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Future prospects of biobased detergent derived from *Jatropha c.* seeds oil (JSO)

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ABSTRACT

Background: Commercialized detergents are synthesized by using either branched-chain *alkylbenzenesulfonate* (ABS) or linear chain *alkylbenzenesulfonate* (LABS) which contributes to environment issues. To alleviate these issues, *Jatropha c.* seeds oil (JSO) was used as a potential feedstock of biobased detergent (biobased detergent) synthesis. The JSO utilization as non-petroleum sources using potassium hydroxide-hydrogen peroxide technique (POHYPET) was conducted at 40 °C. After pretreatment and analysis of JSO, the hydrogen peroxide and sulphuric acid were mixed in a bath stirrer flask. The pH was also controlled, and the added hydrogen peroxide was maintained until the foam quieted down. **Objective:** This work aimed to synthesize biobased detergent from non-edible JSO containing fatty acid as a promising raw material. Effects of processing time, temperature and alkaline concentration on *Jatropha c.* seed oil biobased detergent (JASOB) yield were also investigated. **Results:** The highest biobased detergent yield (88%) was found at the potassium hydroxide concentration of 0.8 M, treatment time of 2 h and operation temperature of 80°C. The physicochemical properties of the examined JASOB was indicated at the foam height (0.7-2.3), emulsification with oil (D), hard water interface (L) and pH (8-9). These performances of JASOB fulfilled the required essential criteria of detergent standard. **Conclusion:** The obtained JASOB using POHYPET provides impactful results compared another biosurfactants sources, and the prospects of JSO can be deliberated as a renewal of fossil derived surfactants for future biobased detergent.

INTRODUCTION

Biobased detergents are a mixture of surfactants with cleaning properties in dilute solutions. The detergents, as well as soaps, are substances that being considered surfactant agents. These compounds are manufactured from crude oil- a fossil fuel of which there is only a limited supply. To deal with these issues, the detergent synthesis by substituting the role of either branched-chain *alkylbenzenesulfonate* (ABS) or linear chain *alkylbenzenesulfonate* (LABS) with vegetable oil has been being extensively developing as a potential raw material. The biobased detergent producers are turning increasingly to detergents made 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). Bio-based detergents or surfactants have attracted much attention from scientific and industrial application due to their renewable feedstock and ecological friendly characteristics. The surfactants are amphiphilic molecules constituted by a hydrophobic and hydrophilic portion, in which it is hydrophobic (polar) is often a hydrocarbon chain, while the hydrophilic (non-polar) portion could

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be ionic (anionic or cationic), non-ionic or amphoteric (Cameotra and Makkar, 2010). Previous reports have been found that biodiesel, biosurfactants and oleochemicals could be derived from vegetable oil such as sunflower oil, soybean oil, palm oil, animal fat etc. containing triglyceride or free fatty acids (Rashid, *et al.*, 2010). However, several plants-based biosurfactants, eg. saponins, lecithins and soy proteins have excellent emulsification properties, but it still have other debatable issue relating to solubility, hydrophobicity and higher cost (Xu *et al.*, 2011). The isolated enzymes can also be used for detergent additive capability (Hasan *et al.*, 2010, Zhou *et al.*, 2012, Chauhan *et al.*, 2013). Hence, other types of oils have been recently investigated in order to reduce the price of biosurfactants and to dispose the used oil effectively. The used *Jatropha c.* seeds oil (JSO) will not only avoid the food chain competition, but it will also manufacture another non-edible oil bio-based products. The JSO confined with high FFA content, and these abundant FFA are advantageous preferences for starting materials of bio-based surfactants. 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 JSO has been being an important issues as a source of biodetergent. Moreover, the economical and feasible conversion of JSO has been being searching for valuable products, eg. surfactants. This effort outlines the substitute of the major constituents of surfactant with JSO for biodetergent (JASOB) using potassium hydroxide-hydrogen peroxide technique (POHYPET) by a stirrer bath flask. Its POHYPET makes preserved and eco-friendly as well as minimization of the feedstock and overhead expenses, and the resulted biosurfactant like biodetergents are commensurable with another commodities and techniques.

MATERIALS AND METHODS

Materials:

The *Jatropha c.* seeds oil (JSO) was obtained from Bionass Sdn Bhd, Kuala Lumpur, Malaysia. The sulphuric acid, sodium chloride, sodium hydroxide, magnesium chloride and hydrogen peroxide were purchased from Chemmart Asia and Sigma Adrich Bhd, Kuala Lumpur, Malaysia.

