Development of a Learning Module Based on Biofuel Synthesis Laboratory Research from CPO Residual of Palm Oil Mill Effluent (POME) with Ultrasonic Irradiation Assistance

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Abstract—**Indonesia is the largest palm oil producer in the world, of which 19 Palm Oil Mills (POM) are in Bengkulu Province. POM in Bengkulu generally processes palm fruit bunches into Crude Palm Oil (CPO) with the by-products of Palm Oil Mill Effluent (POME) which contains CPO residues (CPO-res) as much as 0.6-1.2%. CPO-res are cheap raw materials for the manufacture of biofuels. The purpose of this study was to develop a module based on laboratory research of synthesis of biofuel. Synthesis of biofuels was done by esterification with an acid catalyst, followed by a trans esterification using a base catalyst, both reactions are carried out with ultrasonic irradiation assistance at a frequency of 45 kHz, temperature 60°C, for 30 minutes. This laboratory research was then developed as a module; the module was then used in learning chemistry after being validated by expert judgment. The biofuel has a density of 0.852 g / mL, kinematic viscosity of 1.692 cSt, fog point = 8.84 ° C, pour point = 11°C, acid number = 1.122 mg KOH / g oil and water content = 0.739%. Modules developed from research into biofuel production after being validated by expert judgment on good value (4.71) at the level of trustworthy validation trust (0.846) can be used in learning organic chemistry.**

Keywords—*biofuel; CPO; ultrasonic irradiation; module; POME*

I. INTRODUCTION

The fossil-based energy availability on this earth is dwindling. In Indonesia the use of fossil energy in this case fuel oil from year after year has experienced a significant increase in all sectors. Development of alternative energy is important to minimize the possibility of a future oil crisis. Methyl esters are biofuels that have the same physical and chemical properties as petroleum. So they can be used as alternative energy [1,2]. Methyl ester is environmentally friendly, because it is biodegradable, non-toxic, and the exhaust gas is smaller than petroleum. Methyl ester (biofuel) can be used directly without modifying existing machines. Biofuel is the result of esterification of triglycerides with methanol [3].

Biofuels can be made from animal fats, grains, algae and palm oil [4].

Indonesia is the producer the Crude Palm Oil (CPO) number one in the world [5]. Indonesia still has a competitive forte CPO [6], to increase the production of 32.5 million tons in 2015 to 43.93 million tons in 2020 [7,8]. With the availability of raw materials, Indonesia has a huge opportunity to become a biofuel producer from CPO. Biofuels can be made from palm oil by means of trans esterification using NaOH or KOH catalyst [9,10]. CPO is a food, if then biofuels developed from CPO meal will be competition between the use of palm oil as food oil and biofuels, apart of this, the price of CPO is not cheap as the raw material, for it is better biofuels is developed from CPO off grade [11].

The increase in CPO production of palm oil mills was also followed by an increase in waste in the form of either solids or liquid waste (Palm Oil Mill Effluent = POME). The POME there are still contain 0.6-1.2% CPO. CPO that was extracted from POME (CPO-res) can be converted into biofuel through two reaction steps, namely the esterification reaction using an acid catalyst with a reaction time of 3 hours, followed by a trans esterification reaction using a base catalyst with a reaction time of 3 hours. Trans esterification reactions can be carried out, if the esterification of biofuel ALB has reached a price of ≤2% [12]. In this study biofuel was synthesized from raw materials with low economic value, namely CPO-res through esterification and trans esterification reactions with the help of ultrasonic irradiation to shorten the reaction time of each of them to 20 minutes.

Alternative fuels conversion as a substitute for fossil fuels is a very good knowledge for owned by students. Therefore, research on biofuel synthesis of CPO-res was then developed as an organic chemistry learning module using the ADDIE development model.

