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Research paper

Transesterification of biodiesel from kapok seed oil (ceiba pentandra) using a natural heterogeneous katalyst (rice husk activation)

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Abstract

Biodiesel as a renewable energy source can be produced by a chemical reaction between vegetable oil or animal fat and short-chain alcohol such as methanol, ethanol or buthanol and is supported by a catalyst. This process is called transesterification. From an environmental point of view, the use of biodiesel has several advantages such as reducing carbon dioxide emissions, being non-toxic and biodegradable. Kapok seed oil has potential for exploitation, particularly as a raw material for the manufacture of biofuel. Kapok seeds (Ceiba pentandra) have the potential to be used as a feedstock for biodiesel because their oil content is quite high, around 18-25% oil. The controlled combustion of rice husks produces ash containing high purity amorphous silica. Amorphous silica can be obtained from RHA (rice husk ash) when rice husk is burned at a temperature of 700°C, and it is transformed into crystalline silica when burned at a temperature above 850 °C. This silica has many applications as a filler, adsorbent, catalyst support, star gel component and source for the production of premium silicon and its compounds. The aim of the research is to determine the transisterification process of biodiesel from kapok (Ceiba pentandra) seed oil. using a natural heterogeneous catalyst in It is an activated rice husk. The method used was the preparation of kapok seed samples and the extraction of sokhlet. Determination of free fatty acids (FFA) in kapok seed oil, activation of rice husk, manufacturing of biodiesel from kapok seed with addition of rice husk H2SO4 as catalyst. The characteristics of the biodiesel produced are Density: 859.88572 kg/m3 (SNI: 7182:2015) = 850-890 kg/m3), Viscosity: 2.45824 cSt (SNI: 7182:2015) = 2.3 – 6, 0 cSt, Calorific value: 7,374.5322 cal/g (SNI: 7182; 2015) = 7,100 -11,000 cal/ g, Devil's number: 48 (ASTM: D6751) = 47. Meanwhile, GC-MS with the highest values at all reaction times, namely Hexadec anoic acid, methyl ester (C17H34O2), methyl tetradecanoate (C15H30O2) and 9 - Octadecenoic acid (Z), methyl ester (C19H36O2) . The functional group found in kapok seeds is –OH.

Keywords: *Biodiesel; Kapok Seeds; Rice Husks; Silica.*

1. Introduction

Increasing global energy demand due to rapid industrialization and population growth has led to increased interest in renewable fuel sources, such as biodiesel, biogas and bioethanol. (Demirbas, 2009b; Perea-Moreno et al., 2019). Among them, biodiesel attracts great attention because it is one of the most explored biofuels and can reduce global dependence on it fossil fuels and the greenhouse effect (Demirbas, 2009a; Toldrá-Reig et al., 2020). Biodiesel as a renewable energy source can be produced by a chemical reaction between vegetable oil or animal fat and short-chain alcohol such as methanol, ethanol or buthanol and is supported by a catalyst. This process is called transesterification. From an environmental point of view, the use of biodiesel has several advantages such as the reduction of carbon dioxide emissions, the fact that it is non-toxic and biodegradable (Maceiras et al, 2010).

Kapok seed oil contains 71.95% saturated fatty acids (Nixon Poltak, 2013), which is more than coconut oil. This shows that cottonseed oil goes rancid easily and is therefore not developed as a food oil. However, kapok seed oil has potential for exploitation, particularly as a raw material for the manufacture of biofuel. Kapok seeds (Ceiba pentandra) have the potential to be used as a feedstock for biodiesel because their oil content is quite high, around 18-25% oil. Kapok seed oil as a non-edible oil is relatively cheap and easy to obtain in Indonesia and has a high oil yield (Pooja et al, 2021).

The controlled combustion of rice husks produces ash containing high purity amorphous silica. Amorphous silica can be obtained from RHA (rice husk ash) when rice husk is burned at a temperature of 700°C, and it is transformed into crystalline silica when burned at a temperature above 850 °C (Fernandes et al., 2016).). Silica is a basic raw material widely used in semiconductors, ceramics, polymers and several industries, such as the rubber industry and the pharmaceutical industry (Fernandes et al., 2016). Silica can notably be used for the adsorption of gases (Dhaneswara et al., 2019, Fatriansyah et al., 2019) and the remediation of heavy metals in water (Dhaneswara et al., 2018). In mesoporous form, silica can also be used in gas adsorption applications (Wilson and Mahmud, 2015).

