Production of Biodiesel from Palm Oil using Catalysts Derived from Local Shells in Loei Province

Mallika Lapunt*

Physics Program, Department of Science, Faculty of Science and Technology, Loei Rajabhat University, 42000 Thailand

Received 16 March 2018; Revised 30 June 2018; Accepted 12 July 2018

Abstract

This research studied the use of synthetic calcium oxide derived from shells (Scabies phaselus, Chamberlainia hainesiana and Corbicula javanica) as a catalyst for producing biodiesel from palm oil. When shells are calcined, calcium carbonate changed to calcium oxide, which is an effective for the trans-esterification of palm oil. The temperature of calcination of the shells was 900 °C for 4 hours. The molar ratio of methanol to oil was 9:1 for this reaction and the optimum reaction time and temperature were 60 °C for 30 minutes, When the catalyst level from big shells (Chamberlainia hainesiana) was at about 2, biodiesel yield was 56 ml, or 78.32 of the 71.50 ml of palm oil mixed with methanol to 100 ml, This was the optimum due to the density value being in the ASTM D 1298 standard range of 860 to 900 kg m^{-3} and the viscosity value being in the ASTM D 445 range of 3.50 to 5.00 cSt. The biodiesel obtained was transparent. Other results were that, when the catalyst level from Scabies phaselus shells was about at 2.50, the biodiesel yield was 52.83 ml, or 73.89 and when the Corbicula javanica shell catalyst level was at 2, the biodiesel yield was 49.33 ml, or 69.

KEYWORDS: Biodiesel; Trans-esterification reaction; Calcium oxide Local shells

* Corresponding authors; e-mail: mallika.pud@gmail.com

Introduction

At present, fuel and energy problems in Thailand have become critical, because of insufficient petroleum sources for the needs of Thai people. According to expectations, petroleum came to an end while fuel and energy consumption rapidly increases every year [1]. A search for new energy sources replace petroleum is urgently required. This problem has led to recent studies on alternative energy. An interesting and possible alternative energy source is to produce fuel from agricultural products [2]. To do that, existing agricultural products are processed into biodiesel. Methyl ester or Ethyl ester occurs after the fuels derived from vegetable oil [3] and animal fat [4, 5] are chemically processed. The products can be use in a diesel engine without any engine modification because of having high quality similar to diesel distilled from petroleum. Thailand is an agricultural country; there are a lots of raw materials sources for biodiesel production such as coconuts, palm, sunflower seeds, soybeans, peanuts, Castor beans, sesame, Jatropha, and rubber seed [6 – 8]. Moreover, using vegetable oil can be transformed into biodiesel [9]. However, oil palm has been highly effective for biodiesel production [10], because it is adaptable to changing environmental conditions and the product growth per year is plentifully high. Biodiesel has been produced from palm oil using a calcium catalyst from shells and eggshell. The solid catalyst derived from shells and eggshells was used as a catalyst for biodiesel production by trans-esterification using palm oil. To transform the chemical structure of calcium into calcium oxide depends on various factors such as catalyst type, the amount of catalyst, time, and temperature. In the reaction, these catalysts heighten biodiesel products in trans-esterification [11, 12]. From previous research, in order to assure effectiveness of biodiesel production from palm oil, the results show that using local shells as catalyst can effectively produce international standard biodiesel [13 – 19].

The researchers were interested in studying the quality of biodiesel produced using catalyst derived from local shells, Scabies phaselus, Chamberlainia hainesiana and Corbicula javanica, which are bivalve shells found in the Loei river. The catalysts derived from the shells and palm oil are available in the local area. The significant value added to the useless shells and cheap palm oil was the trans-esterification for biodiesel production.

Materials and Methods

Calcium oxide from Scabies phaselus, Chamberlainia hainesiana and Corbicula javanica shells

The shells of Scabies phaselus, Chamberlainia hainesiana and Corbicula javanica found in the Loei The three types of shells were cleaned without shell size classification. Then, they were dried them in the sun or baked at 100 °C for around 1 to 2 hours. After that, the shells were calcined at 900 °C for 4 hours. After the shell grinding process, particle size selection was effected by the use of an 80 Mesh according to the ASTM E1 1 standard. The particles after the calcining procedure were examined by XRD (Bruker AXS, D8 Advance model) at 40 kV CuK_{α} and 40 mA of current. Shell characteristic are shown in Fig. 1