II. RESEARCH AND METHOD

This research and development (R & D) uses the ADDIE model. The learning material that was developed, as a module was the synthesis of alternative fuels (biofuel) from CPO-res with the help of ultrasonic irradiation

A. Laboratory Researches

1) Processing CPO residues from POME (CPO-res): CPO-res is heated, then the degumming process was carried out by adding 0.6% phosphoric acid (H_3PO_4) as much as 1-3% of the raw material volume, after stirring for 30 minutes, the precipitate was separated. CPO-res was further bleached by adding active zeolites, then determining the level of free fatty acids (ALB). If the ALB level is ≤ 2% then the synthesis of CPO-res becomes a biofuel carried out through a trans esterification reaction to a base catalyst, but if, the ALB level is ≥ 2% then the synthesis was carried out through two reaction steps, namely esterification with H_2SO_4 catalyst followed by trans esterification using NaOH catalyst.

2) Synthesis of biofuels: Esterification assisted by ultrasonic irradiation with sulfuric acid catalysts. Concentrated H_2SO_4 catalyst (1%) was mixed with methanol and CPO-res (6:1). The mixture was irradiated in an ultrasonic cleaner at a frequency of 45 kHZ and a temperature of 60°C, for 30 minutes, after that put into a separating funnel, and then added n-hexane while shaking and finally left for 8 hours. The upper layer were separated from n-hexane. ALB from biofuel was then measured, if ALB was ≤ 2%, after that a trans esterification reaction was carried out.Trans esterification with the help of ultrasonic irradiation with a base catalyst. Biofuel (the result of the esterification stage) was added with methoxy (NaOH in methanol 1:10 g / v). The mixture was irradiated with the help of an ultrasonic cleaner at a frequency of 45 kHZ and a temperature of 60°C for 30 minutes, after that the mixture was put in a separating funnel and then allowed to stand for one night. Biofuel obtained was washed using warm water. Biofuel products were dried with anhydrous Na_2SO_4.

3) Test the physical and chemical properties of biofuels. Physical and chemical properties of biofuels include: density, viscosity, fog point test, pour point test, acid number and moisture content [13].

B. Development of Teaching Materials

This research and development was done to produce learning Module in organic chemistry which was intended for the students of Chemical Education Study Program of Bengkulu University. The research began with data collection of field observations conducted together with students to search for POME of Palm Oil Mill. The observation results were followed by laboratory research to used CPO residue of the POME (CPO-res) for synthesis biofuel. The results of this laboratory study were further developed as learning module with the ADDIE model, through the stages of analysis, design, development, implementation, and evaluation [14]. The analysis was intended to gather information about the implementation of learning before using modules, such as conducting needs analysis, syllabus analysis and analysis of student characteristics. This analysis was used for study material in developing modules. The design used to determine module components such as: cover on module, preface, list of contents, map of material scope, introduction, competencies to be achieved, description of material, closing sections, assessment sheet, and reading list. The development was the process of producing modules in accordance with the results of the analysis and design results. The development module was reviewed by expert judgment. Implementation was a step to implement the learning module in field trials, to see the effectiveness of the modules developed. Students' responses to the trial of the developed modules are very necessary for module improvement. Evaluation was done to improve the module if, there is still something that must be corrected according to the advice received at the time of implementation.

Instruments used in this study include a validation sheet of educational experts. The validation sheet is intended to look at the feasibility of the instructional materials and obtain expert input on aspects of the content presented, language, presentation, and graffiti. The data analysis was solved using the Intracorelation class coefficient (ICC) equation (1).

$$ICC = \frac{RK_b - RK_e}{RK_b + (p-1)RK_e} \qquad (1)$$

Note:

ICC = Intracorelation class koefisien

RK_e = Average squared error

RK_b = Average squares of grains

P = Panelists

III. RESULTS AND DISCUSSION

Conversion to CPO-res into biofuels. The general method for converting vegetable oils into biofuels are trans esterification. Trans esterification is the conversion stage of triglycerides (vegetable oil) to alkyl esters, by reacting with alcohol and producing by-products namely glycerol. In this study vegetable oil used was CPO obtained from POME (CPO-res) and the alcohol used was methanol. Initial treatment of the sample before trans esterification of CPO-res was filtering to separate solids that may exist, heating to remove water, degumming to remove gum and bleaching to reduce color, then clean CPO-res was tested for free fatty acid content (ALB). The high ALB content of CPO-res can cause the trans esterification reaction to be disrupted due to the saponification reaction between alkaline catalysts and ALB to form soap. The ALB content is kept as small as possible (≤ 2%) in order to slow down the saponification reaction in the trans esterification reaction.