This silica has many applications as a filler, adsorbent, catalyst support, star gel component and source for the production of premium silicon and its compounds. Since silica can be produced from RHA, several reports have discussed the extraction of silica from rice husks.

This process not only produces valuable silica, but also reduces pollution problems caused by uncontrolled combustion of rice husks (Bonita et al, 2020). The aim of this research is to determine the process of transisterification of biodiesel from kapok seed oil (Ceiba pentandra) using a naturally heterogeneous catalyst, in this case activated rice husks.

2. Research methodology

2.1. Materials and tools

A set of sokhlet extraction equipment, analytical balance weighing equipment, oven, separating funnel, measuring cup, mixer, mess (filter), magnetic stirrer, flask with three necks, holder and clamp, glass beaker, dropper pipette, volumetric pipette, propipette, thermometer. , bath water, watch glass, Oswald viscometer, Erlenmeyer, biuret, oven, distillation, gegep, ash cup, spatula, condenser, beaker, hot plate and mortar pestle. Kapok seeds, methanol, distilled water, H2SO4, n-hexane solvent, PP indicator, 96% ethanol, rice husk and KOH.

2.2. Research procedure to make biodiesel from kapok seeds

1) Preparation of kapok seed samples

Kapok seeds were collected from the Pali region of South Sumatra. The kapok seeds used were old kapok seeds. The samples were taken randomly or what is usually called a random sampling technique. The samples collected were considered representative of kapok seeds from the Pali region. South Sumatra. The kapok seeds then undergo a first treatment, namely dried in the sun for approximately 7 days. Once dried, they are ground using a blender and filtered so that the kapok seed powder is uniform in size.

2) Sochlet Extraction
a) Samples of fine and dry kapok seeds were weighed 100 grams and then wrapped in filter paper.
b) The sample is then inserted into the Sokhlet extractor sleeve
c) The extraction flask was filled with 500 mL of nhexane solvent.
d) The sample was then extracted for 2 hours
e) The extraction results are in the form of solvents and dissolved substances which are then separated by distillation to obtain kapok seed oil.
3) Determination of free fatty acids (FFA) of Kapok seed oil
a) Kapok seed oil was weighed 5 grams then put into an Erlenmeyer flask
b) Add 50 ml of heated neutral alcohol (ethanol) and 3 drops of phenolphthalein indicator
c) The mixture was titrated with a standardized 0.1 N KOH solution until a pink color was obtained which did not disappear for 30 seconds.
d) Calculations were carried out to determine the FFA content of kapok seed oil.
4) Activation of rice husks
a) Clean the rice husks with water
b) Dry the rice husks in the oven at 110°C
c) Put 100 grams of rice husks in aluminum foil
d) Place the aluminum foil in the oven at a temperature of 500°C for 3 hours
e) Removing rice husk ashes from the oven
f) Cool the rice husk ashes for 30 minutes
g) Soak rice husk ash catalyst in H_2SO_4 for 24 hours
h) Heat the catalyst soaked in H_2SO_4 until all the H_2SO_4 has evaporated.
5) Make biodiesel from kapok seeds by adding rice husk H2SO4 as catalyst
a) Use of catalyst from immersion in the process of transesterification of kapok seed oil
b) Prepare a series of three-necked bottles with a capacity of 1 liter.
c) Prepare the condenser, stirrer, separating funnel and thermometer.
d) Put the methanol in a beaker with the catalyst and stir for 2 hours using a magnetic stirrer.
e) Put 100 ml of kapok seed oil in a trineck, heat it to a temperature of 60°C while stirring with a magnetic stirrer.
f) Put the methanol and catalyst in a three-necked flask for up to 4 hours.
g) Enter the results into a separatory funnel
h) Leave for 24 hours until 2 precipitates of biodiesel and glycerol form
i) Separate the top sediment suspected of being biodiesel.
j) Wash in lukewarm water until clear
k) Repeat the steps above with catalyst mass variations of 3%, 6%, 9%, 12%, 15% for each biodiesel manufacturing process (sample codes B_A, B_B, B_C, B_D and B_E)
l) Heat the results to a temperature of 100°C to remove the methanol and water and analyze the separation product results

