

**TEKNIK, 42 (2), 2021, 218-225** 

# **Reactivation of the Spent Residue Fluid Catalytic Cracking (RFCC) Catalyst through Acid Treatment for Palm Oil Cracking to Biofuels**

Rahma Amalia, Teguh Riyanto, I. Istadi<sup>\*</sup>

Departemen Teknik Kimia Fakultas Teknik, Universitas Diponegoro Jl. Prof. Soedarto, SH, Kampus UNDIP Tembalang, Semarang, Indonesia 50275

# Abstract

This work discusses the treated spent Residue Fluid Catalytic Cracking (RFCC) catalysts using sulfuric or citric acids to examine the impact of acid treatment on the catalyst physicochemical properties and catalytic performance. The catalysts were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), and Brunauer–Emmett–Teller-Barrett–Joyner–Halenda (BET-BJH) methods. The catalyst's performance was examined in a continuous fixed-bed reactor for catalytic cracking of palm oil. It was found that the acid treatment on the spent RFCC catalyst can increase the surface area and pore volume of catalysts as well as the crystallinity. The closed pores in the spent RFCC are opened by acid treatment by eliminating heavy metals. In terms of the catalytic performance, the acid-treated catalysts had better performance than the non-treated catalyst, increasing the selectivity of the kerosene-diesel range fraction from 47.89% to 55.41%. It is interesting since the non-treated catalyst could not produce a gasoline fraction, while the acid-treated catalysts could produce a gasoline fraction at a selectivity range of 0.57 – 0.84%. It is suggested that both sulfuric or citric acids treatment could increase the cracking performance of spent RFCC catalyst by shifting the liquid product to lower hydrocarbons.

Kata kunci: Spent RFCC catalyst; acid treatment; catalyst properties; catalytic cracking; palm oil; biofuels

### 1. Introduction

One of the renewable energy alternatives to replace fossil fuels is biofuels that can be produced from vegetable oils. Vegetable oil, which generally contains triglycerides, is easier to convert into liquid biofuels than biomass containing cellulose, hemicellulose, and lignin. In Indonesia, palm oil is the most favorable raw material for biofuel production (Istadi et al., 2020). Besides, palm oil is one of the most widely used vegetable oils worldwide and continues to experience developments in its production. Currently, Indonesia is the world's largest palm oil producer at 62%, followed by Malaysia at 33%. Furthermore, the biofuels derived from palm oil are among the five national research priorities for new and renewable energy in 2020-2024, based on Indonesia's ministry of research and technology.

Several methods have been used to convert palm oil into bio-hydrocarbons, such as transesterification, hydroprocessing, thermal cracking (pyrolysis), and catalytic cracking (Makertihartha et al., 2020). The catalytic cracking has higher yields from conversion to gasoline, kerosene, and diesel at a relatively lower reaction temperature (~450°C) compared to thermal cracking/pyrolysis (550-800°C) (Riyanto et al., 2020). The catalysts have an important role in reducing the activation energy and increasing the selectivity of desired product so that the choice of the catalyst is essential in the catalytic cracking process. A catalyst with a suitable acid site and structure will encourage cracking with a specific selectivity. Zeolite-based catalysts are generally effective for the cracking process. The zeolite is a major component of the residue fluid catalytic cracking (RFCC) catalysts. The spent RFCC of the refinery unit process could be reused and reutilized for the palm oil cracking process after some treatments (Istadi et al., 2020). This catalyst is still active and can be used in other processes requiring an acidic catalyst to enhance catalytic activity. It also leads to environmentally valuable purposes and the availability of low-cost catalysts to increase cracking products (Bertero et al., 2019). The spent RFCC catalyst was deactivated during the process to reduce the activity of its active sites. This is because the acid site on the catalyst, which plays a

<sup>&</sup>lt;sup>\*)</sup> Corresponding author

E-mail: istadi@che.undip.ac.id

Chamical Component	Chemical	Composition	
Chemical Component	Formula	(wt%)	
Palmitic acid	$C_{16}H_{32}O_2$	43.30	
Oleic acid	$C_{18}H_{34}O_2$	18.51	
1-Nonadecene	$C_{19}H_{38}$	16.27	
11-Hexacosyne	$C_{26}H_{50}$	5.80	
9-Tricosene	$C_{23}H_{46}$	5.68	
2-Monopalmitin	$C_{19}H_{38}O_4$	3.25	
Z-13-octadecenyl acetate	$C_{20}H_{38}O_2$	2.03	
Oleic acid, 3- (oxtadecyloxy)propyl ester	$C_{39}H_{76}O_{3}$	1.47	
2-Pentadecanone	$C_{15}H_{30}O$	1.34	
(Z,Z)-3,9-Cis-6,7-epoxy- nonadecadiene	$C_{19}H_{34}O$	1.18	
1-Heptadecanol	$C_{17}H_{36}O$	1.17	

