling point analysis done by GC of simulated distilation was special for VGO and RBDPO as main feeds having low acidity. FTIR analysis was examined by Shimadzu spectrophotometer to indentify the stretching vibration of molecular group based on fourier-transform of interferogram. Catalysts used for cracking reaction was commercial catalysts containing zeolite REY coming from oil refinery as equilibrium catalysts (E-cats). This catalysts was calcined first at 600°C for 1 hour to remove any residual coke and other contaminants before loaded inside reactor for cracking reaction.

### *2.2. Catalytic Cracking Reaction*

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

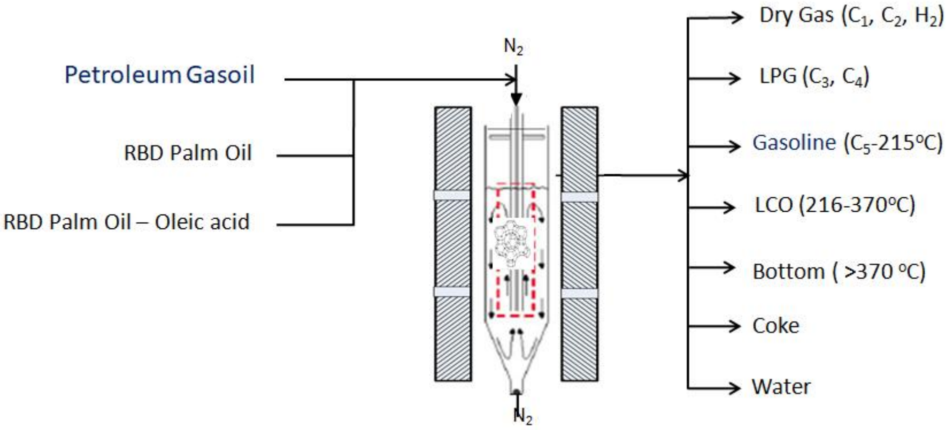

Figure 1. Process flow scheme of catalytic cracking

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 chromatograph of refinery gas analyzer to obtain dry gas component ($C_1$, $C_2$ & $H_2$) and LPG ($C_3$, $C_4$). Liquid product was analyzed using gas chromatograph 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 $CO_2$ formed flowing into catalytic converter, then analyzed by infrared analyzer to obtain coke yield.

Yield of each product fraction ($Y_i$) was calculated according to equation 2 :

$$Y_i = mass\ of\ fraction^i\ /\ total\ mass\ of\ feed\ x\ 100\% \qquad (2)$$

Conversion of reaction was calculated from the sum of dry gas, LPG, gasoline and coke yields plus water content. The water contained in liquid products was analyzed using Karl Fischer method.

Hydrocarbon groups in gasoline was analyzed by gas chromatograph of detailed hydrocarbon analysis using PAC DHA D 6730 Combi System ON 8890 GC system 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 feed properties to be evaluated was shown in figure 2, 3, 4 and 5.

