



RESTORATION OF WASTE COOKING OIL (WCO) USING ALKALINE HYDROLYSIS TECHNIQUE (ALHYT) FOR FUTURE BIODETERGENT

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ABSTRACT

Enormous quantities of waste-cooking oil (WCO) are generated and discharged into environment in diverse countries without proper treatments, especially in Malaysia, it may cause negative impact on human life and ecosystem. However, the WCO pre-treatment reveals rich fatty acids, e.g. oleic, palmitic and linoleic compounds can be used as a potential feedstock of biobased-productions, like biodetergents, etc. The renewal of WCO as non-petroleum sources using alkaline hydrolysis technique (ALHYT) as secondary processing was conducted in a bath stirrer flask at various process parameters. The highest biodetergent yield (90%) was found by the alkaline concentration of 5 M, treatment time of 40 min. and operation temperature of 70 °C. The essential properties of the waste cooking oil biodetergent (WASCOB) was examined using ASTM D-460. The WASCOB provides impressive results compared another biosurfactant sources, and the restoration of WCO can be considered as a replacement of fossil derived surfactants for future biodetergent.

Keywords: restoration, WCO, fatty acids, ALHYT, biodetergent.

INTRODUCTION

Biodetergents are surfactants, short for surface-active agents. Nowadays, the biodetergents become most important biosurfactant because of their benefit. The surfactants constitute an importance class of industrial chemicals. The industrial demand for surfactants has grown to chemical industry need during the last two decades. The surfactants are amphibatic molecules constituted by a hydrophobic and hydrophilic portion, in which its hydrophobic (polar) is often a hydrocarbon chain, while the hydrophilic (non-polar) portion could be ionic (anionic or cationic), non-ionic or amphoteric (Cameotra and Makkar, 2010). The compounds reduce the free energy of the system by replacing bulk molecules of higher energy at an interface. The surfactants compounds are characterized by its capacity to change the surface and interfacial properties of a liquid. These features make biosurfactants suitable for wide industrial application that involve emulsification, solubilisation and phases dispersion, lubrication, foaming capacity and detergents. The detergents, as well as soaps, are substances that being considered surfactant agents. These compounds began to be produced post the Second World War and were modified through the years to improve its properties and solve the environmental problems created by its accumulation and difficulty of natural degradation (Barbosa *et al.* 2013, Silva *et al.* 2014).

Another side, the WCO has been reckoned among the liquid wastes which generated daily from various sources comprising households, restaurants, catering establishments, industrial kitchens, etc. It's reported that a greater quantity of WCO generated all over the world is being discharged in the environment. In Malaysia, around 50000 tons of WCO derived from vegetable oils and/or animal fats are disposed without

proper treatments. All of these large amount of WCO can contribute water pollution, soil contamination, aquatic life destruction, sewer system blockages, increases water and waste management cost, and consequently generates negative effects on the ecological system. Actually, the WCO is expected to be treated and managed in manner that could not be detrimental to human health and environment (Kabir, *et al.* 2014). One of the conducted treatment methods is restoration of WCO for biosurfactants, eg. detergents synthesis.

Nowadays, there are too many researchs and products of biosurfactants and oleochemicals using vegetable oil and liquid waste such as sunflower oil, soybean oil, palm oil, jatropha oil, castor oil, neem seed oil and used oil etc. (Ameh *et al.* 2010, Salimon, *et al.* 2012, Navare *et al.* 2013). The used oil like WCO could be an alternative feedstock as the starting material for biofuel, oleo surfactants, e.g. detergents, etc. (Ghazali *et al.* 2014, Mora *et al.* 2015). The resulted biosurfactants can be utilized for petrochemical industry and remediation of oil spills, biocatalysts (enzymes), etc.. The isolated enzymes can be used for detergent additive capability (Hasan *et al.* 2010, Zhou *et al.* 2012, Chauhan *et al.* 2013). The conversion of WCO to bio-based detergents can be applied as substitutes for entirely petroleum-based surfactants. Analysis of the WCO was found with the high acid value and low moisture content. The major components of WCO are triglyceride esters of glycerol with three long-chain fatty acid (>C12), given priority to oleic, palmitic and linoleic acid. The share of entirely petroleum based surfactants is declining gradually, and the biomass is seen as one of the best material to replace the fossil sources. The WCO has been being an important issues as a source of biodetergent. Moreover, the economical and feasible recycling process of WCO has