**Table 1.** Palm oil composition as raw material forcracking process by GC-MS Analysis

role in the cracking process, has diminished because of the coke and metal blockage that closed the catalyst's active site. In this case, treatment is needed to reactivate or modify this catalyst to conform with the palm oil craking process. There are several ways to increase or modify the acid sites in the zeolite-based catalyst, such as modifying the zeolite with heteroatoms (metals) or treating agents such as acid treatment.

The modification of the spent RFCC catalyst using mixed acids (acetic acid and oxalic acid) increased the heavy oil cracking product, and the loss of metal impurities and dealumination of Al on the catalyst, besides the modified catalyst, led to the increase in the pore volume (Lu et al., 2020). USY zeolites modification using citric acid is preferable to produce liquified petroleum gas (LPG) and diesel in the FCC process. It is indicated that the LPG and diesel yields of citric modified samples were effectively improved, and the coke formation was inhibited (Xin-Mei and Zi-Feng, 2001). Interestingly, the citric acid treatment led to the increasing BET surface area, total pore volume, micropore surface area and volume, and mesopore surface area and volume on HZSM zeolite (Meng et al., 2020), mesopore and macropore volume on SAPO-34 (Jin et al., 2018), and external surface areas on HZSM-5 zeolite (Vieira et al., 2015). Therefore, the citric acid-treated zeolites improve their respective products. Sulfated hierarchical nanoporous HY zeolite improved the sample's acid strength and porosity, and the sulfated zeolite showed better catalytic activity in biodiesel production (Alaba et al., 2017). Likewise, the sulfuric acid treatment on a zeolite clinoptilolite zeolite resulted in the high activity of catalysts and higher surface area and pore volume of modified catalyst (Miadlicki et al., 2021). Also, sulfuric acid-treated HZSM-5 has increased mesopores volume and external surface (Meng *et al.*, 2020). Sulfonated nickel-based meso-Y zeolite catalyst expanded meso-Y zeolite crystal structure and enhanced hydrocracking capacity (Cheng *et al.*, 2019). The previous statement has shown that sulfuric acid has a good ability to modify the catalyst structure, and so citric acid demonstrates an excellent pore-forming ability.

Based on these previous findings, acid treatment is an effective way to increase the activity of zeolitebased catalysts. On the other hand, the study on the effect of sulfuric and citric acid treatments to modify the spent RFCC catalyst for catalytic cracking of palm oil is very limited. Therefore, this study examines the impact of sulfuric or citric acids on the catalyst's physicochemical properties and structural characteristics. This study also discusses the correlation between the characteristics and the catalvtic performance testing of the acid-treated spent RFCC catalysts for palm oil conversion to biofuel

#### 2. Materials and Methods 2.1. Materials and Chamier

2.1. Materials and Chemicals

The spent RFCC catalyst was obtained from a petroleum company in Indonesia as a waste. The chemicals used as an acid treatment are sulfuric acid (96.1 w/w%, Mallinckrodt) and citric acid (99.9 w/w%, Merck). In order to test the performance of the catalysts for the catalytic cracking process, palm oil as a raw material was obtained from the local market (Rose BrandTM), where the composition of palm oil is presented in Table 1. It is known that palmitic acid and oleic acid dominate the palm oil components. In addition, the air in the tubing and reactor system was flushed using  $N_2$  gas (99.9%, UHP) before the cracking process.

