

CRUDE PALM OIL GUM AS ADSORBENT TO REDUCE RESEARCH OCTANE NUMBER AND BOILING POINT OF BIOETHANOL FOR GASOHOL E-85

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ABSTRACT

The mixture of bioethanol with gasoline (gasohol) as vehicle fuel can increase the research octane number (RON) to perfect combustion and reduce carbon monoxide pollution from exhaust gases. The difference in electronegativity polarity causes the two fuels to be incompatible. This study aims to produce a homogeneous and compatible mixture of gasoline (85%) and bioethanol (15%) after the addition of crude palm oil (CPO) gum using degumming and distillation methods. The RON index calculation and physical properties of gasohol E-85 showed that the existence of CPO gum in bioethanol reduced the boiling point from 78 °C to 69 °C and the RON from 120 to 109. FTIR results showed that gasohol E-85 contains phosphatides, hydrocarbons, carboxylic acids, and tocopherols characteristic of CPO gum. The DSC results obtained a melting point of 43.8 °C which indicated that the CPO gum had mixed with bioethanol in gasohol E-85. The GC results of gasohol-85 obtained seven peaks indicating the presence of butylated hydroxytoluene, 1,9-decadiene, 4,4,7,7-tetramethyl, n-hexadecanoic acid, hexadecanoic acid, 2-hydroxy-1-(hydroxyl methyl) ethyl ester, 1-(3-methyl-2-butenyl)-2-phenylcyclopropane, and 9,9-bis(1"-indazolyl) -thioxanthene.

Keywords: CPO; Gasoline, Gasohol E-85, Bioethanol.

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INTRODUCTION

The use of petroleum as an energy source every year continues to increase along with the increase in population. Petroleum is widely used as a fuel for transportation (vehicles), industry, power generation, and households.^{1,2} One of the vehicle fuels that are relatively cheap and sourced from petroleum is gasoline. However, the dwindling availability of petroleum and its unrenowable has resulted in the price of gasoline being increasingly expensive. In addition, the gasoline combustion process is also imperfect, causing toxic gases such as CO, NO_x, HC, and SO_x.³⁻⁵ These problems can be overcome by using alternative renewable and environmentally friendly, such as bioethanol. This bioethanol can be produced from crude palm oil (CPO), containing 35% oxygen. Bioethanol can be applied as a vehicle fuel because it has the advantage that its oxygen content can oxidize fuel and produce complete combustion to reduce CO emissions, CO₂ emissions up to 40-80%, and is environmentally friendly. This bioethanol has properties similar to gasoline, such as volatile, soluble in water and ether, a density of 0.7937 g/cm³, and a boiling point of 78.32 °C, so these two fuels are often mixed. The mixture of bioethanol with gasoline (gasohol) as a vehicle fuel increases the RON value to produce perfect combustion and reduce carbon monoxide pollution from exhaust gases d.^{4,6-8} However, the problem is that bioethanol and gasoline have different electronegative polarities. Bioethanol has a boiling point and RON very high compared to gasoline. Bioethanol has a boiling point of 78 °C with a RON value of 120, while gasoline has a boiling point of 50 °C with a RON value of 88. If bioethanol is mixed with gasoline, it tends to form a separation between two immiscible and incompatible phases.⁹⁻¹¹ It has been previously reported that mixing 20% bioethanol in gasoline is incompatible and results in engine performance being damaged, slow, and prone

to corrosion of automotive components such as copper and carbon steel.¹²⁻¹⁴ One of the efforts made to result in a homogeneous and compatible mixture of bioethanol and gasoline is reducing the boiling point and RON value of bioethanol by using an adsorbent. The adsorbent used is gum from CPO, made via a degumming process. The CPO gum is believed to lower the boiling point and RON value so that bioethanol and gasoline can be mixed homogeneously and compatible because the CPO gum contains phosphatides, hydrocarbons, tocopherols, and carboxylic acid.¹⁵⁻¹⁷ The research aims to study the influence of CPO gum on reducing the boiling point and RON value of bioethanol, which is applied as fuel for gasohol E-85.