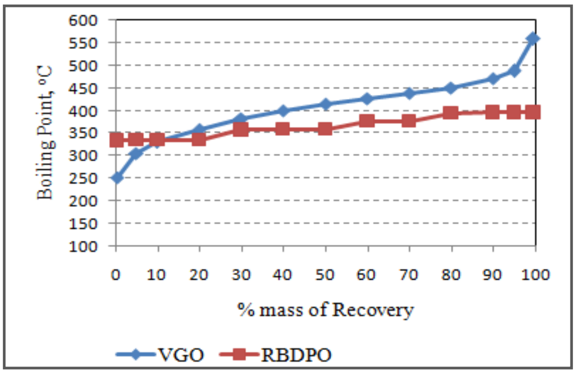

Figure 2. Boiling points of VGO and RBDPO

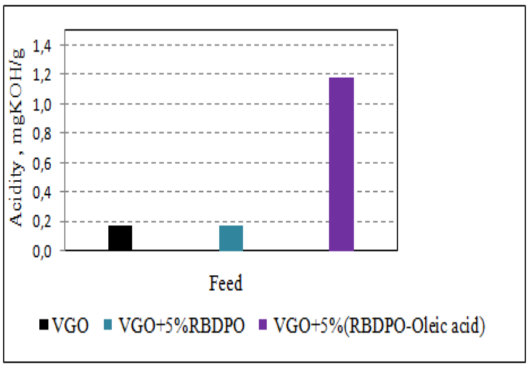

Figure 3. Feed acidity

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% of RBDPO-oleic acid (9:1) as shown in figure 3 had higher acidity than that of VGO and VGO+5%RBDPO, due to oleic acid contribution. The acidity level of feeds about 1.18 mgKOH/g was still in tolerance and safe to feed lines and process unit materials from corrosion effect.

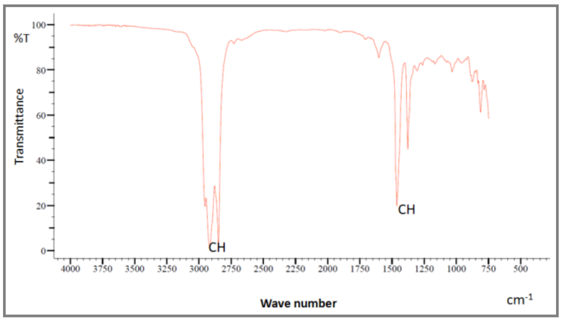

Figure 4. IR spectra of VGO

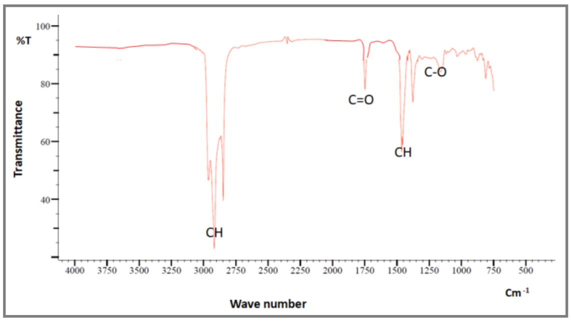

Figure 5. IR spectra of RBDPO

Figure 4 and 5 showed infra-red spectrums of VGO and mixture of its with 5%RBDPO and 5%(RBDPO_oleic acid), respectively that was plotted in percentage of transmittance versus wave number in range of 400 to 4000 cm$^{-1}$. The absorption of infrared 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 infrared light [15]. The IR spectrum of feed samples in figure 5 illustrated the 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$^{-1}$, meanwhile for IR spectra of VGO+5%RBDPO and VGO+5%RBDPO_oleic, there is new spectrums from carboxylate compounds namely C=O stretching absorption of triglycerides and double-bond fatty acid appeared at region 1800–1700 cm$^{-1}$, and C-O stretching absorption at 1200–1100 cm$^{-1}$. The vibration intensity of hydrocarbon molecules in region 1500-1350 cm$^{-1}$ of VGO+5%(RBDPO-oleic) is stronger than that of VGO+5%RBDPO due to double-bond stretching effect of oleic acid.

### *3.2. Catalytic Cracking Products*

The results of catalytic cracking reaction from three different feeds was shown in figure 6. Product yield distribution consisting of dry gas, LPG, gasoline, LCO, bottoms and coke had slightly different patterns according to feed type. Yield gasoline obtained from cracking of VGO+5%RBDPO increased, but LPG, LCO and bottom product decreased, whereas dry gas almost constant and coke 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 effect of unsaturation index of RBDPO is lower than that of oleic acid causing long chain of saturated fatty acid cracked easier to form iso-paraffins in gasoline. LPG and LCO yields appeared contstant, bottom slightly increased, dry gas and coke decreased. The increase of gasoline yield from co-process using this vegetable oil was linked with the promoting effect of olefins through hydrogen transfer reactions on feed hydrocarbon activated by acid sites of catalysts to enhance VGO conversion 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 thermal cracking effect at initial step of reaction where not all of catalyst surface made in contact with oils vapour, also by polymerization and condensation of polycyclic aromatic compounds during catalytic cracking [16]. In cracking of VGO +5%RBDPO_oleic acid, coke yield decreased slightly, whereas dry gas and LCO is almost constant, bottom product increased. There was no water in liquid product found from cracking VGO, but small amount of water around 0,2%wt was detected in liquid product 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 7 which was detected from gas chromatograph of detailed hydrocarbon analysis. Hydrocarbon components in gasoline consisted of n-paraffins, iso-paraffins, olefins, naphthenes and aromatics.