# 2.2. Acid Treatment of Spent RFCC Catalyst

The spent RFCC catalyst was dried in an electric oven (Memmert) at 110°C for 8 hours. Next, the catalyst was calcined in a furnace (NEY VULCAN 3-550) at a temperature of 550°C for 4 hours. The acid treatment on the spent RFCC catalyst used two types of acid solutions: citric acid or sulfuric acid. The calcined catalyst was then soaked and stirred for 3 hours at 80°C in 0.7 M citric acid or 0.7 M sulfuric acid solution, with a solid to liquid ratio of 1:10 w/v (Li et al., 2016). After being treated with acid, the catalyst was filtered, repeatedly washed using demineralized water until it reached pH 7 (neutral), and dried in an electric oven at 110°C for 8 hours. Finally, the catalyst was calcined at 550°C for 4 hours. The treated catalyst was pelleted and crushed, then sieved with particle sizes between 14 and 16 mesh. The non-treated spent RFCC catalyst is denoted as RFCC catalyst. S-RFCC is defined as a sulfuric acid-treated RFCC catalyst, and C-RFCC is defined as a citric acid-treated RFCC catalyst.



**Figure 1.** Schematic diagram of a continuous conventional fixed bed reactor system for catalytic cracking of palm oil: 1) Palm oil raw material tube, 2) Gate valve, 3) Peristaltic pump, 4) Electrical preheater, 5) fixed bed reactor, 6) catalyst bed, 7) Glass wool, 8) heating furnace reactor, 9) Condenser, 10) Gas-liquid separator, 11) Gas products, 12) Organic liquid product (OLP) collector, 13) Gas flowmeter, 14) Nitrogen gas cylinder.

#### 2.3. Catalysts Characterizations

characterization methods Several were implemented on the treated and the non-treated catalysts. The X-ray diffraction (XRD) method analysis (Shimadzu 7000) was used to determine the crystal structure of the catalysts, operate at 30 kV and 30 mA with Cu-Ka radiation, where diffraction patterns were generated at 20 angle ranges of 10-90° with a scanning speed of 3°/min. The percentage of crystallinity is calculated using the total area of the crystal peak and the whole peak (both crystalline and amorphous) area, according to Equation (1). The catalysts' metal content and Si/Al ratio were determined using the X-ray fluorescence (XRF) analysis method (Rigaku Supermini 200 Benchtop WDXRF Spectrometer). The N2physisorption analysis was performed in a TriStar II 3020 surface area and porosity analyzer (Micromeritics) at liquid nitrogen temperature. The surface area of the catalysts was determined using the Brunauer-Emmett-Teller (BET) method. Meanwhile, the pore size distribution and the average pore size were obtained using the Barrett-Joyner-Halenda (BJH) method (Istadi et al., 2020).

$$Crystallinity(\%) = \frac{Area of the crystal peaks}{Area of all peaks} \times 100 (1)$$

## 2.4. Catalytic Performance of Acid-treated Spent RFCC Catalysts

The acid-treated spent RFCC catalysts (S-RFCC and C-RFCC) were tested to perform catalytic cracking of palm oil over a conventional continuous fixed bed reactor (Figure 1). The reactor was constructed by a stainless-steel tube with a diameter of 1 inch. An electric furnace was used to heat up the reactor temperature of 450°C. First, the catalyst (5 g) was introduced into the reactor, then 100 mL/min of N2 gas was flowed for 15 minutes to all parts of the device to remove the presence of oxygen gas. After the required reactor temperature was achieved and stable, palm oil feed was then fed into the reactor at a weight hourly space velocity (WHSV) of  $0.365 \text{ min}^{-1}$ , where the flow rate was controlled by a peristaltic pump (RZ1030-BX). The reaction process was conducted for 3 hours, after which the process reached the steady-state reaction process. In this case, it is assumed that a steady-state was began after the first 30 minutes. After the reaction process, the product was condensed into a liquid or organic liquid (OLP) in an OLP collector, and the non-condensed product was separated. Apart from gas and liquid, the byproduct of the catalytic cracking process was a deposit coke.

The collected OLP was distilled in a batchdistillation apparatus at atmospheric pressure to quantify the amount of gasoline and kerosene diesel. The gasoline was distilled product at a temperature range of  $39-204^{\circ}$ C (CAS 86290-81-5), while the kerosene-diesel was the distilled product at a temperature range of 204- $370^{\circ}$ C (3675 K/24/DJM/2006; 17.K/72/DJM/1999). Yield and selectivity of the cracking product after the distillation was calculated using the Equations 2-6 (Li *et al.*, 2018).