Methods:

Raw JSO pre-treatment:

The raw JSO of 30 mL was filtered using paper filter and followed by heating 100°C. Next, the composition of the pre-treated JSO (10 mL) was analyzed using gas chromatography-mass spectrometry (GC-MS0, Agilent GC, equipped with a capillary column (DB-5HT, 0.25 mm inside diameter and 0.20µm film thickness). These treatments were three times replicated. Treated JSO was ready to be synthesized for biodetergent.

***Jatropha* Seeds Oil Biodetergent (JASOB) synthesis:**

The treated JSO (20 mL) was mixed with various alkaline concentration as KOH (0.2M - 1.2 M), temperature (40°C - 90°C) and time (30 min - 180 min) using a bath stirrer flask (500 rpm). Then, 5 mL of 3M sulphuric acid and 5 mL of hydrogen peroxide were added into the mixture until the foam appeared and subsided. At the same time, the pH was monitored timely at range of 8.0 – 9.5. Next, it was scrubbed using saturated sodium chloride, filtrated and dried in the oven at 60°C for 24 hours. The produced biodetergent was analysed concerning the oil emulsification, pH, foam height and hard water test.

Verification of oil emulsification:

The oil emulsification verification was carried out by a mixture of 4 drop of JSO and 5 mL of the biodetergent into the analysis tube. The tube was shaken carefully and left for 2 min. up to 10 min. Then, the formed oil layer of emulsification was compared with the commercialized detergents for three times of replication analysis.

pH measurement:

The pH measurement was run in 2 test tubes. Both tubes were filled up by 2 g of obtained biodetergent and mixed with 100 mL distilled water. Each solution was stirred with glass rod, and the stirring rod was used to touch a piece of pH paper. The pH of both samples was compared with biodetergent standard.

Foamability examination:

The foamability examination was operated in a tube with stopper. The tube was distributed with 2 g of synthesized biodetergent, and it was diverse with 100 ml of distilled water. The admixture was shaken quickly and left for 2 min. and 10 min. The height of the foam was measured unconsciously, and compared with commercialized detergents.

Hard water test:

The hard water test was done by mixing 2 g of MgSO₄ and 100 mL of distillate water in both test tubes. The test tubes were also strenuously agitated, and the suds height of the operated tubes was measured.

Establishment of *Jatropha* Seeds Oil Biodetergent (JASOB) yield:

The biodetergent yield was calculated the referring to chemical reactions, where the resulted actual mass compared with the expressed theoretical mass. Generally, it can be shown in the following formula:

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

, where biodetergent mass (g), mass of used JSO (g)

RESULTS AND DISCUSSION

Pre-treated JSO analysis:

The pre-treated JSO via filtration, heating and cooling was executed prior to analysis. The JSO fatty acids composition can be compared with previous reports as shown in Table 1. Table 1 shows that the major long fatty acids in the JSO which are linoleic, oleic, palmitic and stearic. The JSO contains high percentage of unsaturated-compared saturated fatty acid. The GC-MS revealed the slightly different of JSO content due to oil sources and extracted methods. It has been also approved by the previous researchers about the potential of JSO as rich fatty acid raw materials for bio-based production, like biodiesel, biodetergent, etc. (Nayak and Patel, 2010, Salimon and Ahmed, 2012, Joshi, *et al.*, 2015).

Table 1: Composition of fatty acids in JSO.

Fatty acids contents, wt., %	This Work	Nayak and Patel, 2010	Salimon and Ahmed, 2012	Joshi <i>et al.</i> , 2015
Stearic (18:0)	7.80	7.67	7.2 ± 0.15	8.1
Oleic (C18:1)	42.46	40.39	43.8 ± 0.5	41.8
Linoleic (C18:2)	32.20	33.09	33.2 ± 0.1	31.5
Palmitic (C16:0)	16.17	16.69	14.9 ± 0.15	17.6
Palmitoleic (C16:1)	0.78	0.96	0.8 ± 0.1	0.7
Others	0.59	-	-	0.3
Σ Unsaturated Fatty Acids	75.44	75.64	77.8 ± 0.7	74
Σ Saturated Fatty Acids	24.56	24.36	22.1 ± 0.3	26