3. Results and discussion

3.1. Fourier transform infrared (FTIR) analysis

1) Analysis of the chemical composition of Kapok seeds

The spectral data in Figure 1 examines the wave absorption peak shown based on the principle of instrumental analysis, Skoog, Holler, Nieman, (1998). From this figure it can be analyzed that the wave number is 1054.22 cm-1 with a strong absorption band and average width found in the area 1300cm-1-1000cm-1 which indicates the presence of compounds esters, namely C-O. With a wave number of 1539.18 cm-1 with a weak absorption band found in the region 1650 cm-1 – 1450 cm-1, it shows the presence of a double bond/aromatic ring of the group C=C. cm-1 with a weak absorption band. In the zone 1820cm-1 - 1600cm-1, we see the presence of a carbonyl group, namely C = O. At wave number 2031.17 cm-1, a weak but strong absorption The band is found in the zone 2150 cm-1, which shows the presence of a triple bond in the C=C group. , and is also found in areas that show the presence of a triple bond in the C-H group. at a wave number of 3273.60 cm-1 with a broad absorption band found in the region 3400cm-1-2400 cm-1 which indicates the presence of acidic compounds with –OH groups. According to this explanation, kapok seeds contain C-O, C=O groups, C=C double bonds, C=C triple bonds, C-H triple bonds and –OH groups, which are a class of carbohydrates under form of polycharides containing lignin, so it shows that kapok seeds can be used as a raw material to make biodiesel.

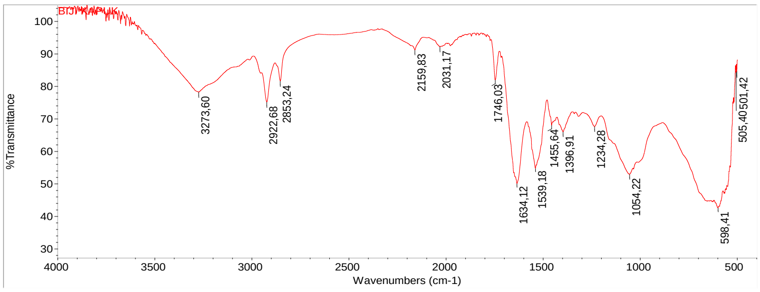

Fig. 1: FTIR Analysis of Kapok Seeds.

2) Analysis of the chemical composition of rice husks

The spectral data in Figure 1 examines the wave absorption peak shown based on the principle of instrumental analysis, Skoog, Holler, Nieman (1998) in Figure 1. They can be analyzed based on the number of wave 1032.90 cm-1 with a strong absorption band and the width of the middle indicates the stretching vibration of Si-O. At a wavenumber of 1506.75 cm-1, it shows the presence of a double bond/aromatic ring of the SiO4 tetrahedral group. Wave number 1635.54 cm-1 with weak absorption band indicates deformation, namely Si-O-Si. Wave-numbers with weak but sharp absorption bands are found in the 2150 cm-1 region, which indicates the O-H silanol stretching vibrations (Manique et al., 2012). Thus, rice husk ash has the potential to be an adsorbent in the biodiesel manufacturing process as a catalytic activation in kapok seed oil refining due to its high silica content.

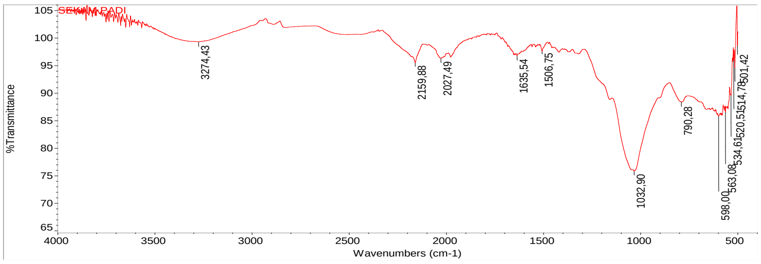

Fig. 2: FTIR Analysis of Rice Husks.

3) Kapok Seed Oil FFA (Free Fatty Acid)

Kapok seed oil used as raw material for biodiesel through transesterification reaction meets the requirements of water content less than 0.5% and FFA (free fatty acid) index > 5%, so that the saponification process does not occur during the manufacturing of biodiesel. (Gardy et al., 2016).

The following constitutes initial data on the characteristics of kapok seed oil before transesterification using a rice husk ash catalyst. According to Table 1, the FFA content of kapok seed oil is 4.6387%, so the transesterification method can be directly used (Lotero et al., 2015).