EXPERIMENTAL

Material

Bioethanol 96% was received from *PT. Energi Agro Nusantara*, Indonesia. Gasoline was purchased from *PT. Pertamina*, Indonesia. Crude palm oil (CPO) was supplied from *PT. Perkebunan Nusantara IV*, Indonesia. Sodium hydroxide and sodium chloride were obtained from Merck, Germany.

Extraction of CPO Gum using the Degumming Process

CPO was put into an Erlenmeyer, reacted with sodium hydroxide 20%% solution (w/v), and heated at 90-110 °C while stirring for 30 min. The oil mixture was put into a dropping funnel, washed using warm water by spraying it evenly over the surface of the oil, and allowed until water and gum were separated from the oil. The CPO gum at the bottom of the funnel is taken by opening the valve, put into an Erlenmeyer, and then added to a hot sodium chloride solution and stirred until the color changes to yellowish-white. The yellowish-white liquid in the form of gum was crystallized. The CPO gum was characterized using FT-IR. Next, the CPO gum was used as an adsorbent in bioethanol.

The Distillation of Bioethanol in the Existence of CPO Gum

CPO gum adsorbent of 4 g was put into a distillation flask containing 500 mL of bioethanol and heated at 80 °C while stirring for 30 min until the mixture was homogeneous. The mixture was distilled in a water bath at a temperature of 68 °C for 20 min. The distillate obtained in the future is called distilled bioethanol. Initial bioethanol and distillate bioethanol were characterized using Fourier Transform Infrared (FT-IR) and Gas Chromatography-Mass Spectra (GC-MS).

The Mixing Process of Bioethanol and Gasoline

150 ml of distillate bioethanol was put into an Erlenmeyer, added 850 ml of gasoline, and stirred for 15 min until homogeneous. The mixture obtained was in the form of gasohol E-85. The functional groups and their contents of gasohol E-85 were characterized using FT-IR and GC-MS. Next, the gasohol E-85 was analyzed for its physical properties and octane number. A similar treatment was also carried out on samples of initial bioethanol.

RESULTS AND DISCUSSION

FTIR Analysis of Bioethanol and CPO Gum

Bioethanol dan CPO gum in this study was characterized by FTIR Spectroscopy Shimadzu-8201PC as shown in

Fig.-1. The initial and distillate bioethanol FTIR spectrum did not significantly differ, but a chemical shift occurred. Initial and distillate bioethanol showed a broad and strong absorption band at 3391 cm^{-1} , which indicates the stretching vibration of the O-H group of the alcohol. The sharp band at 2949 cm^{-1} and 2837 cm^{-1} indicates the aliphatic -CH compounds. The sharp band at 1651 cm^{-1} indicates the presence of a C=C group. The sharp bands at 1451 cm^{-1} and 1391 cm^{-1} showed the bending vibrations of the methylene and methyl groups, and the bands at 1026 cm^{-1} indicate the absorption of -CO groups.¹⁵⁻¹⁷ Meanwhile, The FT-IR spectrum of CPO gum (

Fig.-1c) showed a broad and strong absorption band at 3430 cm^{-1} , which indicated the stretching vibration of the O-H hydroxyl group of carboxylic acids.¹⁸ Sharp bands at 2930 cm^{-1} and 2852 cm^{-1} indicate the presence of aliphatic CH compounds.¹⁹ The sharp and strong band at 1705 cm^{-1} showed the stretching vibration of the C=O carbonyl from the phospholipid group of unsaturated fatty acids, accompanied by the appearance of a sharp band at 1467 cm^{-1} , indicating the bending vibration of the methylene group and supported in the presence of a stretching vibration of the C-O group of the ester at 1126 cm^{-1} and the C-H

rocking of the at 712 cm^{-1} . The FTIR spectrum proved that the CPO gum contains phosphatides, hydrocarbons, carboxylic acids, and tocopherols.²⁰