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The content of ALB at CPO-res is 45%, to obtain the maximum biofuel product and avoid the formation of soap, biofuel synthesis from CPO-res is carried out in two stages, namely esterification and trans esterification. Esterification was a way to convert ALB to methyl ester with H_2SO_4 catalyst. Esterification was carried out with the help of ultrasonic irradiation using an ultrasonic cleaner for 20 minutes. The use of ultrasonic irradiation was intended to make the reaction run faster [15], after esterification, ALB methyl ester was tested to see whether the ALB content had reached $\leq 2\%$, in this study the esterification reaction was carried out three times until the ALB methyl ester was obtained amounting to 0.63%.

Trans esterification was carried out on the results of esterification, the catalyst used at this stage was NaOH which acts as an alkoxide and was a strong nucleophile. The alcohol used in this study was methanol. Stoichiometrically, the trans esterification reaction requires 3 moles of alcohol per mole of triglycerides to produce 3 moles of fatty acid esters and 1 mole of glycerol. Excess alcohol was still needed in the application, so that the formed soap does not form solids, but dissolves in alcohol.

The comparison of the mole between oil and methanol which was too low causes the reaction to run imperfectly. The comparison of the methanol and CPO-res mole ratios used in the study was 6: 1, while the catalyst used was 1% of the CPO-res weight. Trans esterification reaction was carried out using an ultrasonic cleaner for 20 minutes. Trans esterification with ultrasonic irradiation so that the emulsion was easy to occur due to the rupture of cavitation bubbles, if many emulsions are formed, the available surface area for the reaction to two phases (oil-methanol) will increase, thereby increasing the reaction speed.

Excessive use of methanol, in addition to affecting the balance of the trans esterification reaction also encourages the formation of more cavitation bubbles, and resulting in higher yields. Trans esterification reaction begins with the formation of soap, resulting from the reaction to triglycerides with alkaline catalysts (NaOH).

The formation of soap can take place more quickly due to the formation of small droplets from the NaOH catalyst (that was dissolved in methanol) which undergo cavitation such as methanol. The droplet can expand the surface area for the triglyceride saponification reaction by NaOH catalyst. This formed soap acts as a transfer phase and increases the mixing of CPO-res with methanol, so that the reaction to biofuel formation can take place more quickly. The trans esterification process produces 3 layers, namely methanol in the top layer, biofuel in the middle layer and glycerol, water and the

remaining catalyst in the lower layer. Biofuel obtained was washed with warm water (60°C). then a mixture of biofuel and water was separated by using a separating funnel, so that the adsorbed water contained in biofuel was used anhydrous Na_2SO_4. The yield of converting POME oil to biofuel was 75.35%.

Based on the GC-MS chromatogram there are four esters compounds composed of biofuel, as presented in table 1.

TABLE I. COMPONENTS OF BIOFUEL

No	Components	Formula	Molecular weight (g/mol)	Persen (%)
1	Methyl Stearate	$C19H38O2$	298	5,41
2	Methyl Oleate	$C19H36O2$	296	41,09
3	Methyl Palmitate	$C17H34O2$	270	52,36
4	Methyl Meristate	$C15H30O2$	242	1,14

The physical and chemical characteristics of biofuels that are successfully made as presented in table 2.