Table 1: Results of Raw Material Analysis of Kapok Seed Oil Before Transesterification

Physical/chemical properties of biodiesel	FFA
Free fatty acids (mgKOH/g) maximum	4,6387

4) Performance analysis of biodiesel results

Theoretically, variations in the catalyst of a process will affect the amount of biodiesel produced, i.e. the longer the transesterification process, the higher the yield of the resulting product. The longer the transesterification time, the more likely the molecules between the reactants will collide (Supardan, et al., 2014). In this study, the yield of the biodiesel product produced was BA<BB<BC<BD> BE. This is evident from the biodiesel yield results in Table 2.

Table 2: Biodiesel Yield Analysis Results

Code example	Oil mass (gr)	Mass biodiesel (gr)	Rendemen %
B_A	45,2200	32,0825	70,9576
B_B	46,0800	35,2625	76,5245
B_C	47,1165	38,0116	80,6758
B_D	48,3811	39,2842	81,1972
B_E	48,1103	38,9867	81,0361

5) Density Analysis of Biodiesel Results

Based on the biodiesel test results on each sample of B_A, B_B, B_C B_D and B_E at different temperatures, the stirring time in the transesterification reaction will produce different density values, even slightly. This research shows that the higher the number of catalysts used during the transesterification process, the higher the density value of biodiesel, as shown in Table 3. Phillips and Mattamal (2015) explain that the density value of esters d Carboxylic fatty acids are influenced by molecular weight. According to Ramirez et al (2012), density will decrease with increasing molecular weight and increase with increasing fatty acid saturation.

In SNI 7182:2015 regarding biodiesel, it is shown that the density value of biodiesel at 40°C is between 850 and 890 kg/m3. Test results for B_A, B_B, B_C, B_D and B_E biodiesel meet SNI 7182:2015 specifications. This shows variations in catalyst mass in the transesterification reaction of 3%, 6%, 9%, 12%, 15%, producing biodiesel with density values consistent with SNI 7182:2015.

Table 3: Density Analysis Results of Biodiesel Results

Code example	Catalyst %	Density (kg/m^3)	SNI 7182:2015 (kg/m^3)
B_A	3	855,4452	
B_B	6	858,7703	
B_C	9	859,9311	850-890
B_D	12	863,0792	
B_E	15	862,2528	

6) Viscosity analysis of biodiesel results

Viscosity is a number that indicates the amount of resistance a liquid material must flow or a measure of the amount of frictional resistance a liquid has.

The standard value of SNI 7182:2015 for biodiesel shows that the viscosity of biodiesel at 40 ^oC is between 2.3 and 6 cSt. The test results carried out on B_A, B_B, B_C, B_D and B_E biodiesel have a viscosity that exceeds the viscosity value of SNI 7182:2015. This shows that the catalyst mass variations in the transesterification reaction were 3%, 6%, 9%, 12%, 15% with stirring time of 120 minutes to produce biodiesel with conforming viscosity value. to the SNI 7182: 2015 standard. The viscosity results can be seen in table 4.

Table 4: Results of Viscosity Analysis on Biodiesel Results

Code example	Catalyst %	Viskositas mm^2/s(cSt)	SNI 7182:2015 mm^2/s(cSt)
B_A	3	2,3841	
B_B	6	2,4305	
B_C	9	2,4603	2,3-6,0
B_D	12	2,5120	
B_E	15	2,5043	

7) Calorific value

The calorific value of combustion indicates the amount of heat produced by a fuel that undergoes combustion with air or oxygen (Endang et al., 2015).

Table 5: Calorific Value Results of Biodiesel

Code example	Catalyst %	Calorific value (Cal/gr)
B_A	3	3.153,9234
B_B	6	3.578,9727
B_C	9	4.476,4369
B_D	12	7.374,5322
B_E	15	6.197,2017

Based on Table 5, it can be seen that the combustion power of the five types of biodiesel in the fourth sample is within the range of the calorific value of fuel oil, namely 7,100 to 11,000 cal/g.

8) Cetane number of biodiesel

The Satana index is an indication of how easily the fuel ignites when injected into the engine (Setyawardhani, et al, 2010). It is believed that a high cetane number allows for easier and better engine operation. The ASTM D6751 standard for biodiesel requires a minimum cetane number of 47, as shown in Table 5. Looking at the cetane number of the ASTM standard, in this study it meets the standard with a cetane number of 48. Thus, kapok seeds with the addition of activated rice husks and H_2SO_4 can be used as raw materials for biodiesel.