yield of OLP (%) = 
$$\frac{m_{OLP}}{m_{feed}} \times 100$$
 (2)

yield of coke (%) = 
$$\frac{m_{coke}}{m_{feed}} \times 100$$
 (3)

yield of gas (%) = 
$$100 - \frac{m_{OLP} + m_{coke}}{m_{feed}} \times 100$$
 (4)

selectivity of gasoline (%) = 
$$\frac{m_{gasoline}}{m_{OLP}} \times 100$$
 (5)

selectivity of kerosene - diesel (%) =  $\frac{m_{kerosene-diesel}}{m_{OLP}} \times 100$ 



Figure 2. XRD patterns of non-treated and acid-treated spent RFCC

Where  $m_{feed}$  represents the mass of feed,  $m_{OLP}$  is the mass of OLP,  $m_{coke}$  is the mass of coke,  $m_{gasoline}$  is the mass of gasoline fraction, and  $m_{kerosene-diesel}$  is the mas of the kerosene-diesel fraction.

#### 3. Result and Discussion

#### **3.1.** Catalyst Characterizations

3.1.1. XRD and XRF Characterizations of Spent RFCC Catalysts

XRD analysis was performed to determine the crystallinity of the catalysts. The percentage of crystallinity was calculated according to Equation (1), and the crystallinity results were 27.364%, 35.935%, 32.908% for RFCC, C-RFCC, and S-RFCC catalysts, respectively. This crystallinity of the catalysts increases after being treated with acid. It is suggested that acid treatment has a beneficial effect on crystallinity enhancement. The fundamental reason can be attributed to part of the crystal surface eroding with acid, increasing crystallinity. Good crystallinity precursor to a strong zeolite and making the catalyst more stable under (hydro) thermal conditions (Li et al., 2017). As previously mentioned, the spent RFCC catalyst was deactivated because the coke and metal block the catalyst's active sites. The acid treatment leads to removing the metals blocking the active sites on the catalysts. As a result, the metals are leached out, leaving the crystalline structure so that the crystallinity of the catalysts increases. It is true since the XRD pattern of non-treated and acid-treated catalysts is relatively unchanged. This fact confirms that the acid treatment does not significantly change the crystal structure or phases of the catalysts, as reported by Istadi et al. (2020). Moreover, it also confirms that the crystallinity change is caused by the metal leaching that leaves the

	Metal Content (wt%)				
	RFCC	S-RFCC	C-RFCC		
Si/Al ratio	0.944	2.013	1.453		
Al	13.971	5.751	8.509		
Si	13.186	11.576	12.366		
Р	0.122	0.028	0.045		
S	0.034	0.013	0.015		
K	0.150	0.114	0.136		
Ca	0.115	0.079	0.095		
Ti	0.394	0.413	0.473		
V	0.043	-	0.048		
Fe	0.427	0.254	0.349		
Co	0.037	0.025	0.040		
Ni	1.336	1.044	1.275		
Zn	0.010	0.008	0.011		
Sr	0.010	-	0.008		
Zr	0.009	0.012	0.008		
La	0.590	-	0.240		
Ce	0.510	0.110	-		
Y	0.005	-	-		
Pr	0.083	-	-		
Nd	0.207	-	-		

 Table 2. Si/Al ratio and metal content of acid-treated and non-treated spent RFCC catalysts

crystalline structure. This finding follows the previous study, which stated that the acid leaching of intra-porous EFAl and amorphous material increased the crystallinity of the catalyst (Meng *et al.*, 2020).

The Si/Al ratio and the composition of the metals in the catalysts were determined using XRF analysis (Table 2). The non-treated spent RFCC catalyst has a lower Si/Al ratio than the acid-treated spent RFCC catalyst. This is due to the dealumination process during the acid treatment (Table 2), where the Al content decreases after both sulfuric or citric acid treatments. This trend corresponds to the previous study reporting that the acid treatment causes the dealumination of the zeolite (Ishihara, 2019). As can be seen in Table 2, the Si and Al contents decrease after the acid treatments. However, the dealumination degree is different for the sulfuric and the citric acid treatment because of selective desilication during the acid treatment. As suggested by Jin et al. (2018), citric acid treatment tends to attack the P-Al-Si particular domain causing selective desilication in the zeolite framework of SAPO-34. Likewise, the sulfuric acid treatment causes the dissolution of Al and Si; however, the dealumination process remains more dominant in this acid treatment (Wang et al., 2016).