(a) (b) (c)

Fig. 1 Shell characteristics of (a) Corbicula javanica (b) Scabies phaselus and (c) Chamberlainia hainesiana

Biodiesel production

Palm oil is the main factor affecting the quality of biodiesel. In the experiment, new oil could not be used to produce biodiesel directly, so palm oil and methanol were mixed together in a 300 ml beaker. The molar ratio of methanol to oil was 9:1. In 100 ml, there were 28.50 ml of methanol and 71.50 ml of palm oil. Then, the mixture was boiled on a hot plate at 60 °C for the reaction. The calcium oxide catalyst was used at 2, 2.5, 3, 3.5, and 4 per palm oil weight.

The liquid mixing rate was 600 RPM for 30 minutes of reaction. After finishing, the resulting product was rest for 2 hours so that methyl ester and glycerol were cracked. The upper layer was filtered in order to separate the catalyst from the oil. Then, it was boiled on an electric stove at 60/70 °C for ethanol evaporation. The experiment was repeated with different catalysts 3 times. Then, the average score was compared with the yield percentage of biodiesel with different catalysts. The synthetic biodiesel procedure is shown in Fig. 2.

(a) (b) (c)

Fig. 2 Synthetic biodiesel procedure (a) the ratio of methanol to oil was 9:1, boiled on an electric stove at 60 °C (b) the oil after adding calcium oxide catalyst (c) oil filtration to separate catalyst from biodiesel

The analysis of biodiesel properties compared with standard

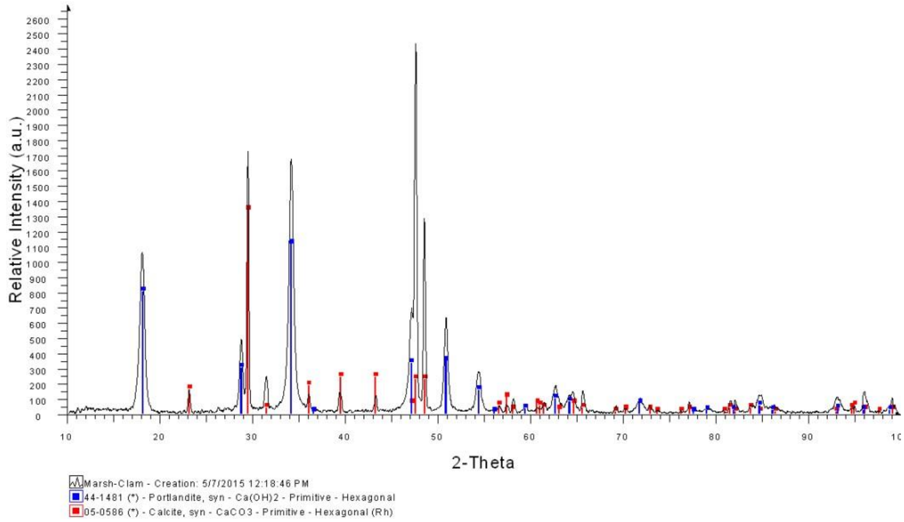
Biodiesel synthesis at optimum conditions was conducted to examine the chemical properties (yield percentage of biodiesel and approximate percentage of methyl ether by microwave) and fuel properties (color, density, and viscosity) according to the ASTM D 6751 standardized test.