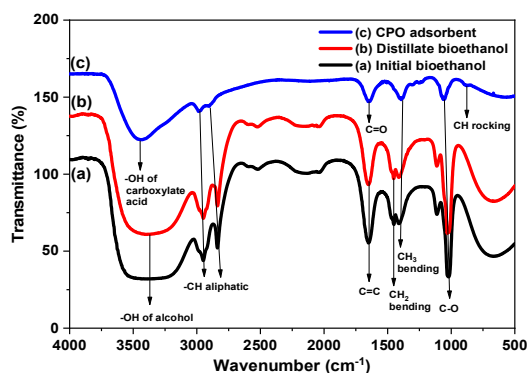


Fig.-1: FTIR Spectrum of (a) Bioethanol before Adsorption; (b) Bioethanol after Adsorption; and (c) CPO Gum

GC-MS Analysis of Initial and Distillate Bioethanol

Initial and distillate bioethanol was characterized using GC-MS QP-2010S Shimadzu to determine the compounds contained in the distillate bioethanol sample after the adsorption process using CPO. The GC-MS bioethanol chromatogram analysis data is shown in Fig.-2.

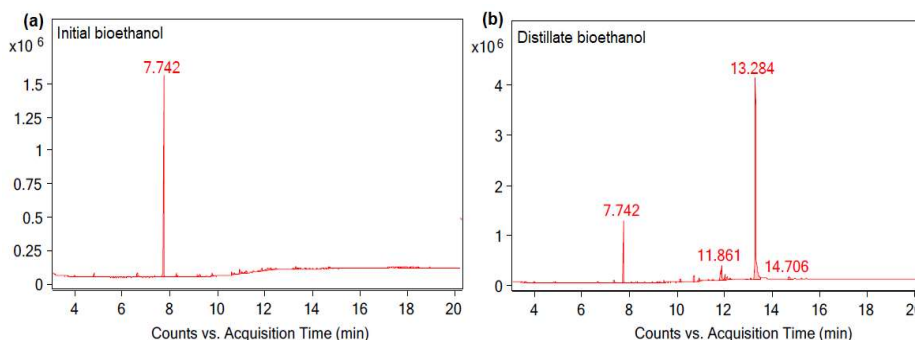


Fig.-2: GC-MS Chromatogram of (a) Initial Bioethanol; and (b) Distillate Bioethanol

Based on the result of the initial bioethanol (Fig.-2a), there is a sharp peak at the retention time of 1.581 min. It proves that the compound contained in the sample is initial bioethanol injected into a gas chromatograph.²⁰ Meanwhile, the analysis results of distillate bioethanol (Fig.-2b) showed four peaks with different retention times and areas. The highest peak was at peak 3 with a retention time of 13.284 min, while the lowest peak was at peak 4 with a retention time of 14.706 min. The content of compounds in the distillate bioethanol sample is presented in Table-1.

Table-1: Content of Distillate Bioethanol

No	Compound	Molecular Formulas	Retention Time (min)	Area (%)
1	Butylated Hydroxytoluene	$\text{C}_{15}\text{H}_{24}\text{O}$	7.742	8.13
2	9-Octadecenoic acid, methyl ester, (E)-	$\text{C}_{19}\text{H}_{36}\text{O}_2$	11.861	3.52
3	Methyl Ester of Ricinoleic Acid	$\text{C}_{19}\text{H}_{36}\text{O}_3$	13.284	45.35
4	bis[(Dimethyldithiocarbamoyl]-methane	$\text{C}_7\text{H}_{14}\text{N}_2\text{S}_4$	14.706	2.19

Based on the peak obtained, it is shown that CPO gum can reduce the boiling point and RON value of bioethanol. It can be seen that the presence of short-chain hydrocarbons in the first peak indicates the presence of butylated hydroxytoluene ($\text{C}_{15}\text{H}_{24}\text{O}$) compound of 8.13% with a retention time of 7.742 min. The third peak shows the presence of methyl ester of ricinoleic acid ($\text{C}_{19}\text{H}_{36}\text{O}_3$) compound, amounting to 45.35% with a retention time of 13.284 min. These constituent components prove the formation of bioethanol with a boiling point of 69°C and a concentration of 45.35%.