TABLE II. PHYSICAL AND CHEMICAL CHARACTERISTICS OF BIOFUELS

Parameter	Unit	SNI M E	Biofuel	Gasoline	Kerosine
Density	g/cm^3	0,85-0,89	0,852	0,7732	0,7937
Kinematic viscosity 40°C	cSt	2,3 - 6,0	1,6925	0,45	1,05
Pour point	°C	Maks 18°C	11	0	0
Fog point	°C	Maks 18°C	8,835	1	1
Water content	% weight	Maks 0,05	0,739	0,26	0,46
Acid number	mgKOH /g oil	Maks 0,8	1,122	0,33	0,47

Based on table 2 the characteristics of biofuel synthesized from CPO-res have met SNI, except the acid and water contents that was still quite high. Acid values in biofuels depend on various factors including the type of raw material used, the acid catalyst used and free fatty acids produced during the production process [16]. A high acid value can result in corrosive properties and can cause a crusts on the engine injector, high acid numbers also have a large potential for polymerization which results in blockage of the injector.

Good fuels quality requirements were free of water. The water contained in biofuels will cause corrosion and condition the environment suitable for microorganisms so that it will encourage oxidation which can increase sediment and acid numbers during storage [16]. The presence of water in the fuel will cause a short filter life or fuel blockages in the filters and this was also the main cause of the decrease in quality of the fuel in the engine. The amount of water also causes corrosion in the engine. High water content in biofuels allows hydrolysis reactions that can cause an increase in ALB levels and are corrosion if it acts with sulfur because it will form acid.

The results of the analysis of the syllabus, the implementation of learning, interviews with subject lecturers, and needs analysis and student learning in the Bengkulu region as producers of palm oil, then when linked to the possibility of

an energy crisis. so that students have extensive knowledge about energy problems alternative, then students need to be given knowledge about the development of alternative energy with raw materials for CPO. Therefore, the research on CPO-based biofuel synthesis was conducted using the ADDIE model. The results of the development module were validated by expert judgment in order to find out whether the module was suitable for use for learning, the average validity test score is presented in table 3.

TABLE III.   THE AVERAGE MODULE VALIDITY TEST SCORE

No	Validator	Score	Average	Criteria
1	V1	153	4,5	Good
2	V2	165	4,9	Good
3	V3	163	4,8	Good
Total		481	4,71	Good

The trust level test was also carried out on the module validation value to see if the value given has the same variants so that it can be accepted and feasible to be used in the field learning. The results of the module value confidence level test are presented in table 4.

TABLE IV.   TEST OF CONFIDENCE LEVEL OF MODULE VALIDATION RESULTS

SV	JK	df	Variance	ICC
validator	17437,73	2	8718,863	0,846
Item	-900,245	33	-27,2802	
Error	-16516,7	66	-250,253	
Total	20,7549	101	8441,329	

Note: interclass correlation, if ICC $\geq$ 0,6= reliable and if ICC $\leq$ 0,6 = not reliable

The average value of validity were in a good category, with the ICC validation module 0.846 providing added value to be able to use the module as a trial tool.

IV. CONCLUSION AND RECOMMENDATION

A. Conclusion

Biofuel made from CPO residues from POME (CPO-res) can be synthesized with the help of ultrasonic irradiation. The yield obtained was 75.35%, the composition of biodiesel was a mixture, methyl meristate (1.14%), methyl palmitate (52.36%), methyl oleate (41.09%) and methyl stearate (5.41%). The characteristics of biofuels are as follows: density 0.852 g / mL; kinematic viscosity 1.6925 cSt, pour point 11 °C, fog point 8.835 °C, moisture content 0.739%, acid number 1.122 mg KOH / g oil. The number of acid and water content still does not meet SNI.

Modules developed from research on biofuel synthesis after being validated by expert judgment received good grades (4.71) with trust validation levels (0.846), therefore the modules developed can be interpreted in the learning of organic chemistry in class

B. Recommendations

It is necessary to do esterification with heterogeneous catalysts to avoid difficulties when separating biofuels and catalysts

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