Results and Discussion

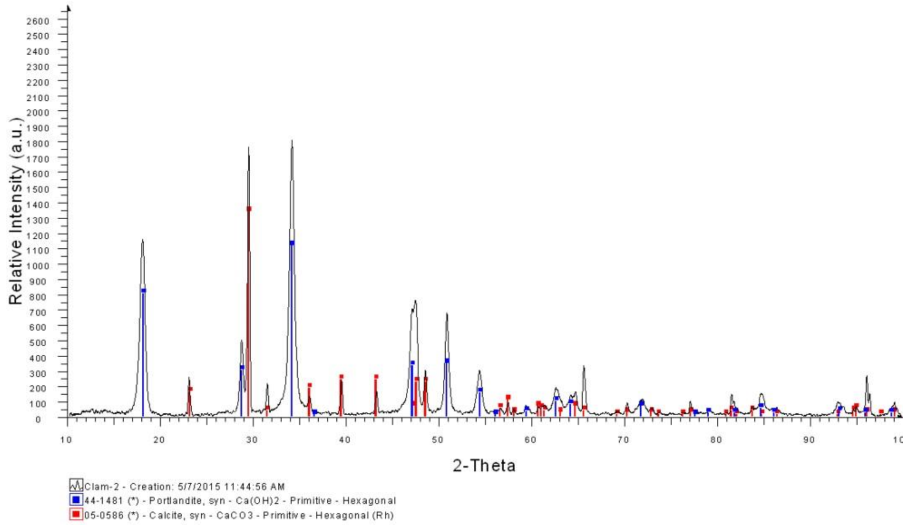
After Scabies phaselus, Chamberlainia hainesiana, and Corbicula javanica shells were used in the calcite procedure for 4 hours, $CaCO_3$ was observed with peaks at 29.48°, 39.44°, 43.17°, 47.72° and 48.62°, (in comparison with the JCPDS data base, registered number 72-1651). The calcite reaction is shown in equation (1) . During the experiment, three types of shells were kept at room temperature and humidity, and the peaks of calcium hydroxide ($Ca(OH)_2$) appeared. Calcium oxide from the three types of shells absorbed the humidity well [20], as indicated in equation (2) and Fig. 3.

$$CaCO_3(s) \xrightarrow{heat} CaO(s) + CO_2(g) \quad (1)$$

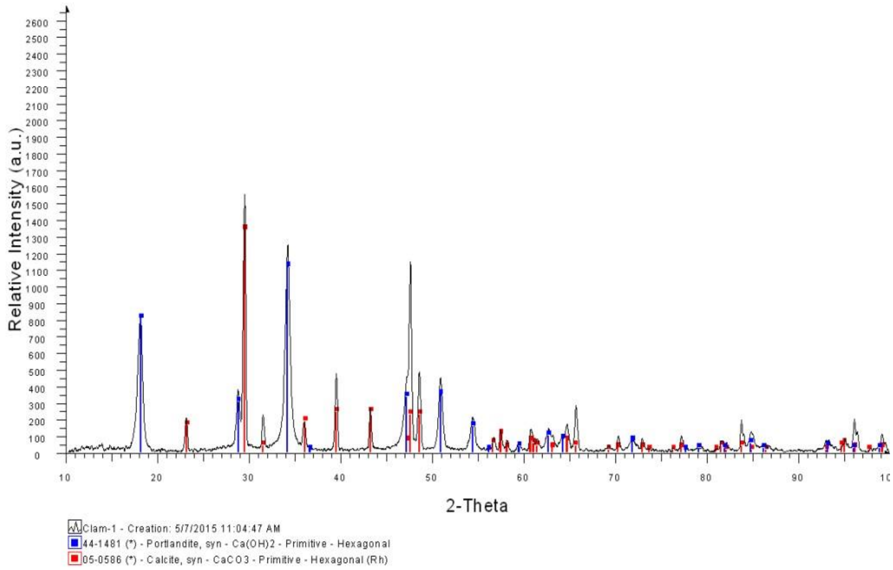
$$CaO(s) + H_2O(l) \xrightarrow{\Delta} Ca(OH)_2(s) \quad (2)$$



(a)



(b)



(c)

Fig. 3 XRD spectra from the shells (a) Scabies phaselus (b) Corbicula javanica and (c) Chamberlainia hainesiana.

From Table 1, the results show that the catalyst obtained from the big shells (Chamberlainia hainesiana) use at 2%, had biodiesel yield of 56 ml, or 78.32% of the initial 71.50 ml of palm oil, which was the highest yield. Secondly, the catalyst from Scabies phaselus shell at about 2.50%, gave biodiesel yield of 52.83 ml, or 73.89%. Lastly, the catalyst from Corbicula javanica shell at about 2%, gave biodiesel yield of 49.33 ml, or 68.99%. The biodiesel color was transparent yellow which was to the ASTEM D 6751 biodiesel standard, as shown in Fig. 4. To find the density affecting oil viscosity, the range of biodiesel standard density was from 860 to 900 kg m^{-3} according to ASTM D 1298 standard. The value for biodiesel catalyzed using Scabies phaselus shell exceeded the standard by 4%. After using the Digital Display Viscometer, it was revealed that the viscosity value of biodiesel according to ASTM D 445 standard was a minimum of 3 . 5 0 cSt and a maximum of 5 .0 0 cSt. From Table 1, it is seen that the catalyst viscosity from Scabies phaselus shell at 23.50 was in the standard range. The viscosity from Corbicula javanica shell catalyst at 2 3 was in the standard range. Similarly, viscosity from Chamberlainia hainesiana shell catalyst at 2, 3 was in the standard range. After the analysis to find methyl ester percentage, the approximate methyl ester percentage of biodiesel corresponded with the EN 14103 standard.