FTIR Analysis of Gasohol E-85

Gasohol E85 consists of gasoline (85%wt) with initial bioethanol or distillate bioethanol (15%wt). The FT-IR spectrum for the gasoline/bioethanol mixture is shown in Fig.-3. Based on the FT-IR spectrum, gasoline/bioethanol (gasohol E-85) using both initial and distillate bioethanol indicated no significant difference. However, there is a slight chemical shift in gasohol E-85 using distillate bioethanol. The similarity between the two spectra is that bioethanol using initial and distillate bioethanol is not different from each other.

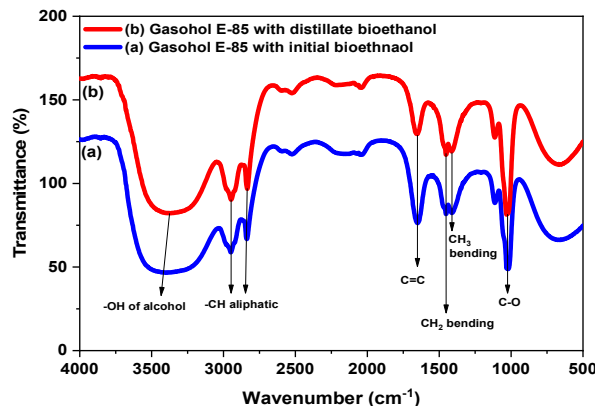


Fig.-3: FTIR Spectrum of Gasohol E-85 with (a) Initial Bioethanol; and (b) Distillate Bioethanol

In the FT-IR spectrum of gasohol E-85 with initial bioethanol (Fig.-3a), it is shown that there is a wide and strong band at 3393 cm^{-1} , which indicates the presence of stretching vibrations of the O-H from alcohol. The FT-IR spectrum of gasohol E-85 with distillate bioethanol showed a slight chemical shift at 3369 cm^{-1} . It is due to the difference in electronegative polarity between the atoms in the group. The mixing of bioethanol and gasoline was due to the different polarities in the hydroxyl group, which is the most polar chemical group.^{21,22} The existence of bioethanol in gasoline will cause the hydroxyl group to widen and become strong because of its shorter molecular structure. In contrast, gasoline is a complex mixture of non-polar alkane compounds to polar aromatic hydrocarbon. The two spectra also show strong and sharp absorption bands at 2948 cm^{-1} and 2838 cm^{-1} , indicating aliphatic -CH group stretching vibrations. The sharp and strong band at 1653 cm^{-1} indicated the presence of a C=C band from bioethanol. The bands at 1453 cm^{-1} and 1391 cm^{-1} indicated the presence of methylene and methyl groups. The band at 1045 cm^{-1} indicates the -CO group.²³⁻²⁶

GC-MS Analysis of Gasohol E-85

The addition of CPO gum into bioethanol decreased the boiling point and RON value so that bioethanol and gasoline can be mixed perfectly to achieve a compatible and homogeneous mixture because CPO gum contains phosphatides, hydrocarbon, carboxylic acids, and tocopherols.²³ The mixture of bioethanol and gasoline using distillate bioethanol is shown in Fig.-4.

