PLANT OIL AND FATS LIPOLYSIS USING PLANT LATEX LIPASE: MILD CONDITION PRE-TREATMENT FOR METAL SOAP SYNTHESIS

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Abstract: Metal soap is an intermediate substance in oleochemical industry which also is a potential precursor for biofuel. Synthesis of metal soap requires high pressure operation, otherwise, partial or total conversion of triglyceride into fatty acid is necessary. In this paper, an enzymatic hydrolysis using plant latex lipase was proposed to pretreat triglyceride prior to metal soap synthesis. Physical characteristic and reduction of acid value confirmed the saponification reaction of fatty acid. Two procedures based on references were compared. Overall, it is concluded that lipolysis with plant lipase is an effective pretreatment to produce metal soap in atmospheric pressure.

Index terms: Metal soap, saponification, lipolysis, plant latex lipase, fatty acids

I. INTRODUCTION

In the last decades, high demand of energy along with sustainability concern have driven researchers to develop production of renewable fuels. Among various renewable fuels, the most utilized form by far are biodiesel (1st generation, which basically is fatty acid methyl esters compounds) and bioethanol. Nevertheless, with current automotive engine, both are only applicable in restricted amount. Utilization of FAME and bioethanol as biofuels requires blending with their respective predecessor, i.e. diesel fuel and gasoline.

Conventional fossil fuels consist of hydrocarbons, either long, unbranched chain (for diesel fuel) or medium chain with aromatics (for gasoline). Similar compounds can be synthesized by removing oxygen atoms in bio-based fuels, thus making it directly applicable onto current automotive engine. This kind of fuels are also known as drop-in biofuels. Attempts have been reported to convert triglycerides and fatty acids into biohydrocarbons[1]. Aside from hydrodeoxygenation, which requires hydrogen and high pressure, removal of oxygen atoms can also be established with decarboxylation[2].

Several reports claimed that conversion of triglyceride to metal soap prior to cracking has some advantages. It produces more liquid product with less oxygenated compounds[3], reduces acid value to higher extent[4], avoids polymerization and produces less sludge[5]. Most metal soaps were synthesized with calcium or magnesium. Each metal plays specific role in promoting of certain substances desired in the final products[6], thus in some cases metals were mixed to attain certain hydrocarbon composition[7].

In 1982, Blachford[8] claimed procedure of metal soaps synthesis from triglyceride. However, it requires high pressure and high operational cost. Metal soap synthesis in atmospheric pressure from mixture of triglyceride and fatty acid was reported using ketone solvents[9]. Alternatively, metal soap can also be produced with high yield in atmospheric pressure from fatty acid[10]. Nevertheless, conversion of triglyceride to fatty acids requires a hydrolysis reaction, which currently established in oleochemical industry via thermal hydrolysis. This process (250 ^{o}C, 50 bar)[11] demands high amount of energy and prone to side reactions[12]. Enzymatic hydrolysis of triglyceride was feasibly established using microorganism lipase, nevertheless it is costly and requires complex separation step[13]. Alternatively, plant lipase offers high availability, and ease of handling. Lipase can be found in castor seed[14], rice bran[15], frangipani latex[16], and other sources. Utilization of plant latex lipase is a low-cost pretreatment process to convert most of triglyceride into fatty acids, making them ready for saponification.

The aim of this study is to evaluate metal soap synthesis from lipolysis product. Lipolysis was performed with plant latex lipase as biocatalyst, and palm olein, palm stearin, and coconut oil as triglyceride sources.

II. METHODS

Preparation of plant latex lipase

Latex lipase was obtained from frangipani (*Plumeria rubra*) local tree in Bandung, Indonesia. Suspension of latex was settled in 7^{o}C and decantated to remove its liquid phase. Solid phase was dried and stored in 7^{o}C.

Lipolysis of triglycerides

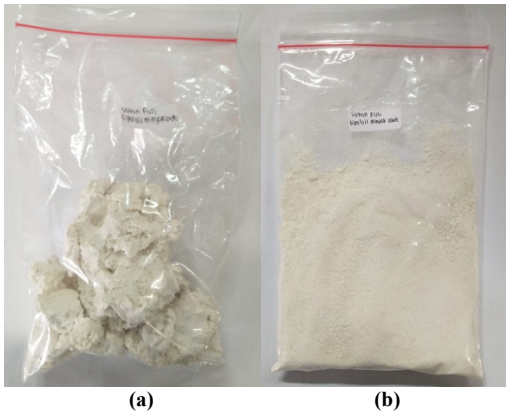
Oil or fats was mixed with buffer NH_3-NH_4Cl pH 8.25 (1 mL/g oil or fats) and crude lipase (1%-oil or fats mass) for 24 hours. For coconut oil

and palm olein, stirring was done in room temperature. For palm stearin, the reaction mixture was heated to 52°C prior to stirring until stearin was liquified. At the end of lipolysis, acid value (AV) and saponification value (SV) of product were determined.

Synthesis of metal soap

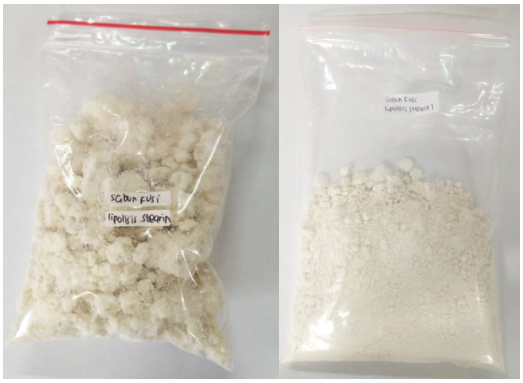
Saponification of lipolysis products into metal soap was performed using two methods: fusion reaction[10] and solvent-based[9]. Metal hydroxides (Ca-Mg-Zn) used in this experiment were prepared with procedure describes on reference[7].

