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How Refinery Industry Waste (Spent Bleaching Clay/Earth) Related to the Energy Fuel Demand: A Review

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Abstract

Biodiesel is an extender for traditional petroleum diesel and can be defined when the color show slightly yellow, oily liquid with a slight aromatic odor and a bitter taste. Commonly used as fuel for stationary diesel engine like pump sets, other agricultural implements and also in the diesel car. Realizing the importance of alternative energy sources, this research had come out with cost effective and versatile method for biodiesel preparation. In this research, the raw material feedstock had been taken from the refinery palm oil waste called spent bleaching clay. Refinery industry waste usually was dumped into landfill and cause environmental problems. This waste called spent bleaching clay. It is about 20-40 wt. % oil remains in spending bleaching clay which are taken from palm oil refinery. The transesterify between the oil and methanol can convert the oil into an alternative to fossil diesel fuel. This review had lined up all the transesterification method, the conversion yield, catalyst and other applications . The prospective of refinery waste will cover the future of biodiesel using waste as cost effective feedstock.

Keywords: Waste; Spent bleaching clay; Transesterification; Biodiesel; Feedstock

1. Introduction

In this century, the depletion of petroleum based diesel gives major impact for industry and human itself. The alternative energy fuel had been discovered and one of them called biodiesel. Biodiesel or fatty acid methyl ester found to be the best substitute for petrol-diesel because it has many benefits. The benefits covered the lower toxic emission, biodegradable, excellent lubricity, carbon neutral and environmental friendly [1]. In industry, the oil (triglyceride) was subjected to the transesterification process to produce biodiesel. This triglyceride reacts with methanol by one mole of triglycerides react with three moles of methanol to produce three moles of methyl ester and one mole of glycerol. This reaction takes same reaction condition with suitable parameters to get the excellent methyl ester conversion. Other than to mention before, the feedstock selection is very important to maintain this alternate energy fuel production. Spent bleaching clay (SBC) or spent bleaching earth (SBE) from any refinery industry can be used as feedstock. The SBC from palm oil refinery industry contains 17% to 35% of residual oil, metallic impurities and other organic compounds [2]. As a byproduct from refinery industry, people usually dump into landfill and caused environmental issue. Bleaching clay dosage of 0.5-1% is usually used for crude palm oil refineries. In Malaysia, estimated about 150 000 tonnes or more of clay utilized yearly in the refining palm oil industry (based on 19 million tonnes of palm oil production yearly) (MPOB). The remaining oil retained in SBC after refining process can be extracted and sold as a raw material to lubricant and biodiesel industries [3, 4].

Figure 1 shows the palm oil refinery process flow in Malaysia. From the figure, the spent bleaching clay was used at bleaching stage Bleaching stage covered the absorptive purification process in which a wide range of unwanted components (soaps, phospholipids, oxidation products, trace metals, contaminants) are removed prior to deodorization [5] and also has been used in the process of reducing the color pigments, primary various pheophytins and carotenes, in fats and oil. Haslenda [6] from the studied framework stated that SBC appears as the most profitable by-product as it is demanded in a huge amount by the customers. Besides, the selling price of SBC is considerably higher, which is MYR30/kg.

2. Availability of spent bleaching clay

Asia country such as Malaysia and Indonesia is one of the largest palm oil hub and supplier of world palm oil demand. Other than these two, Saudi Arabia has large refinery industry. Yearly, the estimated of the SBC from Malaysia is about 15 000 tonnes compared to Saudi Arabia only 6000 tonnes per year. According to the MPOB 2013 data statistic, the total CPO production is around 19 million tonnes in 2013. The SBC was calculated as 0.8% of CPO production (MPOB).

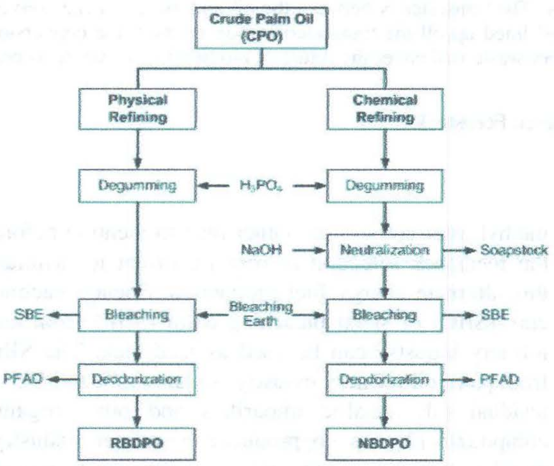

Figure 1: Refinery palm oil process flow chart

The SBC waste depends on the CPO production. Taiwan refinery edible oil is about 5000-6000 tonnes per year. India has approximately 90 units of edible oil refineries located in different states. The sources of edible oil are soybean, groundnut, rapeseed, sunflower, safflower, cotton, sesame, coconut, palm, mustard, rice bran, watermelon, neem, etc.