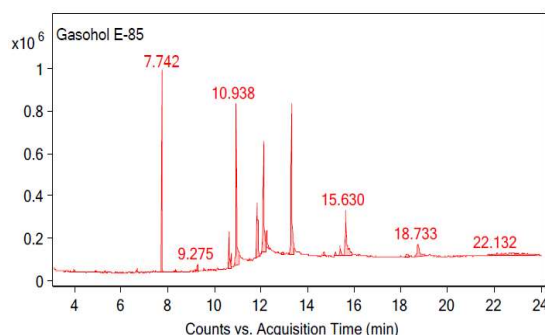


Fig.-4: GC-MS Chromatogram of Gasohol E-85 with Distillate Bioethanol

Chromatogram analysis of gasohol E-85 in the existence of distilled bioethanol resulted in six peaks with different retention times and areas. The highest peak was at peak 1 with a retention time of 7.742 min,

while the lowest peak was found at peak 6 with a retention time of 22.132 min. The content of compounds in the gasohol E-85 with distillate bioethanol sample is presented in Table-2.

Table-2: Content of Gasohol E-85 with Distillate Bioethanol

No	Compound	Molecular Formulas	Retention Time (min)	Area (%)
1	Butylated Hydroxytoluene	$C_{15}H_{24}O$	7.742	90.54
2	1,9-Decadiene, 4,4,7,7-tetramethyl	$C_{12}H_{26}$	9.275	20.98
3	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	10.938	87.03
4	Hexadecanoic acid, 2-hydroxy-1-(hydroxyl methyl)ethyl ester	$C_{19}H_{38}O_2$	15.630	49.9
5	1-(3-Methyl-2-butenyl)-2-phenyl cyclopropane	$C_{14}H_{18}$	18.733	23.51
6	9,9-bis(1"-Indazolyl)-thioxanthene	$C_{27}H_{18}N_4S$	15.722	22.132

Based on the chromatogram peaks (Fig.-4), it is known that CPO gum can reduce the boiling point and RON value of bioethanol, it is shown by the presence of short-chain hydrocarbons at the third peak, which indicates the presence of n-hexadecanoic acid ($C_{16}H_{32}O_2$) of 87.03% with a retention time of 10.938 min, and the first peak showed butylated hydroxytoluene ($C_{15}H_{24}O$) compound of 90.54% with a retention time of 7.742 min. The constituent components prove that bioethanol is formed with a boiling point of 69 °C and content of 90.54%, so obtained gasohol E-85 is shown in Table-3.

Table-3: Physical Properties Analysis of Gasohol E-85 with Distillate Bioethanol

No	Properties	Unit	Method	Result	Specification
1	Density at 15oC	kg/m ³	ASTM D 1298	809.1	Reported
2	Lead Content (Pb)	g/L	ASTM D 3341	-	-
3	RON		ASTM D 2699	109	Min.88
4	Distillation				
	IBP	°C		69	Reported
	10% Vol. Evaporation	°C		70	Max. 74
	50% Vol. Evaporation	°C		72	75-125
	90% Vol. Evaporation	°C		75	Max. 180
	End Point	°C		88	Max. 215
	Residue	%vol.		0.5	Max. 2.0
5	RVP at 37.8 °C	kPa	ASTM D 323	-	Max.62
6	Existent Gum	mg/100ml	ASTM D 381	-	Max.4.0
7	Sulfur Content	% mass	ASTM D 4294	-	Max.0.10
8	Copper Strip Corrosion test		ASTM D 130	No. 1	Max No. 1
9	Doctor Test		IP-30	-	Negative
10	Color		visual	Clear & Bright	Yellow
11	Induction Period	minutes	ASTM D 525	-	Min.240

Based on Table-3, gasohol E-85 has a boiling point of 69 °C, and RON 109, which means that the RON of gasohol from the bioethanol component can reduce, and the boiling point can reduce to 10 °C from the initial. The decrease in RON value from bioethanol was caused by the adsorption process of the CPO gum, where the CPO gum has adsorbed carbon chains in the bioethanol. Where gasohol E-85 with initial ethanol has a boiling point of 78 °C and RON 120, this study proves that gasohol E-85 can be reduced in the value of RON and boiling point by adsorption bioethanol using CPO gum.