Dependence of reaction time:

The dependence of reaction time with various temperature on the yield of biodetergent (JASOB) at constant alkali concentration (5M) is shown in Fig. 1. In general, the curves grew to the same tendency of resulted JASOB during 30 min to 90 min of reaction time at temperatures of 50°C, 60°C, 70°C and 80°C. The graphs still increase and give the highest yield at 90 min up to 120 min. After 120 min. the overall treatment reveals the less yields, the curve reflects the identical performance. It is caused by evaporation process for long time of chemical reactions. The reaction time has also a crucial dependance on the other synthesis modification of chemicals, like malenized oil based oleo-chemicals from JCO, WCO, etc. (Chandelkar and Karadbhajne, 2014). The highest biodetergent yield (88%) is found at 80°C for 120 min of optimal treatment time.

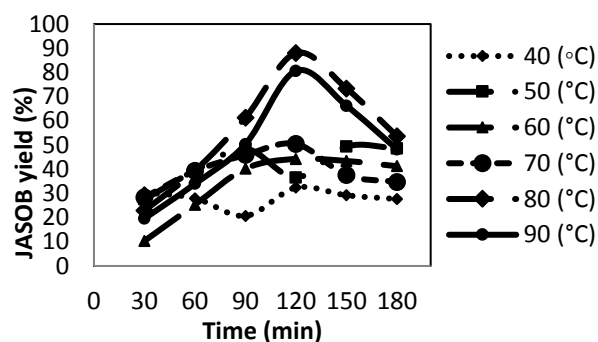


Fig. 1: Effect of reaction time and temperature on JASOB yield at constant alkali concentration of 5 M.

Operation temperature response:

The response of temperature with various alkali concentration at constant time (120 min) on the yield of JASOB is presented in Fig. 2. The overall yields still increase at temperature range of 60°C-80°C. The surfactants, like detergents or soaps making need to be retained at substantial temperature. The temperature has obsessed also on emulsifying properties. The majority of the modern industrial applications work at temperatures above 40 °C, the significance of thermostable biosurfactants, like biodetergents is of extraordinary importance (Elazzazi, *et al.*, 2015). Apparently, the temperature magnifies micellization, and upper 80°C elimination arises.

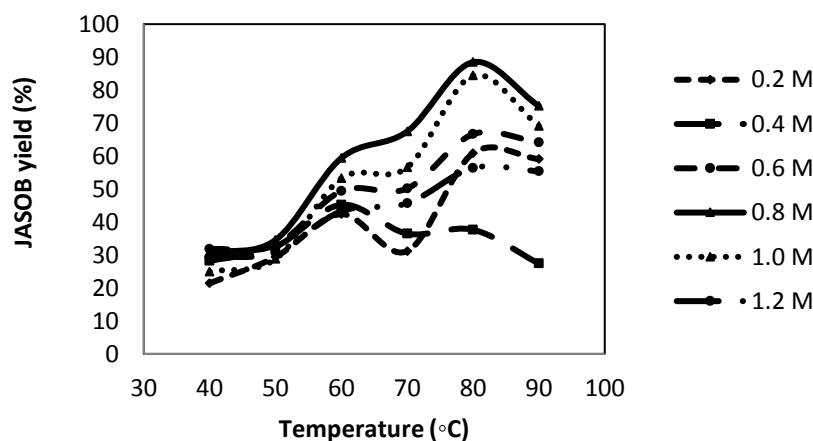


Fig. 2: Effect of temperature and alkali concentration on JASOB yield at constant reaction time of 120 min.

Collision of potassium hydroxide:

Fig. 3 shows the collision of potassium hydroxide concentration with various reaction time on the biodetergent yield at constant temperature (80°C). The detergent yield fluctuates at time 30 min., the obtained detergent starts with 31.36 % at 0.2 M concentration, and then it keeps on decreasing at 0.4 M and 0.6 M. By the low concentration of potassium hydroxide indicates insufficient separation of many fats remains in the mixture. The produced biodetergent shoots up growing > 0.6 M to 0.8 M, but after 0.8 M to 1.2 M the yield decreases sharp. This tendency occurs at overall of treatment times. The conversion starts to increase tremendously reaching 88% at 0.8 M. It reflects the highest JASOB yield by the optimal of the hydroxide concentration. At the concentration of alkali is too high, the water saponifies the oil and reacts would be less. The use of alkaline treatment has also been examined for bioethanol synthesis and the alkaline process is based on utilization of dilute bases. Sodium, potassium, etc. are the suitable alkaline agents for biodetergents or another biosurfactants synthesis (Talebnia, *et al.*, 2010).