Metal contaminants found in spent RFCC came from the feed oil in the refinery unit process (Akah, 2017). Therefore, the amount of these metal contaminants depends on the metal contents of the feed

Sample	BET Surface Area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)
RFCC	106.19	0.106	-
S-RFCC	223.11	0.137	6.29
C-RFCC	175.47	0.136	7.53

**Table 3.** Textural properties of acid-treated and non-treated spent RFCC

refinery oil. Ni, V, and Fe are common contaminants often found in spent RFCC catalysts (Le et al., 2019). As shown in Table 2, the spent RFCC catalyst contains many metals, including Ni, V, and Fe, leading to coking formation and producing gas affecting the catalytic activity in the cracking process (Akah, 2017). However, both acid treatments could completely eliminate some metals, while the sulfuric acid treatment can eliminate total V metal. Both acid treatments could reduce Ni and Fe slightly. The metal removal mechanism using citric acid, a weak organic acid, differs from Sulfuric acid. The citric acid can directly remove metal ions by hydrogen ions or specifically adsorbing mineral surfaces making soluble complexes with metal (Astuti et al., 2016). These mechanisms lead to citric acid's effectiveness in attacking metals and making citric acid as good as sulfuric acid.

3.1.2. Surface Area and Pore Properties of Spent RFCC

The surface area was determined using the BET method, while the pore volume and pore size were determined using the BJH method. The surface area, the pore volume, and the average pore size of the RFCC, S-RFCC, and C-RFCC catalysts are presented in Table 3, while the pore size distribution of the catalysts is shown in Figure 3. Depending on IUPAC classification, this sorption isotherm indicates the type IV isotherm of typical sorption isotherm. Furthermore, it suggests that

spent RFCC catalyst has micropore and mesopore. The surface area of catalysts increases after being treated with sulfuric or citric acids, where an increase follows an increase in surface area in the pore volume of the acid-treated catalyst. As shown in Figure 3, the adsorption volume of the spent RFCC compares to acidtreated samples increases obviously, and the adsorptiondesorption hysteresis increases. It demonstrates that pore volumes of the acid-treated catalysts are much larger than the spent RFCC because the acid treatment cleans the closed pores by removing the heavy metals that block the pores of the catalyst. It is true since the metal content of spent RFCC catalysts decreases after acid treatment (Table 2). This process can open the pores and increase the surface area. This finding is supported by the fact that the surface area of the S-RFCC catalyst is higher than the C-RFCC catalyst with respect to the metal leaching degree. As shown in Table 2, the number of metals released in S-RFCC is higher than in C-RFCC. Therefore, it is highly suggested that the metal leaching causes the increase in surface area and pore volume by acid role during the acid treatment (Lu et al., 2020). The same finding was reported in several previous studies that the surface area increased due to the release of matrix material (Kumar et al., 2000; Bertero et al., 2019). It is also suggested that the release of Si and Al by the acid solution causes changes in the textural properties of the catalyst (Istadi et al., 2021).

# **3.2. Catalytic Performance of Spent RFCC Catalyst**

The effect of the acid treatment on the spent RFCC catalyst activity is investigated in the catalytic cracking palm oil process using the continuous fixed-bed catalytic reactor to produce biofuels, as presented in Table 4. Based on Table 4, the yield of OLP produced by all catalysts is not significantly different, with the value is higher than 90%. This fact confirms that the spent RFCC catalyst is still active enough even though it is not being treated. Unfortunately, the RFCC catalyst tends to have



Figure 3. N<sub>2</sub> sorption isotherms and pore size distribution of non-treated and acid-treated spent RFCC

Copyright © 2021, TEKNIK, p-ISSN: 0852-1697, e-ISSN: 240-9919

# TEKNIK, 42 (2), 2021, 223

Table 4. Catalytic performance of the non-treated and the acti-treated spent KI CC catalysis			
Parameters	RFCC	S-RFCC	C-RFCC
The yield of OLP (%)	91.18	90.90	93.53
Selectivity of Gasoline (%)	0.00	0.57	0.84
Selectivity of Kerosene-Diesel (%)	47.89	55.41	48.25
The yield of coke (%)	1.91	1.14	1.20
The yield of gas (%)	6.91	7.96	5.28