Table 5: Cetane Index Analysis Results in Biodiesel Results

Code example	Catalyst %	Cetane Index	ASTM D6751-08 Min
B_D	12	48	47

9) GC-MS Analysis of Biodiesel Results

The methyl esters resulting from the transesterification of kapok seed oil to biodiesel were analyzed by gas chromatography-mass spectroscopy (GC-MS). This analysis is a qualitative analysis that can be used to determine the type of fatty acid content of biodiesel and its quantity. The biodiesel methyl esters that were analyzed by GC-MS exhibit three dominant peaks, as presented in Table 6.

Table 6: Results of GC-MS Analysis of Biodiesel Results

Compound Name	Quantity (% Area)
Methyl ester, Hexadecanic acid	12,35
Methyl tetradecanoate	9,69
Methyl ester , 9-Octadecenoic acid (Z)	8,53

The results of GC-MS analysis of the methyl ester content of the obtained biodiesel include hexadecanoic acid methyl ester, methyl tetradecanoate, and 9-octadecenoic acid (Z) methyl ester.

4. Conclusion

1) Features of biodiesel research results include:

Density: 859.88572 kg/m3 (SNI: 7182:2015) = 850-890 kg/m3)
Viscosity: 2.45824 cSt (SNI:7182:2015) = 2.3 – 6.0 cSt
Calorific value: 7,374.5322 cal/g (SNI: 7182; 2015) = 7,100-11,000 cal/g
Cetane Index: 48 (ASTM: D6751) = 47

2) GC-MS with the highest scores at all reaction times, namely hexadecenoic acid, methyl ester ($C_{17}H_{34}O_2$), methyl tetradecanoate ($C_{15}H_{30}O_2$) and 9-octadecenoic acid (Z), the methyl ester ($C_{19}H_{36}O_2$). The functional group found in kapok seeds is –OH

References

[1] Demirbas.2009b. Biofuels securing the planet's future energy needs. Energy Convers. Manag., 50 (2009), pp. 2239-2249 https://doi.org/10.1016/j.enconman.2009.05.010.

[2] Demirbas.2009a. Progress and recent trends in biodiesel fuels. Energy Convers. Manag., 50 (2009), pp. 14-34 https://doi.org/10.1016/j.enconman.2008.09.001.

[3] Dhaneswara, D., Fatriansyah, J.F., Mahagnyana, A.B., Delayori, F., Putranto, D.A., Adriyani Anwar, S.U.A., 2018. The Role of Modification SBA-15 Mesoporous Silica with CPTMS in Cd Adsorptions. *In:* International Conference on Chemistry and Material Science, Volume 299(1), pp. 1–11 https://doi.org/10.1088/1757-899X/299/1/012063.

[4] Dhaneswara, D., Fatriansyah, J.F., Yusuf, M.B., Abdurrahman, M.H., Kuskendrianto, F.R., 2019. Study of Si Surface Adsorption Towards Hydrogen Molecule. *In:* IOP Conference Series: Materials Science and Engineering, Volume 547(1), pp. 1–7 https://doi.org/10.1088/1757-899X/547/1/012038.

[5] Donanta Dhaneswara., Jaka Fajar Fatriansyah., Frans Wensten Situmorang., Alfina Nurul Haqoh.2020. Synthesis of Amorphous Silica from Rice Husk Ash: Comparing HCl and CH_3COOH Acidification Methods and Various Alkaline Concentrations. International Journal of Technology (IJTech). Vol 11. No.1 https://doi.org/10.14716/ijtech.v11i1.3335.

[6] Dwi Ardiana Setyawardhani.,Sperisa Distantina.,Hayyu Henfiana.,Anita Saktika Dewi.2010.

[7] Pembuatan biodiesel Dari asam lemak jenuh minyak biji karet. Seminar Rekayasa Kimia Dan Proses 2010 ISSN : 1411-4216

[8] Endang Dwi Siswani, Susila Kristianingrum, Tohari. 2015. Sintesis Biodiesel Dari Minyak Biji Kapuk Randu (Ceiba Pentandra L) Pada Variasi Lama Pengadukan Pada Reaksi Transesterifikasi.Jurusan Pendidikan Kimia, FMIPA, Universitas Negeri Yogyakarta.