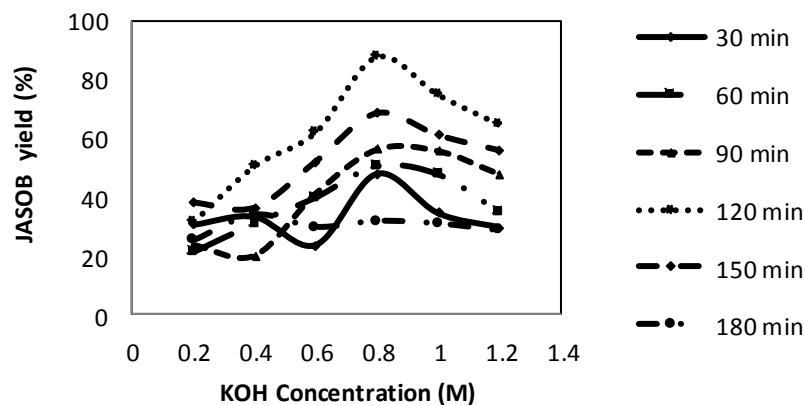


Fig. 3: Effect of KOH concentration and reaction time on JASOB yield at constant temperature of 80°C.

JASOB analysis:

Analysis of JASOB were examined to determine whether the resulted JASOB can accomplish the criteria of standard detergent stated by ASTM D-460. Three of JASOB samples were prepared with the highest yield as the possible specimen, and the results are as stated in Table 2. All analysed samples of JASOB can be affirmed, the oil dissolves in the detergent as commercialized emulsification criteria. Dispersion of liquid into another liquid has approved by the mixing of two immiscible liquids as known as emulsification (Satpute *et al.*, 2010). The emulsification is realible in detecting biodetergent, and it designates the strength of surfactant (Velioglu and Urek, 2015). Next, JASOB hard water test from samples 1 up to 3 form layer without drizzle. It matched the water hardness examination of laundry detergents, and no formed precipitation of used detergents in soft water (Abeliolitis, 2015). The JASOB foamibility was examined for three samples, and the foam height nearly the commercialized detergent compared neem oil detergent (Ameh, *et al.*, 2010). Foam displayed an acceptable detergent properties. The higher foam height induces a surface tension which ultimately results in better washing action (Meshram *et al.*, 2014). Furthermore, the pH measurement of JASOB was tested for samples 1 up to 3, and all samples were adequate for proposed cleaning products, e.g. range pH of 7 to 10. The samples of saporo lipids jatropha oil detergent existed also in the range (Navare *et al.*, 2013).

Table 2: JASOB compared ASTM D-460.

JASOB Samples (This Work)	1	2	3	ASTM D-460 (Commercialized detergent)	Neem oil detergent (Ameh <i>et al.</i> , 2010)	Saporo lipids jatropha oil detergent (Navare <i>et al.</i> , 2013)
pH	8	9	8	8	9.3	5-8
Foam height (cm)	1.3	0.7	2.3	1.8	3.0	-
Oil emulsification	D	D	D	D	-	D
Hard water test	Laye r	Laye r	Laye r	Layer	-	Layer
Biodetergent yield (%)	83. 22	85. 43	88	-	-	-

Conclusion:

The biobased detergent derived from *Jatropha c.* seeds oil (JSO) has been successfully synthesized using POHYPET. The highest *Jatropha c.* seed oil biodetergent (JASOB) yield (88%) was distinguished by process condition at temperature of 80 °C, time of 120 min and KOH concentration of 0.8 M. The physical-chemical features of the accumulated JASOB examination was expressed at the foam height (0.7-2.3), emulsification with oil (D), hard water interface (L) and pH (8-9). The resulted JASOB using potassium hydroxide-hydrogen peroxide methods accomplishes the required ASTM D-460, and it could be a favorable technique for nature friendly treatment carrying non-edible *Jatropha* oil. For upcoming development, it might be formulated via additives (enzymes, etc.), chemical agents (polymers, etc.) for biodetergent multitude enhancement.

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