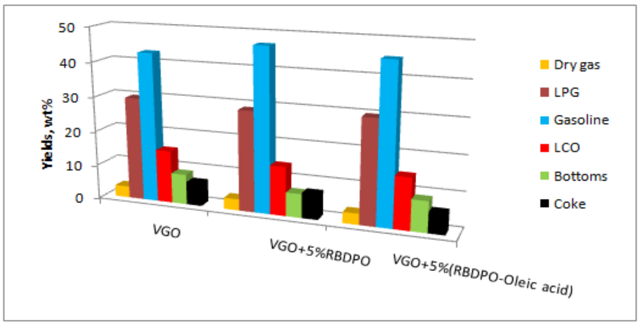

Figure 6. Product yields from each feed

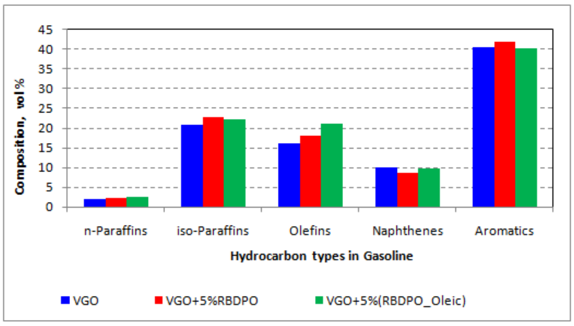

Figure 7. Composition of gasoline hydrocarbon

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-bounds 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 8.

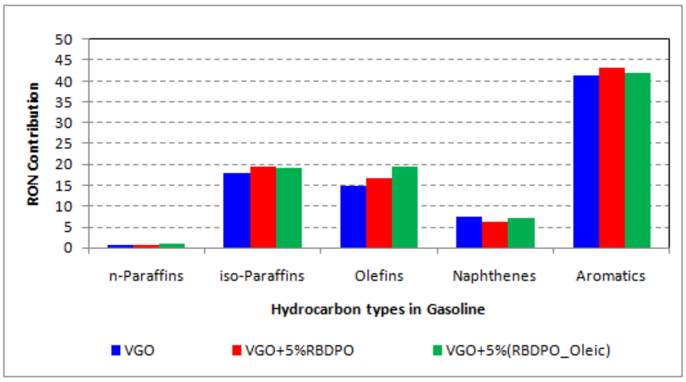

Figure 8. RON contribution of gasoline hydrocarbon

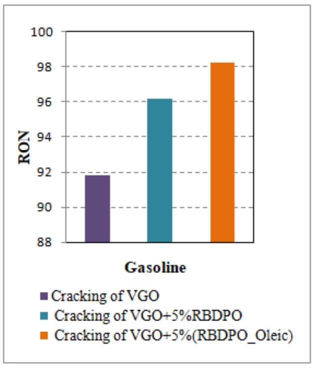

Figure 9. RON of gasoline

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 9. The highet 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 10.

