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BIODEGRADABILITY OF PALM-BASED LUBRICANTS

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ABSTRACT

In the European countries, around 600 000 t of lubricants are released into the environment through normal use such as chain saw oils, railway point's greases and two-stroke engine oils every year. The toxicity and biodegradability of lubricants are a crucial aspect in managing the sustainability of environmental. This article is intended to evaluate the biodegradability of palm-based lubricants in order to establish their environmental-friendliness. The respirometric method was used to monitor the biodegradation of lubricant samples over 28 days as described in the OECD 301F Test Method. The results showed that palm-based lubricants; mould oil, BO-20 and BO-18, readily biodegraded in aquatic environment with the biodegradability of mould oil reached 62.7% within 23 days, BO-20 reached 62.8% within 11 days and BO-18 reached 63% within 14 days which surpassed the 60% pass level within the test period. Meanwhile, the petroleum-based lubricants, mineral oil and motor oil, were not readily biodegraded when tested according to standard method OECD 301F as their biodegradability did not surpass the 60% pass level within the 28 days test period. The viscosity of a lubricant may also be used as an indicator in predicting the biodegradability of that lubricant. The petroleum-based white oil for example, has a low viscosity and it is readily biodegradable. The petroleum-based lubricant which is not readily biodegradable may cause problems when it comes to loss lubricants, accidental spillage and disposal. The use of palm-based lubricants are more environmental-friendly and are one of the alternatives to reduce adverse effects of lubricants on ecosystem.

Keywords: lubricant, biodegradation, respirometry method, OECD 301F, environmental management.

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INTRODUCTION

Lubricants, either plant or petrochemical-based, had been used since 1650 B.C. The biggest markets for lubricants are engine and gear oils for automotive, with about 450 000 t usage per year (Andreas, 2001). Besides petroleum, about 400 000 t yr^{-1} of oils and fats are used for similar applications such as grease and metal working fluids (Andreas, 2001).

About 13% and 32% of all used lubricants in European countries and USA, respectively, are released into the environment (Adolf, 2002). The majority of lubricants used in lubrication frictional contacts and in circulation systems, are disposed to environment and not recycled back. Other than that, lubricants can also be released to the environment through leaks, and traces in filters and containers (Adolf, 2002). Although mineral oils are the major lubricants used in the various field of industry, they are not biodegradable enough to meet the demands of the times. Actually, as alternatives to mineral oils, there have been many kinds of materials developed, such as polyalkylene glycol, vegetable oils and fats,

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and fatty acid esters (Yamada, 2006). The replacement of mineral oils with biodegradable products is one of the ways to reduce adverse effects of lubricants on ecosystem. In 1997, the use of biolubricant worldwide is still very small, for example only 3.6% in the Western European market and 1.5% in the US market (Yeong *et al*. 2007). Currently, there is a renewed interest in using vegetable oils as lubricants, basically due to its inherent good biodegradability. The use of biolubricant globally was estimated at 1.3 million pound in 2013, which is valued about USD 2 billion and in 2014 it was forecasted at 1.4 million pounds (USD 2.1 billion) (Industry Experts, 2014).

Biodegradation is a process whereby microorganisms decompose the organic matter in the environment through utilisation of carbon as food. In primary biodegradation, microorganisms may convert the original organic into different products, but, in ultimate biodegradation they may assimilate the organic molecule completely to a simple molecule (such as carbon dioxide/methane, nitrate/ammonium, and water) (Betton, 2009). The ability of the chemical compound to degrade is the most significant parameter to determine adverse effects on the ecosystem. The percentage of biodegradability of the chemical compound must fulfill the standard regulation requirement such as, the EU requirement for eco-labels, ISO 15380 and the German water hazard class classification (Adolf, 2002). To ensure reproducible and comparable results are achieved in different laboratories, standardised methods have been used globally. There are a number of standardised biodegradability test methods available, such as the ISO standard methods like ISO/TR 15462 on water quality-selection of test for biodegradability and Organisation for Economic Co-operation and Development (OECD) standard methods (OECD, 1992). A substance that gives a positive result in one of the 'ready biodegradability' tests is assumed to be able to rapidly biodegrade, releasing non-toxic products like carbon dioxide and water (ultimate biodegradation). Hence, a substance that is readily biodegradable should cause no adverse effects to living organisms in the environment (Painters, 1992).

The OECD tests for ready biodegradability, *i.e.* the OECD Test Guideline (TG) 301, represent the most prominent group of standardised biodegradation screening tests in the laboratory. These tests are conducted under aerobic conditions, in which the test system is inoculated with microorganisms derived from domestic sewage, activated sludge or secondary effluent of the sewage treatment plants. The OECD has published six tests on ready biodegradability, *i.e.* DOC Die-Away Test (TG 301 A), CO_2 Evolution Test (TG 301 B), Modified MITI Test (I) (TG 301 C), Closed Bottle Test (TG 301 D), Modified OECD Screening Test (TG 301 E) and Manometric Respirometry Test (TG 301 F).

In this study, the respirometric method was used due to its suitability to test poorly water-soluble compounds such as lubricants. The respirometry technique is a quantification of the amount of biogas generation rate (anaerobic conditions) or biological oxygen consumption rate (aerobic conditions) under standard condition of experimental set-up. Generally, respirometry is a technique to measure oxygen consumption by microorganisms during biodegradation process in wastewater samples or activated sludge under aerobic conditions (Katri, 2009). This respirometric technique was based on manometry. This technique involved analysis of changes in the pressure of the gas in closed measuring system. The purpose of this study is to evaluate the biodegradability of poorly water-soluble substances, *i.e.* palm-based and petroleum-based lubricants, by using the manometric respirometry method in order to determine its environmental performance in aquatic environment.