**Table 4.** Catalytic performance of the non-treated and the acid-treated spent RFCC catalysts

**Table 5.** Comparison of palm oil cracking to biofuels

Catalysta	Temperature	The yield of	Selectivity (%)			Deferences
Catalysis	(°C)	OLP (%)	Gasoline	Kerosene	Diesel	Kelefences
CaO	480	72.50	n.a.	n.a.	n.a.	(Junming et al., 2010)
Na <sub>2</sub> CO <sub>3</sub>	450	60.00	n.a.	n.a.	n.a.	(Mancio et al., 2016)
HZSM-5	450	65.00	45.00	17.00	3.00	(Bhatia et al., 2009)
MCM/Beta (komposit)	450	43.70	30.60	10.40	2.70	(Ooi et al., 2004)
Ni-Co/HY	450	40.00	11.79	28.54	57.95	(Istadi et al., 2021)
S-RFCC	450	90.90	0.57	55.4	1	This study
C-RFCC	450	93.53	0.84	48.2	5	This study

n.a. : not available

high coke formation due to the presence of many metal contaminants, as suggested by previous research where some metals in spent RFCC catalysts, especially Ni, V, and Fe, can increase coke formation (Akah, 2017). This spent RFCC property is not beneficial for the catalytic cracking process because the coke formation can shorten the catalyst's lifetime due to the deactivation process. In this case, the acid treatment to the spent RFCC catalyst is required, improving the catalytic activity by increasing the surface area and crystallinity of the catalysts through metals leaching.

With respect to the cracking product selectivity, the distribution of gasoline and kerosene-diesel selectivity in the liquid product is utilized to compare the catalytic activity of the non-acid and the acid-treated RFCC catalysts. The distribution of gasoline and kerosene-diesel selectivity is investigated by the batch-distillation process at atmospheric pressure, as presented in Table 4. Overall, the gasoline and kerosene-diesel selectivity in the acidtreated catalysts is higher than that of the spent RFCC catalyst. Compared to the spent RFCC, the selectivity of kerosene-diesel in the S-RFCC catalyst increases by about 17%. In contrast, the selectivity of kerosene-diesel obtained by the C-RFCC catalyst increases slightly. This result can be attributed to the role of the surface area of catalysts. As Hartati et al. (2020) discussed, one of the most influential properties of catalyst activity is surface area, which relates to pore structure. Zeolite was extensively investigated as porous acid catalysts for catalytic cracking due to the unique pore structures. Hence the shape and the porosity of zeolite influenced the selectivity and the composition of biofuel. Acid treatment on the catalyst reopens the pore and enhances both acidtreated samples' gasoline and kerosene-diesel product selectivity. As reported in Table 3, the S-RFCC catalyst has the highest surface area, which is reasonable, showing the highest selectivity. Istadi *et al.* (2021) reported that a larger surface area provides a larger active site area. On the other hand, a catalyst with a high surface area can increase the mass transfer efficiency so that the conversion process occurs efficiently.

Concerning the gasoline and kerosene-diesel selectivity obtained by the S-RFCC and the C-RFCC catalysts, it is found that the S-RFCC catalyst obtains higher kerosene-diesel selectivity than the C-RFCC catalyst leading to more gasoline productivity by the C-RFCC catalyst. However, the total gasoline and kerosenediesel selectivity of the S-RFCC catalyst are higher than the C-RFCC catalyst. In this case, the catalysts' surface area is responsible for the product selectivity, which is in line with the suggestion of Istadi et al. (2021), in which a larger surface area provides a larger area for the activity for adsorption reactants and surface reaction, leading to more mass transfer efficiency. In addition, it is probably attributed to the presence of higher crystallinity and surface areas coupling with solid acidity (Li et al., 2017). However, it is suggested that both sulfuric and citric acid treatment can increase the performance of the spent RFCC catalysts.

As can be seen in Table 5, it is found that the acidtreated RFCC catalysts produce a better result than the other results reported in some previous studies. The yield of OLP produced in this study is high. However, the selectivity of gasoline is still low. It shows that the reactivation of spent RFCC catalyst is still not adequate for gasoline production. However, it is noticeable that the selectivity of the kerosene-diesel fraction is high. Therefore, it is concluded that the reactivation of spent RFCC catalyst through acid treatments using sulfuric acid or citric acid can increase catalyst activity to produce kerosene-diesel fraction due to better catalysts properties after acid treatments.