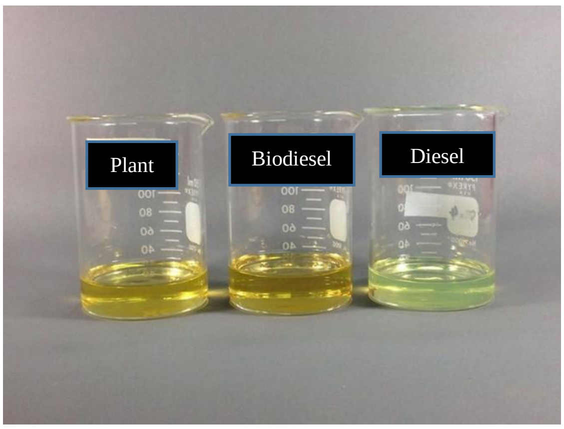


Fig. 4 Biodiesel color compared with vegetable oil color and diesel color

Table 1 The properties of synthetic biodiesel with standard interpretation.

Type of catalyst	Catalyst (%)	Yield (%)	Color (ASTEM D 6751)	Average density (kg m^{-3}) (ASTM D 1298)	Average viscosity (cSt) (ASTM D 445)	Approximate percentage of methyl ester (%) (EN 14103)
Scabies phaselus shell	2	66.67	Transparent yellow	895.04	4.82	99.43
	2.5	73.89	Transparent yellow	889.63	4.86	99.54
	3	65.50	Transparent yellow	889.65	4.45	99.33
	3.5	63.86	Transparent yellow	890.49	3.88	99.11
	4	54.54	Transparent yellow	871.78	2.39	98.50
Corbicula javanica shell	2	68.99	Transparent yellow	878.37	4.96	99.34
	2.5	64.80	Transparent yellow	899.17	4.80	99.18
	3	67.13	Transparent yellow	882.34	4.24	98.98
	3.5	67.59	Transparent yellow	875.85	3.22	98.74
	4	67.13	Transparent yellow	902.89	2.29	97.98
Chamberlainia hainesiana shell	2	78.32	Transparent yellow	898.85	5.03	99.53
	2.5	63.64	Transparent yellow	901.20	3.95	99.52
	3	69.23	Transparent yellow	888.95	3.92	99.23
	3.5	66.20	Transparent yellow	880.13	3.58	98.98
	4	63.87	Transparent yellow	949.11	3.14	98.75

Conclusion

The analysis results of catalyst from the shells of Scabies phaselus, Chamberlainia hainesiana, and Corbicula javanica showed that calcium was structurally transformed into calcium oxide, and the graphs of Scabies phaselus and Corbicula javanica shells showed peaks at almost equal levels. Calcium oxide derived from shells (Scabies phaselus, Chamberlainia hainesiana, and Corbicula javanica) can be used as a catalyst. In the experiment, biodiesel was produced by three types of shells calcined at 900 °C for 4 hours. It was reacted at 60 °C for 30 minutes. The molar ratio of methanol to palm oil was 9:1. The liquid mixing rate was 600 RPM, and the amount of catalyst was varied from 2 4 by palm weight. According to ASTEM D 6751 biodiesel standard, the color of the oil was transparent yellow. The density range was from 560 to 900 kg m^{-3}.

Only the density value from Scabies phaselus shell at 4 percent was over the ASTM D 1298 standard. After viscosity analysis, the results showed that the value range was from 3.50 cSt to 5 .0 0 cSt according to ASTM D 445 biodiesel standard. The viscosity of biodiesel derived from the catalyst from Scabies phaselus shell at 23.50 was in the standard range. The viscosity of biodiesel using catalyst from Corbicula javanica shell at 2 3 was in the standard range. Also, the viscosity of biodiesel using Chamberlainia hainesiana shell catalyst at 2 3 was in the standard range. The minimum percentage of methyl ester in biodiesel was 96.50%, which was according to the EN 14103 standard. At catalyst percentage from Chamberlainia hainesiana shell of about at 2 %, the highest biodiesel yield was 56 ml, or 78.32%. Secondly, biodiesel yield derived using catalyst from Scabies phaselus shells at 2.50% was 52.83 ml, or 73.89%. Finally, biodiesel derived from synthetic catalyst of Corbicula javanica shell at 2% was 49.33 ml, or 69.00%.