Table-4: Analysis of Calculated Octane Index

Parameters	Units	Results	Methods
Calculated Octane Index	Gasohol E-85 with initial bioethanol	120	ASTM D4737-10 (2016)
	Gasohol E-85 with distillate bioethanol	109	

CONCLUSION

The function of CPO gum as an adsorbent has succeeded in reducing the RON value and boiling point of bioethanol which is applied together with gasoline to form gasohol E-85. The results of the GC-MS

analysis showed that CPO gum has phosphatides, hydrocarbons, carboxylic acids, and tocopherols that can be used as adsorbents for bioethanol. The results of the FTIR analysis showed that the use of CPO as an adsorbent did not affect changes in the functional group of bioethanol after distillation. Gasohol E-85 with initial bioethanol has a boiling point of 78 °C and a RON value of 120. While gasohol E-85 with distillate bioethanol after using CPO gum as an adsorbent, the boiling point decreases to 69 °C and the RON value of 109.

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REFERENCES

1. S. P. Choudhury, B. Saha, I. Haq, and A. S. Kalamdhad, *Advanced Organic Waste Management*, 277(2022), <http://doi.org/10.1016/B978-0-323-85792-5.00021-6>
2. E. Pursiheimo, H. Holttinen, and T. Koljonen, *Renewable Energy*, **136**, 1119(2019), <http://doi.org/10.1016/j.renene.2018.09.082>
3. H. K. S. Panahi, M. Dehghani, G. J. Guillemain, V. K. Gupta, S. S. Lam, M. Aghbashlo, and M. Tabatabaei, *Current Opinion in Food Science*, **43**, 71(2022), <http://doi.org/10.1016/j.cofs.2021.11.001>
4. S. N. A. Yusof, S. M. Basharie, N. A. C. Sidik, Y. Asako, and S. B. Mohamed, *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, **86(2)**, 136(2021), <http://doi.org/10.37934/arfmts.86.2.136146>
5. M. N. Dudin, E. E. Frolova, O. V. Protopopova, O. Mamedov, and S. V. Odintsov, *Entrepreneurship and Sustainability Issues*, **6(4)**, 1704(2019), [http://doi.org/10.9770/jesi.2019.6.4\(11\)](http://doi.org/10.9770/jesi.2019.6.4(11))
6. S. A. Aitkeldiyeva, E. R. Faizulina, L. G. Tatarkina, M. B. Alimzhanova, S. T. Daugaliyeva, O. N. Auezova, A. V. Alimbetova, G. A. Spankulova, and A. K. Sadanov, *Rasayan Journal of Chemistry*, **13(2)**, <http://dx.doi.org/10.31788/RJC.2020.1325580>
7. L. R. Sassykova, K. A. Kadirbekov, N. K. Zhakirova, A. S. Zhumakanova, S. Sendilvelan, T. S. Abildin, A. A. Batyrbayeva, R. N. Azhigulova, O. I. Ponomarenko, and R. G. Ryskaliyeva, *Rasayan Journal of Chemistry*, **13(4)**, 2085(2020), <http://dx.doi.org/10.31788/RJC.2020.1345852>
8. T. Güney, *International Journal of Sustainable Development & World Ecology*, **26(5)**, 389(2019), <http://doi.org/10.1080/13504509.2019.1595214>
9. H. X. Phong, N. N. Thanh, B. H. D. Long, and P. Thanonkeo, *Rasayan Journal of Chemistry*, **13(4)**, 2167(2020), <http://dx.doi.org/10.31788/RJC.2020.1345923>
10. Y. L. Calvin, P. A. T. Hariyanto, A. I. Usman, M. Masuku, C. S. Wibowo, R. Anggarani, N. A. Fathurrahman, and B. Sugiarto, *Fuel*, **307**, 121850(2022), <http://doi.org/10.1016/j.fuel.2021.121850>
11. A. Demirbas, M. A. Balubaid, A. M. Basahel, W. Ahmad, and M. H. Sheikh, *Petroleum Science and Technology*, **33(11)**, 1190(2015), <http://doi.org/10.1080/10916466.2015.1050506>
12. L. M. Baena, M. Gómez, and J. A. Calderón, *Fuel*, **95**, 320(2012), <http://doi.org/10.1016/j.fuel.2011.12.002>
13. L. M. Baena, F. A. Vásquez, and J. A. Calderón, *Heliyon*, **7(7)**, 07585(2021), <http://doi.org/10.1016/j.heliyon.2021.e07585>
14. M. M. Ali, T. T. Irawadi, N. Darmawan, M. Khotib, and Z. A. Mas'ud, *Makara Journal of Science*, **23(3)**, 6(2019), <http://doi.org/10.7454/mss.v23i3.11263>
15. S. Kaniapan, S. Hassan, H. Ya, K. Patma Nesan, and M. Azeem, *Sustainability*, **13(6)**, 3110(2021), <http://doi.org/10.3390/su13063110>
16. A. S. Peter, M. P. Alias, M. P. Iype, J. Jolly, V. Sankar, K. J. Babu, and D. K. Baby, *Materials Today: Proceedings*, **42(2)**, 1002(2021), <http://doi.org/10.1016/j.matpr.2020.11.995>
17. L. M. Serrano-Bermúdez, C. A. Monroy-Peña, D. Moreno, A. Abril, A. D. I. Niño, C. A. M. Riascos, G. B. Hurtado, and P. C. N. Rincón, *Food and Bioproducts Processing*, **129**, 75(2021), <http://doi.org/10.1016/j.fbp.2021.07.005>
18. N. Bakar and S. A. Muhammad, *Malaysian Journal of Analytical Sciences*, **23(5)**, 870(2019),