#### 4. Conclusion

The results showed beneficial changes in the catalyst structure characterizations and components with sulfuric acid or citric acid treatment. The S-RFCC and the C-RFCC catalysts have increased surface area and pore volume, while according to the pore distribution curve, the acid-treated samples have larger pore sizes slightly than spent RFCC. Thus, it can be concluded that the changes in the textural properties were caused by removing heavy metal from the spent RFCC catalyst and the Si/Al ratio change due to the acid-treatments. Along with changes in the structure and components of the catalyst, the performance of catalytic cracking improves, where the acid-treated catalyst produces higher gasoline and kerosene-diesel selectivity rather than the spent RFCC catalyst, which produces lower coke. The spent RFCC tends to produce more coke because of the higher metal content of Ni and Fe.

## Acknowledgement

The authors would like to express their sincere gratitude to Research Institution and Community Ser-vice, Universitas Diponegoro, Indonesia, for the finan-cial support through the World Class Research Universi-tas Diponegoro (WCRU) research project category A with contract number 118-22/UN7.6.1/PP/2021.

## References

- Akah, A. (2017). Application of rare earths in fluid catalytic cracking: A review. J. Rare Earths, 35(10): 941–956.
- Alaba, P.A., Sani, Y.M., Mohammed, I.Y., Abakr, Y.A. and Daud, W.M.A.W. (2017). Synthesis and characterization of sulfated hierarchical nanoporous faujasite zeolite for efficient transesterification of shea butter. J. Clean. Prod., 142: 1987–1993.
- Astuti, W., Hirajima, T., Sasaki, K. and Okibe, N. (2016). Comparison of effectiveness of citric acid and other acids in leaching of low-grade Indonesian saprolitic ores. *Miner. Eng.*, 85: 1–16.
- Bertero, M., García, J.R., Falco, M. and Sedran, U. (2019). Equilibrium FCC catalysts to improve liquid products from biomass pyrolysis. *Renew. Energy*, 132: 11–18.

- Bhatia, S., Mohamed, A.R. and Shah, N.A.A. (2009). Composites as cracking catalysts in the production of biofuel from palm oil: Deactivation studies. *Chem. Eng. J.*, 155(1–2): 347–354.
- Cheng, J., Zhang, Z., Zhang, X., Liu, J., Zhou, J. and Cen, K. (2019). Sulfonated mesoporous Y zeolite with nickel to catalyze hydrocracking of microalgae biodiesel into jet fuel range hydrocarbons. *Int. J. Hydrogen Energy*, 44(3): 1650–1658.
- Hartati, H., Trisunaryanti, W., Mukti, R.R., Kartika, I.A., Firda, P.B.D., Sumbogo, S.D., Prasetyoko, D. and Bahruji, H. (2020). Highly selective hierarchical ZSM-5 from kaolin for catalytic cracking of Calophyllum inophyllum oil to biofuel. *J. Energy Inst.*, 93(6): 2238–2246.
- Ishihara, A. (2019). Preparation and reactivity of hierarchical catalysts in catalytic cracking. *Fuel Process. Technol.*, 194(May): 106116.
- Istadi, I., Riyanto, T., Buchori, L., Anggoro, D.D., Gilbert, G., Meiranti, K.A. and Khofiyanida, E. (2020). Enhancing Brønsted and Lewis Acid Sites of the Utilized Spent RFCC Catalyst Waste for the Continuous Cracking Process of Palm Oil to Biofuels. *Ind. Eng. Chem. Res.*, 59(20): 9459– 9468.
- Istadi, I., Riyanto, T., Buchori, L., Anggoro, D.D., Pakpahan, A.W.S. and Pakpahan, A.J. (2021). Biofuels Production from Catalytic Cracking of Palm Oil Using Modified HY Zeolite Catalysts over A Continuous Fixed Bed Catalytic Reactor. *Int. J. Renew. Energy Dev.*, 10(1): 149–156.
- Jin, W., Wang, B., Tuo, P., Li, C., Li, L., Zhao, H., Gao, X. and Shen, B. (2018). Selective Desilication, Mesopores Formation, and MTO Reaction Enhancement via Citric Acid Treatment of Zeolite SAPO-34. Ind. Eng. Chem. Res., 57(12): 4231– 4236.
- Junming, X., Jianchun, J., Jie, C. and Yunjuan, S. (2010). Biofuel production from catalytic cracking of woody oils. *Bioresour. Technol.*, 101(14): 5586– 5591.
- Kumar, S., Sinha, A.K., Hegde, S.G. and Sivasanker, S. (2000). Influence of mild dealumination on physicochemical, acidic and catalytic properties of H-ZSM-5. J. Mol. Catal. A Chem., 154(1–2): 115– 120.
- Le, T., Wang, Q., Ravindra, A. V., Li, X. and Ju, S. (2019). Microwave intensified synthesis of Zeolite-Y from spent FCC catalyst after acid activation. J. Alloys Compd., 776: 437–446.
- Li, C., Ma, J., Xiao, Z., Hector, S.B., Liu, R., Zuo, S., Xie, X., Zhang, A., Wu, H. and Liu, Q. (2018). Catalytic cracking of *Swida wilsoniana* oil for hydrocarbon biofuel over Cu-modified ZSM-5 zeolite. *Fuel*, 218: 59–66.