3. Spent bleaching clay applications and the properties

Other than being applied as a feedstock for biodiesel production, SBC oil can be applied as a substitute for marine fish oil in the diets of Nile tilapia, *Oreochromisniloticus.* Palm oil-laden SBC can totally replace added fish oil. The use of this presently discarded waste product from palm oil refining in tilapia diets will significantly give to reducing the impact of rising feed costs in the culture of tilapia in many tropical countries. Other potential benefits may include acting as a feed binder, removal of mycotoxins in fish feeds as well as adsorbing toxic substances present in the culture water [7]. Composted SBC has a progressive impact on soil physical attributes for plant growth and microbial rejuvenation due to adequate amounts of beneficial mineral elements; improved organic carbon (OC); cation exchange capacity (CEC); water-holding capacity and C: N ratio. The pot and field trials carried out indicate highly significant increases in the productivity of okra (*Abelmoschusesculentus*), kangkung (*Ipomoea aquatic*) and groundnut magenta with 2-fold increase (35–60%) on average in fresh and dry matter production [8]. Abdulbari [9] work on the grease composed from spent bleaching clay has a promising future as consistent lubricating grease for plenty of applications. Spent bleaching clay consists of very fine particles of clay, able to absorb oil and hold the oil. This special property is important for any thickener, the ability to hold and to release oil when needed. As a conclusion, spent bleaching clay can be used as a novel application for grease formulation even without adding of additives.

But, from these other application, biodiesel production from SBC had become major subjected into the energy problem because the depletion of energy sources will affect others industry. Therefore, this review will cover the biodiesel production from SBC itself and how it can tolerance with other factors.

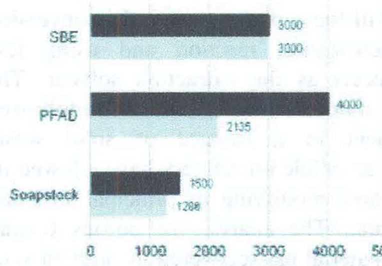

Figure 2: Quantity of by product

The oil content was calculated using the formula:

$$\text{Oil content: } \frac{M1}{M0} \times 100$$

M1 and M0 is the mass of obtaining oil and SBC in g, respectively.

In terms of solvent used, the solvent can be classified polar and non-polar solvent. Table 4 shows the polarity of solvent. Boey [10]discuss about the polarity deeply. Ethanol extraction highest yield compares to non-polar solvent extraction. It happens because the crude palms oil less soluble in polar solvent. Methanol consists of smallest chain which only attracted a small number of oil and non-polar components in SBC. But, both non polar solvent petroleum ether and hexane gave similar results.

Al Zahrani [11]discussed about the effect of solvent type, solvent to clay ratio, time of extraction and extent of mixing on the percentage of oil extracted (POE) were investigated. The corresponding optimum conditions for the four solvents were: extraction time time = 5 minutes, solvent to clay ratio = 4 to 5, extraction temperature = 25 °C (room temperature) and mixing rate = 150 to 200 RPM. The bleaching efficiency (compared to fresh clay) of the clay deoiled by methylethylketone, acetone, petroleum ether and n-hexane were 77%, 65%, 51% and 27%, respectively. Fatah[12] prove that subcritical water has been used as a new pathway for oil extraction from spent bleaching clay by using optimum oil extraction temperature is 270°C, the optimum extraction time is 20 minutes, and the optimum feed: solvent ratio is 1:3.

King [13] describes the use of SC-CO_2 for processing both neutral and acidic clays used in the refining of soybean oil. Rapid extractions of spent bleaching clay can be affected at 10,000–12,000 psi by proper preparation of the clay substrate. Experiments utilizing both laboratory and pilot-plant extractors have yielded almost 100% of the adsorbed oil. Extraction of the clay can be facilitated by cross blending the clay with a diatomaceous clay-based dispersion. The oils recovered by the supercritical fluid extraction (SFE) process have properties (free fatty acid content, color ratio, and phosphorus content) similar to those found in degummed-bleached oils.

Waldmann [14] compared the extractability of different spent bleaching clay from rapeseed oil refinery using a high pressure extraction plant with carbon dioxide as solvent. The results show more than 97% of oil yield can be recovered with good oil quality.

4. Oil absorbed on spent bleaching clay as a feedstock for biodiesel

Approximately 50–90% of the biodiesel production cost arises from the cost of raw material such as vegetable oils, animal fats, and waste cooking oils [15]. To lower the production cost of biodiesel and to expand its usage, using less expensive raw materials is preferred. Waste oil adsorbed on spent bleaching clay during the crude oil refining process is a potential feedstock and can reduce the disposal cost of industrial waste.Table 1 and 2 shows summary of the oil content and biodiesel production base on their condition.