been being looking for valuable products, eg. surfactants. This work reports the replacement of the main ingredients of surfactant with WCO for biodetergent (WASCOB) using alkaline hydrolysis technique (ALHYT) by a stirrer bath flask. It's restoration process makes safe and environmental friendly as well as reducing the raw material and operation cost, and the resulted biosurfactant like biodetergents are comparable with another methods and products.

MATERIALS AND METHODS

Materials

The WCO was provided by the restaurants in Gambang, Kuantan, Pahang Malaysia. The sodium hydroxide, magnesium chloride and hydrogen peroxide were ordered from Sigma Adrich Bhd, Kuala Lumpur, Malaysia. The sulphuric acid and sodium chloride were procured by Chemmart Asia, Malaysia.

Methods

Pre-treatment of WCO

The sample of WCO was filtered as preliminary treatment. Next, the filtrate was heated at 60°C, and cooled at room temperature. The composition of the treated WCO was analyzed using Gas Chromatography (GC), and then it was ready to be restored for biodetergent synthesis.

Synthesis of biodetergent

About 10 mL of WCO was heated up to 40°C. The sodium hydroxide solution was diluted with distilled water and mixed with the heated WCO. The mixture was stirred using magnetic stirrer with hot plate. Then, 5 mL of 3M sulphuric acid was added and the pH was monitored timely using pH meter. Next, 5 mL of hydrogen peroxide was added until the foam formed. The mixture was stirred continuously up to the foam subsided. Then, it was washed using saturated sodium chloride, filtrated and dried in the oven at 60°C for 24 hours. The work steps were repeated for various temperature (30°C, 40°C, 50°C, 60°C, 70°C and 80°C), time (20 min., 30 min., 40 min., 50 min., 60 min. and 70 min.), and alkaline concentration as NaOH (1 M, 2 M, 3 M, 4 M, 5 M and 6 M). The resulted biodetergent was analyzed based on the foam height, pH, oil emulsification and hard water test.

Foamability measurement

The foamability measurement was conducted in a tube with stopper. The tube was filled with 2 g of synthesized biodetergent, and it was mixed with 100 ml of distilled water. The mixture was shaken vigorously and leaved for 2 min. and 10 min. The height of the foam was measured spontaneously. The other commercialized detergents was also compared for three times of repetition measurements.

Hard water examination

The hard water examination was prepared by adding 100 mL of distillate water and 2g of magnesium sulfate, MgSO₄. The mixture was stirred, half-fill of the test tube was added with tap water, and then about pea-sized of detergent was inserted to the both test tubes. The test tubes were also shaken vigorously to take the reading of height of the suds in both test tubes.

Oil emulsification test

The oil emulsification test was provided by a mixture of 4 drop of cooking oil and 5 mL of the biodetergent into the analysis tube. The tube was shaken vigorously and leaved for 2 minutes and 10 minutes. Then the height of produced foam was compared with the commercialized detergents for three times of repetition analysis.

Biodetergent yield determination

The yield of biodetergent was determined based on the chemical reactions, where the produced actual mass compared with the expressed theoretical mass. Generally, it can be shown in the following formula:

$$\text{Biodetergent Yield (\%)} = \frac{\text{Biodetergent mass}}{\text{Mass of used WCO}} \times 100 \quad (1)$$

where the biodetergent mass (g), mass of used WCO (g)

RESULTS AND DISCUSSION

Purification and analysis of WCO

The purification and analysis of WCO were conducted simultaneously as pre-treatment. The WCO was pretreated via filtration and centrifugation. The oil phase of WCO was filtered, acidified and washed with the water, and then it was dried prior to analysis. The analysis of the treated WCO can be compared with others as shown in Table-1.