- Li, W., Zheng, J., Luo, Y. and Da, Z. (2016). Effect of hierarchical porosity and phosphorus modification on the catalytic properties of zeolite Y. *Appl. Surf. Sci.*, 382: 302–308.
- Li, W., Zheng, J., Luo, Y., Tu, C., Zhang, Y. and Da, Z. (2017). Hierarchical Zeolite Y with Full Crystallinity: Formation Mechanism and Catalytic Cracking Performance. *Energy and Fuels*, 31(4): 3804–3811.
- Lu, G., Lu, X. and Liu, P. (2020). Reactivation of spent FCC catalyst by mixed acid leaching for efficient catalytic cracking. J. Ind. Eng. Chem., 92: 236– 242.
- Makertihartha, I.G.B.N., Kadja, G.T.M., Gunawan, M.L., Mukti, R.R. and Subagjo, S. (2020). Exceptional aromatic distribution in the conversion of palm-oil to biohydrocarbon using zeolite-based catalyst. *J. Eng. Technol. Sci.*, 52(4): 584–597.
- Mancio, A.A., da Costa, K.M.B., Ferreira, C.C., Santos, M.C., Lhamas, D.E.L., da Mota, S.A.P., Leão, R.A.C., de Souza, R.O.M.A., Araújo, M.E., Borges, L.E.P. and Machado, N.T. (2016). Thermal catalytic cracking of crude palm oil at pilot scale: Effect of the percentage of Na<sub>2</sub>CO<sub>3</sub> on the quality of biofuels. *Ind. Crops Prod.*, 91: 32–43.
- Meng, X., Lian, Z., Wang, X., Shi, L. and Liu, N. (2020). Effect of dealumination of HZSM-5 by acid treatment on catalytic properties in nonhydrocracking of diesel. *Fuel*, 270(February): 117426.

- Miądlicki, P., Wróblewska, A., Kiełbasa, K., Koren, Z.C. and Michalkiewicz, B. (2021). Sulfuric acid modified clinoptilolite as a solid green catalyst for solvent-free α-pinene isomerization process. *Microporous Mesoporous Mater.*, 324(April): 111266.
- Ooi, Y.S., Zakaria, R., Mohamed, A.R. and Bhatia, S. (2004). Synthesis of composite material MCM-41/Beta and its catalytic performance in waste used palm oil cracking. *Appl. Catal. A Gen.*, 274(1–2): 15–23.
- Riyanto, T., Istadi, I., Buchori, L., Anggoro, D.D. and Dani Nandiyanto, A.B. (2020). Plasma-Assisted Catalytic Cracking as an Advanced Process for Vegetable Oils Conversion to Biofuels: A Mini Review. *Ind. Eng. Chem. Res.*, 59(40): 17632– 17652.
- Vieira, S.S., Magriotis, Z.M., Ribeiro, M.F., Graça, I., Fernandes, A., Lopes, J.M.F.M., Coelho, S.M., Santos, N.A. V. and Saczk, A.A. (2015). Use of HZSM-5 modified with citric acid as acid heterogeneous catalyst for biodiesel production via esterification of oleic acid. *Microporous Mesoporous Mater.*, 201: 160–168.
- Wang, X., Wang, K., Plackowski, C.A. and Nguyen, A. V. (2016). Sulfuric acid dissolution of 4A and Na-Y synthetic zeolites and effects on Na-Y surface and particle properties. *Appl. Surf. Sci.*, 367: 281– 290.
- Xin-Mei, L. and Zi-Feng, Y. (2001). Optimization of nanopores and acidity of USY zeolite by citric modification. *Catal. Today*, 68(1–3): 145–154.