Acknowledgements

This research was entirely supported by the Science Center, Loei Rajabhat University in terms of chemicals preparation and instruments for analyzing biodiesel properties and was funded by Loei Rajabhat University.

References

[1] F. Ma and M.A. Hanna, Biodiesel production: a review, Biores Technol. 70 (1990) 1 – 15.
[2] B.K. Barnwal, M.P. Sharma, Prospects of biodiesel production from vegetable oils in India, Renewable Sustainable Energy Rev. 90 (2005) 363 – 78.
[3] C.L. Peterson., D.L. Auld, Technical overview of vegetable oil as a transportation fuel, FACT. 12 (1991) 44 – 53.
[4] P.R. Muniyappa, S.C. Brammer, H. Noureddini, Improved conversion of plant oils and animal fats into biodiesel and co-product, Biores Technol. 56 (1996) 19 – 24.
[5] F. Ma, L.D. Clements, M.A. Hanna, The effect of mixing on transesterification of beef tallow, Biores Technol. 69 (1999) 289 – 293.
[6] X. Lang, A.K. Dalai, N.N. Bakhshi, M.J. Reaney, P.B. Hertz, Preparation and characterization of bio-diesels from various bio-oils, Biores Technol. 80 (2000) 53 – 62.
[7] K. Ramezani, S. Rowshanzamir, M.H. Eikani, Castor oil transesterification reaction: A kinetic study and optimization of parameters, Energy. 35 (2010) 4142 – 4148.
[8] A.S. Ramadhas, S. Jayaraj, C. Muraleeharan, Biodiesel production from high FFA rubber seed oil, Fuel. 84 (2005) 335 – 340.
[9] R. Alcantara, J. Amores, L. Canoira, E. Fidalgo, M.J. Franco, A. Navarro, Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow, Biomass Bioenergy. 18 (2000) 515 – 27.
[10] D. Darnoko, M. Cheryan, Kinetics of palm oil transesterification in a batch reactor, J. Am Oil Chem Soc. 77 (2000) 1263 – 1267.
[11] H. Fukuda, A. Kondo, H. Noda, Biodiesel fuel production by transesterification of oils, J. Biosci Bioeng. 92 (2001) 405 – 416.
[12] H. Noureddini, D. Zhu, Kinetics of transesterification of soybean oil. J. Am Oil Chem Soc. 74 (1997) 1457 – 1463.
[13] C. Nangwieng, Biodiesel production by using activated carbon and calcium oxide as a heterogeneous catalyst, Master's Thesis, Silpakorn University, Nakhon Pathom, 2010.
[14] N. Sungthing, A. Nonting, Biodiesel production from palm oil by using calcium-based catalyst, Master's Thesis, Khon Kaen University, Khon Kaen, 2012.
[15] R. Sittikan, Biodiesel production using polymer supported phase transfer catalyst, Master's Thesis, Silpakorn University, Nakhon Pathom, 2011.
[16] P. Benjapreechaphat, Biodiesel production from palm oil using lipase immobilized on montmorillonite, Master's Thesis, Srinakharinwirot University, Bangkok, 2012.
[17] C. Chaiburi, P. Sumanatrakul, Biodiesel production from palm oil using cutlebone as catalyst, Burapha Sci. J. 18 (2556) 1 – 7.
[18] S. Hatthason, R. Pairintra, K. Krisnangkura, Comparison of Biodiesel Production Using CaO of Cockle Shell and Mud Crab Shell Catalysts, Agricultural Sci. J. 44 (2013) 553 – 556.
[19] S. Boonyuen, S. Ruengsuttinaruebhap, Y. Amnuaybhanich, T. Thapkri, Biodiesel production using synthetic heterogeneous catalyst from useless shells, Technol. Sci. J. 21 (2013) 526 – 532.
[20] M. Mustakimah, Y. Suzana, M. Saikat, Decomposition study of calcium carbonate in cockle shell, J. Eng. Sci. Tech nol. 7 (2012) 1 – 10.