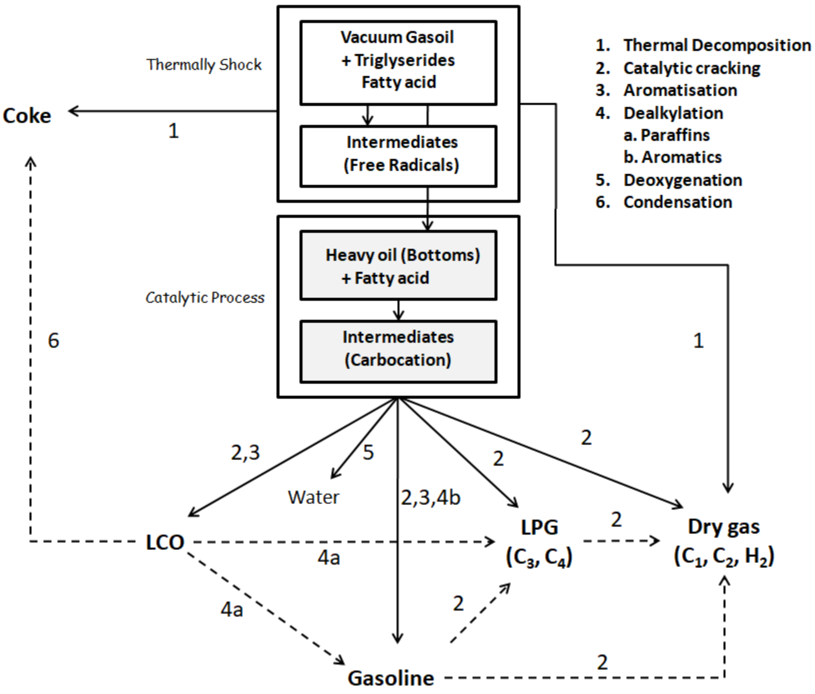

Figure 10. Proposed reaction pathway for catalytic cracking of vacuum gasoil mixed with triglycerides fatty acid over zeolite REY based catalyst

The reaction pathway for cracking of vacuum gasoil 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 data obtained in this research work. The first step in short time involves thermal decomposition of gasoil hydrocarbon and triglycerides to form intermediates, heavy oil and fatty acid by means of radical mechanism forming coke and dry gas as by-products. Further transformation of heavy oil and fatty acids occurs in the pores surface of catalysts including cracking reactions, aromatization, dealkylation, deoxygenation and condensation. In primary reactions, heavy oil converts into LCO, gasoline, LPG and dry gas through cracking reaction. In addition to catalytic cracking, isomerisation and hydrogen transfer reactions play important role in the formation of gasoline. In secondary reaction, LCO undergone dealkylation of paraffinic fragments to form gasoline and LPG, and condentation of polyaromatics in LCO to form coke. Further cracking of gasoline can occur to form LPG and dry gas. Fatty acid reacts with hydrogen gas occurring deoxygenation to form water, whereby hydrogen gas created from dehydrogenation of n-paraffins to olefins and from naphthenes to aromatics [16].

## 4. Conclusions

Mixtures of petroleum gasoil with RBD palm oil and oleic acid have been demonstrated to be potential of coprocessing in fluid catalytic cracking to improve gasoline yield and octane quality. For a given catalyst type of REY zeolite, catalyst-oil ratio and reaction temperature, gasoline yield increased higher from cracking of vacuum gasoil with 5%RBD palm oil, whereas higher increase of gasoline octane quality was obtained from addition of 5%RBDPO-oleic acid. Yields of dry gas and LCO diesel seem unchanged, LPG and coke slightly decreased, bottom slightly increased. These of process routes has beneficial gain for gasoline octane improvement from 91.8 to 96.2 and 98.2. The increase of gasoline RON was supported by formation of more iso-paraffins, olefins and aromatics. There was not oxygenates detected in gasoline product indicating that completely conversion of oxygen into water occured through deoxygenation. The increase of gasoline RON was supported by the presence of double-bond fatty acid in the feedstock that promoted aromatisation and hydrogen transfer reactions of olefins to raise iso-paraffins and aromatics in gasoline. The higher unsaturation index of oleid acid than that of RBDPO contributed to form more olefins in gasoline increasing octane number.

## Acknowledgments

Authors wishing to acknowledge for financial support of 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 Determintaion 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., Nasikin, 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.