Table-1. The composition of fatty acids in WCO.

Fatty acids contents, wt., %	This Work	Lam et al., 2010	Ghazali et al., 2014	Zhang et al., 2015
Stearic (C18:0)	4.91	4.50	5.19	8.12
Oleic (C18:1)	39.43	40.50	38.45	40.72
Linoleic (C18:2)	10.42	10.10	10.01	25.81
Linolenic (C18:3)	-	0.20	-	7.19
Margaric (C17)	0.74	-	0.61	-
Palmitic (C16:0)	33.84	42.80	32.88	18.16
Palmitoleic (C16:1)	1.35	-	1.38	-
Myristic (C14:0)	0.78	1.00	0.80	-
Lauric (C12:0)	-	0.10	-	-

Table-1 shows the abundant fatty acids contents are oleic, palmitic and linoleic. It has been also approved by the previous researchers about the potential of WCO as



starting feedstocks of bio-based production, like biodiesel, biodegreaser, etc. (Lam. *et al.* 2010, Ghazali *et al.* 2014, Chang *et al.* 2015).

Impact of alkaline concentration on biodegreaser yield

Figure-1 shows the impact of alkaline concentration on the yield of biodegreaser at various time and constant temperature (70 °C). The yield was considered from the weight of produced biodegreaser. The detergent yield fluctuates at time 30 min., the yield starts with 15.24 % at 1 M concentration, and then it keeps on decreasing at 2 M and 3 M. By the low concentration of hydroxide indicates insufficient separation of many fats remains in the mixture. The produced biodegreaser shoots up growing at 4 M to 5 M, but after 5 M the yield decreases sharp. This tendency occurs at overall of treatment times. The conversion starts to increase tremendously reaching 90% at 5 M. It reflects the highest biodegreaser yield by the optimal of the hydroxide concentration.

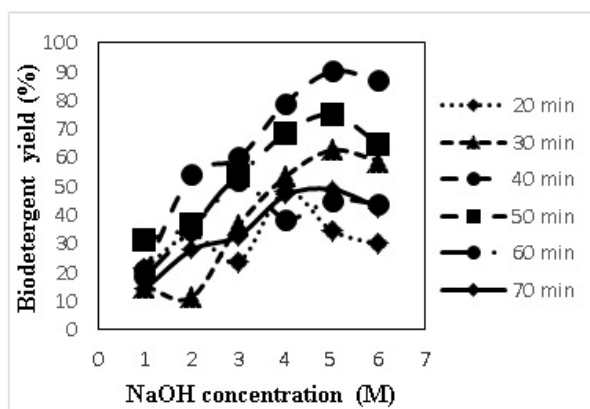


Figure-1. Impact of alkaline concentration on biodegreaser yield (70 °C).

If the concentration of alkali is too high, the water saponifies the oil and reacts would be less. The use of alkaline treatment has been also reviewed for bioethanol synthesis. The alkaline process is based on utilization of dilute bases. The sodium, potassium, etc. are the suitable alkaline agents (Talebinia *et al.* 2010).

Effect of treatment time on biodegreaser yield

The effect of various time on the yield of biodegreaser at constant alkali concentration as shown in Figure-2. Generally, the graph gives the same tendency of resulted biodegreaser at 20 min. to 30 min. at temperatures of 40°C, 50°C, 60°C and 70°C. The curves still increases and grows rapidly to highest yield at 30 min. up to 40 min. After 40 min. the overall treatment reveals the less yields, the curve reflects the identical performance. It's predicted due to evaporation process for long time of alkaline treatment.

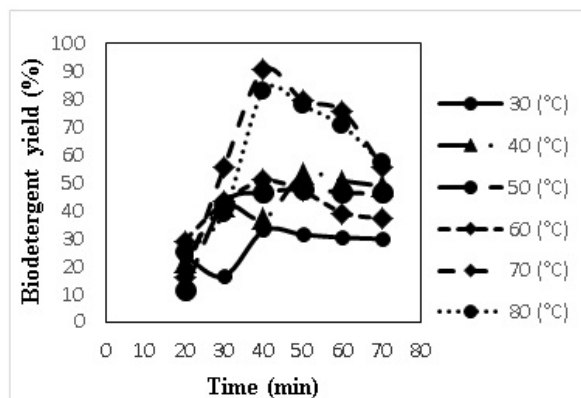


Figure-2. Effect of treatment time on biodegreaser yield (5 M).