[9] Fatriansyah, J.F., Dhaneswara, D., Abdurrahman, M.H., Kuskendrianto, F.R., Yusuf, M.B., 2019. Modeling of Nitrogen Adsorption Phenomena in Amorphous Silica using Molecular Dynamics Method. AIP Conference Proceedings, Volume 2169(1), pp. 030001-1–030001-8 https://doi.org/10.1063/1.5132651.

[10] Fernandes, I.J., Calheiro, D.F., S?nchez, A.L., Camacho, A.L.D., de Campos Rocha, T.L.A., Moraes, C.B.A.M., de Sousa, V.C., 2016. Characterization of Silica Produced from Rice Husk Ash: Comparison of Purification and Processing Methods. Materials Research, Volume 20(2), pp. 512–518 https://doi.org/10.1590/1980-5373-mr-2016-1043.

[11] Gardy, J., Hassanpour, A., Lai, X., Ahmed, M.H., 2016. Synthesis of Ti (SO4) O solid acid nano-catalyst and its application for biodiesel production from used cooking oil. Appl. Catal. Gen. 527,81-95. https://doi.org/10.1016/j.apcata.2016.08.031.

[12] Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., & Goodwin,.G., 2005. Synthesis of Biodisel via Acid Catalysis, Indrustrial & Engineering Chemistry Research. 44(14), 5353-5363. https://doi.org/10.1021/ie049157g.

[13] Maceiras R, Rodrı´guez M, Cancela A, Urréjola S, Sánchez A. Macroalgae: Raw material for biodiesel production. Appl. Energy. [Internet]. 2023, 13 September]; 88(10):3318-23. Available from: http://www.sciencedirect.com/science/article/pii/S0306261910004903 https://doi.org/10.1016/j.apenergy.2010.11.027.

[14] Manique, M. C., Faccini, C. S., Onorevoli, B.,Benvenutti, E. V., dan Caramao, E.B .2012. Rice husk ash as an adsorbent for purifying biodiesel from waste frying oil, 92(2012), 56-61. https://doi.org/10.1016/j.fuel.2011.07.024.

[15] Miguel-Angel Perea-Moreno.,Esther Sameron-Manzano.,Alberto-Jesus Perea-Moreno.2019. Biomass as Renewable Energy: Worldwide Research Trends. *Sustainability*, *11*(3), 863; https://doi.org/10.3390/su11030863.

[16] Muhammad Dani Supardan, Satriana, Ryan Moulana., 2014. In Situ Transesterification of Jatropha Seed Using Hydrodynamic Cavitation., Jurusan Teknik Kimia, Universitas Syiah Kuala

[17] Nixon Poltak. F, 2013. Making Biodiesel from Kapok Seed Oil with esterification process of transesterification, Journal Technolgy Of Chemical Industrial, 2(2) p.262-266

[18] Phillips JC dan Mattamal GJ.1978. Effect of number of carboxyl groups on liquiddensity of esters of alkyl carboxylic acids.*J.Chem Eng.* 23(1): 1-6. https://doi.org/10.1021/je60076a031.

[19] Pooja.S.,Anbarasan.B.,Ponussami.V.2021. Efficient production and optimization of biodiesel from kapok (*Ceiba pentandra*) oil by lipase transesterification process: Addressing positive environmental impact.Renewable Energy.Volume 165,Part 1.Page 619-631 https://doi.org/10.1016/j.renene.2020.11.053.

[20] Skoog, Holler, Nieman, 1998, Principle of Instrumental Analysis, Stanford University, United States of America.

[21] Ramirez-Verduzco LF, Rodriguez-Rodriguez JE, Jaramillo-Jacob A. 2012.Predicting cetane number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acidmethyl ester composition.*J Fuel.* 91 (1): 102-111. https://doi.org/10.1016/j.fuel.2011.06.070.

[22] Wilson, L.D., Mahmud, S.T., 2015. The Adsorption Properties of Surface-modified Mesoporous Silica Materials with ß-Cylodextrin. International Journal of Technology, Volume 6(4), pp. 533–545 https://doi.org/10.14716/ijtech.v6i4.2036.

[23] Toldrá-Reig, L. Mora, F. Toldrá.2020. Trends in biodiesel production from animal fat waste. Appl. Sci., 10 (2020), p. 3644. https://doi.org/10.3390/app10103644.