Metal soap products were evaluated by their yield (product mass compared to total mass of reactants), acid value (evaluated by titration with 0.1 N alcoholic KOH).



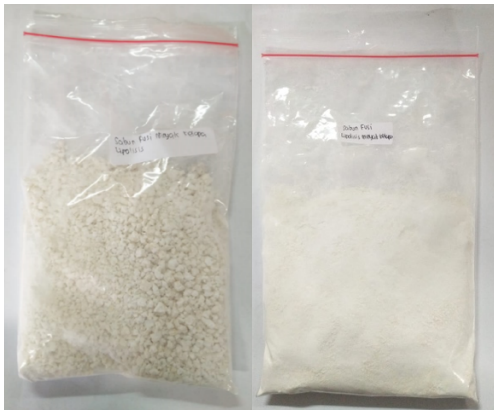
(a) (b)

Figure 1: Metal soap from saponification of lipolyzed palm olein: (a) before grinding, (b) after grinding



(a) (b)

Figure 2: Metal soap from saponification of lipolyzed stearin: (a) before grinding, (b) after grinding



(a) (b)

Figure 3: Metal soap from saponification of lipolyzed coconut oil

III. RESULTS AND DISCUSSION

Experiment results are shown in Table 1. Lipolysis converts most of triglycerides in palm olein and coconut oil into fatty acids, for more than 50% in room temperature. Conversions were calculated from ratio of acid value (representing fatty acids formed during lipolysis) to saponification value (representing total saponifiable matters in reaction mixture, i.e. glycerides and fatty acids. Lower conversion was attained in lipolysis of stearin, indicating the decreasing lipase activity along with heating. Heating above melting point of stearin (55 °C) was required to keep stearin in liquid form and makes it agitable. Meanwhile the optimum conditions of plant lipases, such as canola seeds, physic nuts, and African oil bean, are mostly in 37 °C[17]. Increasing temperature above enzyme optimum condition affects its conformation, reducing its ability to catalyze specific substrates.

Saponification turns thick fluids of lipolysis products into white, soapy granules. Unlike lipolyzed coconut oil, metal soaps from lipolyzed palm stearin were slightly sticky, causes problem in grinding. Acid value in metal soap from lipolyzed stearin was low, indicating that the stickiness of product was rather caused by unlipolyzed triglyceride than fatty acids. Although saponification of lipolyzed stearin was effective (according to low acid value and high saponification yield), low conversion of lipolysis affects product quality significantly. In case of stearin lipolysis, it appears that utilization of organic solvent is required. Aside from increasing substrate solubility, organic solvent utilization also eases immobilization, enzyme recycling, and separation step[18]. On the other side, it also might decrease enzyme activity[19], thus suitability of solvents in lipolysis needs to be determined. In our previous work, nonpolar solvents with low viscosity increases conversion in lipolysis with plant latex lipase.

With lower operation cost and less organic solvent needs, saponification with fusion reaction appears to be more effective than solvent-based

method. Yields are significantly higher, acid value was more decreased, and changing form of reactants confirm conversion of fatty acids (and probably triglyceride) into metal soaps. Fusion reaction is known to be effective to saponify fatty acids[10], while solvent-based procedure was claimed to convert mixture of fatty acids and triglyceride into metal soaps[9]. However, experiment in this study indicates that hydrolyzing triglycerides into fatty acids prior to saponification is important to ensure product quality, and triglyceride presence in reaction mixture was undesirable.

The experiment also shows that lipolysis with plant latex was feasible to pretreat triglyceride into saponifiable fatty acids although lipase used was in crude form and the exact composition is still unclear. Thus, the overall processing plant oils into metal soap was established in atmospheric pressure and relatively mild temperature. (<100 ºC). Low cost preparation of metal soaps from plant oil will increase economic feasibility in biohydrocarbons production via decarboxylation or pyrolysis. However, maximum conversion of lipolysis needs to be improved, especially in the case of solid fats (i.e. stearin). The effects of metal soap preparation via lipolysis with plant latex to biohydrocarbons characteristics after decarboxylation or pyrolysis are also important to be recognized.

CONCLUSION

Lipolysis with plant latex as pretreatment of plant oils prior to saponification was proved to be feasible, producing white, solid granule metal soaps. Acid values were decreased, indicating the saponification reaction was occurring. With lower operational cost, fusion reaction was significantly more effective than solvent-based method. It is potentially developed further for synthesis of metal soap with mild condition process. It also reduces operational cost of metal soap preparation, which is important to produce economical biofuels.

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Table 1
Characteristics of metal soap synthesized from lipolysis product

Method	Substance	Yield	Acid Value (AV)		Saponification Value (SV)
			Post lipolysis	Post saponification	
Solvent based	Palm olein	19,2%	132,8	15,6	180,0
	Palm stearin	34,3%	73,4	17,7	196,4
	Coconut oil	18,8%	178,7	101,1	271,8
Fusion reaction	Palm olein	93,4%	141,0	10,1	180,0
	Palm stearin	83,9%	95,8	1,6	196,4
	Coconut oil	67,6%	237,5	9,0	271,8

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