The treatment time has also a significance effect on the other synthesis modification of chemicals, like malenized oil based oleo-chemicals from WCO, etc. (Chandelkar and Karadbhaje, 2014). The highest biodegreaser yield (90%) is found at 70°C for 40 min. of optimal operation time.

Temperature influence on biodegreaser yield

The influence of various temperature at constant time (40 min.) on the yield of biodegreaser is presented in Figure-3. The all curves show the same tendency at temperature of 40 °C to 50 °C for diverse alkaline concentration. The overall yields still increase up to the temperature of 70 °C. Otherwise, the less results is found post 70 °C treatment. Therefore, the highest biodegreaser yield (90%) is found at temperature of 70 °C.

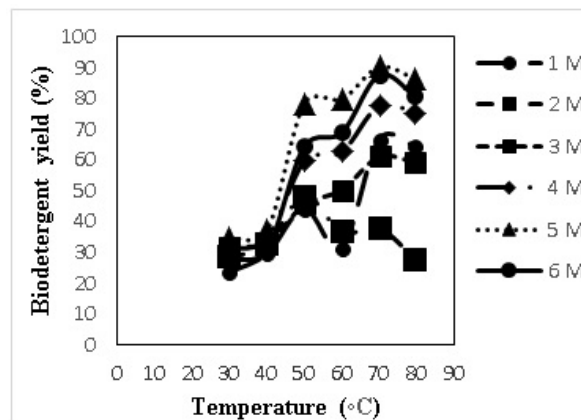


Figure-3. Temperature influence on biodegreaser yield (40 min).

The surfactants, like detergents or soaps making need to be held at considerable temperature. The temperature has influenced also on emulsifying property (Navare *et al.* 2013). Probably, the temperature enhances micellization, and upper 70 °C destruction occurs.



Analysis of biodetergent

Few analysis were run to determine whether the biosynthesis can achieve the criteria of standard detergent stated by ASTM. Three samples were chosen with the highest yield as the possible specimen, and the results are as stated in Table-2 below.

Table-2. WASCOB compared ASTM D-460.

WASCOB Samples (This Work)	1	2	3	ASTM D-460 (Commercialized detergent)	Castor oil detergent (Isah, 2006)	Neem oil detergent (Ameh et al., 2010)
pH	8	9	8	8	-	9.3
Foam height (cm)	1	0.5	2.5	1.8	2.6	3.0
Oil emulsification	D	D	D	D	-	-
Hard water test	Layer	1.2	Layer	Layer	-	-
Biodetergent yield (%)	81.23	84.46	90	-	-	-

Analysis of the resulted biodetergent relates with the pH parameter as shown in Table-2. The hydrogen (H^+) ions which are atom or groups of atoms with negative or positive charge that can control acidity levels prior to liquid containing detergent is released to the stream or another water resources. The level of pH is so important because the aquatic organism needs the pH of their water body to be within a certain range for optimal growth and survival. Furthermore, toxic will be released and compounds from sediments into the water where they may be taken up by aquatic animals or plants if the pH value was low. The water condition is "acidified" due to the less than 5, and the aquatic organisms may be stressed in acidified lakes. Usually, the sea water pH criteria is 6.5 to 10 and for fresh water pH of 6.5 to 9 or as what occurs naturally. The recommended pH for cleaning products, eg. detergent, etc. range between 7 to 10. All of the WASCOB tested samples can be accepted and preferred because nearly to the pH of commercialized and neem oil detergent (Ameh, *et al.* 2010). Otherwise, if the pH more than allowable standard, and the detergents are also linear alkyl benzene sulfonate, and attack the horny layer of the skin and increase its permeability with little or no inflammatory change, it may result in handeczema, which is very distressing and incapacitating. Besides that, the linear alkyl benzene sulfonate is agreed that the poor biodegradability of surfactant due to under anaerobic

condition may sometimes result in a high sludge load (Mungray and Kumar, 2009, Austoria *et al.* 2010).