- <http://doi.org/10.17576/mjas-2019-2305-12>
19. P. M. Ramos, T. M. R. Maria, A. C. Guimaraes, P. C. Prieto, S. H. Navarro, and Jesus Martín Gil, *International Journal of Food Properties*, **20(3)**, S2739(2017), <http://doi.org/10.1080/10942912.2017.1372470>
 20. N. H. Azeman, N. A. Yusof, and A. I. Othman, *Asian Journal of Chemistry*, **27(5)**, 1569(2015), <http://doi.org/10.14233/ajchem.2015.17810>
 21. M. Amine, E. N. Awad, V. Ibrahim, and Y. Barakat, *Egyptian Journal of Petroleum*, **27(4)**, 567(2018), <http://doi.org/10.1016/j.ejpe.2017.08.007>
 22. S. A. Shirazi, B. Abdollahipoor, J. Martinson, B. Windom, T. D. Foust, and K. F. Reardon, *Fuel*, **252**, 542(2019), <http://doi.org/10.1016/j.fuel.2019.04.105>
 23. A. H. Ritonga, N. Jamarun, S. Arief, H. Aziz, D. A. Tanjung, B. Isfa, V. Sisca, and H. Faisal, *Journal of Materials Research and Technology*, **17**, 2326(2022), <http://doi.org/10.1016/j.jmrt.2022.01.125>
 24. A. H. Ritonga, N. Jamarun, S. Arief, H. Aziz, D. A. Tanjung, and B. Isfa, *Rasayan Journal of Chemistry*, **15(1)**, 190(2022), <http://doi.org/10.31788/RJC.2022.1516720>
 25. C. B. Labari, A. A. Goni, I. B. Pardo, M. G. Peinado, and J. F. Carrasquilla, *Materials & Design*, **32(1)**, 441(2011), <http://doi.org/10.1016/j.matdes.2010.06.017>
 26. Q. Xia, L. Yuan, X. Chen, L. Meng, and G. Huang, *Applied Sciences*, **9(24)**, 5336(2019), <http://doi.org/10.3390/app9245336>

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