Huang [4] proved that residual oils recovered from SBC generated at the soybean oil refinery could be converted into biodiesel via a two-step esterification. The residual oil contained hexadecenoic acid (58.19%), stearic acid (21.49%) and oleic acid (20.32%), which were similar to those in vegetable oils. The biodiesel properties were found suit both EN 14214 and ASTM D6751 standards. Boey [16]declared the ultrasound aided in situ transesterification of crude palm oil adsorbed on SBC with co-solvent can convert the residual oil into methyl esters. The reaction conditions used were methanol to oil molar ratio of 150:1, 20% KOH catalyst concentration, with best condition. The SBC containing about 24.2–27.0% residual oil gave methyl ester yield of 75.2 ± 1.7% when petroleum ether (PE) was used as a co-solvent and 60.0 ± 0.8% when ethyl methyl ketone was used.

Table 2: Biodiesel from SBC oil

Method	Technique	Type of catalyst	Catalyst	Reaction condition				Conv. (wt.%)	Ref
				T(°C)	MeOH:oil (mol:mol)	Cat. (wt.%)	t (h)		
In situ Transesterification	Ultrasound	Homogeneous	KOH	60	150:1	20	2	75.20	[16]
	Mechanical stirring	Homogeneous	NaOH	68.74	0.6:1	-	<5	15.98-16	[18]
			H_2SO_4			-	>5		
Transesterification	Mechanical stirring	Heterogeneous	CaO	65	0.5:1 (mass: mass)	6	2.5	98.60	[17]
Two step : Esterification (A) Transesterification (B)	Mechanical stirring	Homogeneous	Sulfuric acid followed by NaOH	60 (A)	0.29:1 (mass: mass)	1	1		[4]
				80 (B)	6:1	1	1.5	90.08	
			Sulphonated ion exchange followed by NaOH	80 (A&B)	-	-	3		[20]
					-	-	0.5	82.00	

Table 1: Oil content from SBC

Sources	Method	Solvent		Oil Yield (wt.%)		Ref
		1st	2nd	1st	2nd	
Palm oil refinery	Double step extraction using Soxhlet Extractor	Methanol	Petroleum Ether	21.5	11.7	[17]
			Hexane		12.0	
		Ethanol	Petroleum Ether	35.6	0.6	
			Hexane		0.7	
		Petroleum Ether	Methanol	28.2	6.3	
			Ethanol		3.1	
		Hexane	Methanol	28.8	6.0	
			Ethanol		3.4	
	Single step using soxhlet extractor	Methanol		24.4		[4,20,21,22]
		Ethanol		42.4		
		Isopropanol		44.2		
		Petroleum Ether		36.6		
		Pentane		38.0		
		Hexane		21-37.7		
		Heptane		37.6		
	Manual extraction	Hexane		26.6		[23]
		Ethyl methyl ketone		27.0		[16]
		Petroleum Ether		24.2		
	Supercritical fluid ($SC-CO_2$) extraction	Carbon dioxide		20-27		[20]
Corn oil refinery	Soxhlet extractor	Methyl ethyl ketone		73-95.3		[11,24,25]
		Benzene + Ethanol		84.6		
		Acetone		65-80.8		
		Trichloroethylene		76.5		
		Dichloromethane		75.4		
		Chloroform		73.0		
		Benzene		71.3		
		Petroleum Ether		51-66.7		
		Hexane		27-62.5		
		Methanol		52.9		

Lim [17] revealed that heterogeneous base-catalyzed transesterification had been proposed using CaO. Studied has been conducted and the optimal conditions were found to be: methanol/oil mass ratio 0.5:1; catalyst amount 6 wt.%, and at 65°C. The utmost purity of 98.6 ± 0.8 % was achieved within 2.5 h. Biodiesel yield under the solid catalyst was counted as 90.4% as compared to 45.5% and 61.0%, respectively for conventional NaOH and KOH homogeneous catalysts.

Mat [18] stated the best biodiesel yield was obtained when the methanol to spent bleaching clay ratio was 3.2:1 (gram of methanol: gram of SBC) and hexane to methanol ratio of 0.6:1 (volume of hexane: volume of methanol). The studies were carried out in an in-situ biodiesel reactor system using the alkali catalyst produced the highest yield of biodiesel.

5. Prospective of refinery industry waste

Future work will focus on improving the conversion of the transesterification reaction and using less expensive chemicals as the extraction solvent. The impregnation by ammonium chloride solution followed by heat treatment in a furnace of solid waste originating from an edible oil refinery have allowed its regeneration without modifying its principal structure of montmorillonite. The analysis of porous texture reveals that the material has recovered its original state (mesoporosity) off before use. Moreover, the decomposition of NH_4Cl under the heat effect caused an increase in micro porosity in the regenerated material. The results of the porous texture show that spent bleaching clay, a polluted industrial waste can be regenerated and reused as a low cost mineral adsorbent [19]. The application of wastes in industries is a wise way to decrease pollution from industries as well as to preserve the environment. At the same time this trend is hoping to further utilize and give added value of wastes by converting the waste to wealth. The implementation of such regeneration steps to spent bleaching clay in the edible oil refining industries would greatly contribute to reducing environmental pollution problems in these and similar industries.

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