The hard water examination connects with calcium ions, Ca^{2+} , and magnesium ions, Mg^{2+} . The greater the concentration of these minerals, the harder the water. The hard water interferes with almost every cleaning task from washing clothes, dish washing, bathing, personal care and many more that involved with cleaning. Furthermore, the hard water may cause a film on bathtubs, shower doors, sinks, faucets, etc. If the hard water touches with skin surface, the skin become itchy and dry. However, positively charged magnesium ions (Mg^{++}) and calcium ions (Ca^{++}), which are present in hard water, tend to bind themselves to the negatively charged heads of these surfactant molecules. Surfactant molecules that have reacted with the water in this way fall out of solution, as they no longer have the electrically charged head as it was this 'polar' end that was keeping them dissolved. Hardness minerals also react with carbonate builders commonly found in non-phosphate detergents. The resulting product is a white precipitate, calcium and magnesium carbonate that makes fabrics stiff and harsh and leaves a film on fabrics which tends to make colours appear faded or streaked with white. No precipitate is formed when the carbonate-built detergents are used in soft water (Abeliotitis *et al.* 2015). From the analysis result reveals the sample 1 and 3 of WASCOB can be accepted because it indicates the form layer for hard water test.

Emulsions are either oil suspended in an aqueous water or water suspended in oil. Emulsifiers contain both hydrophilic head group and hydrophobic tail. Hydrophilic head is water loving or others name as polar while hydrophobic tail is oil loving or others name as non-polar. Emulsifiers will be attracted to both compounds. Surfactants, like detergents are able to clean lies in its ability to disperse water insoluble molecules. In the process of the mixture is started to agitate, the oil is begun to emulsify due to the charge on the surface and it causes the mixture dispersion. The dispersion of a liquid into another liquid, leading to the mixing of two immiscible liquids as known as emulsification (Satpute *et al.* 2010). All analyzed samples of WASCOB can be affirmed, the oil dissolves in the detergent as commercialized emulsification criteria. The emulsification is reliable in detecting biodetergent, and it designates the strength of a surfactant (Velioglu and Urek, 2015).

Foam can be prescribed as the gasification process in a liquid. The foamability measurement is also done for three samples. The sample detergent gives the foam during contacts with the water. The foam is unstable and may disappear gradually but it can be stabilized with the aid of certain additives. To protect the fiber, stable foam is needed by reducing the mechanical action. While for surfactant, like detergent cases, high foaming is neither necessarily important nor desired. The samples 1 can accomplish nearly the commercialized detergent, but lower than castor oil detergent. The castor oil detergent reveals the foam height of 2.6 cm (Isah, 2006). This resulted foam height is equivalent to the tested sample 3 of



WASCOB (2.5 cm). Otherwise, the sample 2 is less in view of low foam height. The WASCOB has enough efficiency for the results of foamability test. Usually, the efficiency of a washing powder is assessed through amount of produced foam. The present of persistence foam exemplifies a good detergent. The higher value of foam height reflects a reduction of surface tension which ultimately results in better cleaning action (Meshram *et al.* 2014).

CONCLUSIONS

The biode detergent has been successfully restored from waste cooking oil (WASCOB) using alkaline hydrolysis technology (ALHYT). The highest eco-friendly WASCOB yield (90%) was found by the alkaline base concentration of 5 M, treatment time of 40 min. and operation temperature of 70°C. The characteristics of the formed WASCOB test was shown at the pH (8-9), interaction with hard water (Layer), emulsification with oil (D) and foam height (0.5 cm-2.5 cm). The synthesized WASCOB using alkaline methods fulfils the ASTM D460, and it can be a promising technique for environment friendly treatment carrying waste cooking oil. For the future work, it could be simulated via builders (inorganics, organics & polymer builders and additives (enzymes, etc.) for biode detergent formulation.

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