MATERIALS AND METHODS

Test Substances

The samples studied were commercial petroleum-based lubricants, *i.e.* mineral oil, white oil and motor oil, and palm-based lubricants, *i.e.* mould oil, BO-20 and BO-18. The palm-based lubricant samples were formulated by the Malaysian Palm Oil Board (MPOB). Reference compound used was aniline, 99% from AnalaR-BDH, UK.

Fourier Transforms Infrared Spectroscopy (FTIR) Analysis of Lubricant Sample

The FTIR spectrum for lubricant sample was recorded using Nicolet Magna-IR 550 spectrometer series II FTIR (Nicolet Instrument Corporations, USA). The sample was scanned between wavenumbers 4000 – 500 cm^{-1}, 64 times with a resolution of 6 cm^{-1}. Samples were analysed by grinding with potassium bromide (KBr) powder and pressing into a disc prior to the analysis.

Nuclear Magnetic Resonance (NMR) Analysis of Lubricant Sample

The ^{13}C-NMR analyses were carried out using a Bruker NMR, model Avance III 150MHz (Switzerland).

Determination of Lubricants Viscosity

The viscosity of the lubricants was determined at 40°C using a Herzog HVM472 Automated viscometer, USA.

Source of Inoculum

The inoculum used in this biodegradation study was derived from the activated sludge of a wastewater treatment plant treating predominantly domestic sewage. The sludge was collected from the Indah Water Konsortium (IWK), Putrajaya, Malaysia and was diluted in the mineral medium to the concentration as stated in the OECD 301F Test Method. Thereafter, the sludge was pre-conditioned by aerating it (in mineral medium) for four to five days at the test temperature (22 ± 2^{o}C). The pre-conditioning process allows microorganisms to overcome the shock of transfer and to reduce the rate of oxygen uptake by blank controls (Painter, 1992).

Viability of Inoculum

The viability of bacteria in the inoculum was measured by doing the plate count. The sludge from IWK in mineral medium was diluted to 10^6 dilutions. About 0.1 ml of the diluted sludge was pipetted onto the surface of a solidified 1% nutrient agar (NA) and spread with a sterilised, bent, glass rod. All platings were made in triplicate. All plates were incubated at 37°C. After 24 hr of incubation, colonies observed were counted and the number of bacteria in the inoculum was calculated.

Preparation of OECD 301F Mineral Medium Stock Solution and Test Medium

The following stock solutions were prepared using analytical grade reagents as in *Table 1*. A total of 3 ml of each solution A, B, C and D were mixed and made up to 1 litre with deionised water.

Preparation of Bottles

The six biochemical oxygen demand (BOD) bottles were prepared as in *Table 2*.

Procedure for Readily Biodegradation OECD 301F, Manometric Respirometry

All BOD bottles were inoculated with a small volume of the inoculum to give a concentration of 30 mg litre^{-1} of suspended solids. The oxygen uptakes in all bottles were measured directly using the BOD EVO (Velp, Italy) system for 28 days to produce a BOD curve.

Measurement of the Biochemical Oxygen Demand (BOD)

The BOD to degrade the lubricant was measured using the BOD EVO system (Velp, Italy). This system includes an individual number of glass bottles reactors (510 ml) with a carbon dioxide trap (soda lime) in the headspace and magnetic stirrer to make the mixture homogenised during the biodegradation test. The total volume of the test mixture is 300 ml. The bottles are provided with a cap containing a BOD sensor. This BOD sensor will display the BOD value directly in mg litre^{-1}. An incubator was used to maintain the respirometer units at a constant temperature during the test. The BOD value was monitored and recorded for 28 days.

Determination of the Theoretical Oxygen Demand (ThOD)

For complete biodegradation of the test substance, the degree of biodegradation is expressed as a percentage of the ThOD or carbon dioxide production (theoretical inorganic carbon, ThIC). This maximum value is normally calculated from the molecular formula of the test substance. But, the calculation of ThOD using molecular formula is impracticable since normally most of the chemical composition for lubricant in unknown.

Studies have shown that elemental analysis can be used to calculate both ThOD and ThIC (Gerike, 1984). In this study, the theoretical values for lubricants were calculated on the basis of values from elemental analysis (CHNS Analyser, LECO, USA). The ThOD for each lubricant was calculated using the following formula (Gerike, 1984).

$$\text{Thod} = \frac{2.67\,(C\%) + 8(H\%) - 0.23\,(Cl\%) - 1.71\,(N\%) + 1.5\,(S\%) + 1.29\,(P\%) + 0.35\,(Na\%) - O\%}{100}$$

$= \text{mg } O_2/\text{mg test substance}$

Percentage of Biodegradability

The percentage of biodegradability of a compound is calculated using the following formula.

$$\%\ \text{Biodegradation} = \frac{\text{BOD (mg } O_2/\text{mg test substance)}}{\text{ThOD (mg } O_2/\text{mg test substance)}} \times 100$$

where,

$$\text{BOD} = \frac{[(\text{mg } O_2/\text{litre uptake by test and/or reference item}) - (\text{mg } O_2/\text{litre uptake by inoculum blank})]}{\text{mg test and/or reference test item/litre}}$$

RESULTS AND DISCUSSION

FTIR Analysis of Lubricant Samples

FTIR spectra can be used as a tool for fingerprint identification of a lubricant. *Figure 1* show the FTIR spectra of petroleum-based white oil and palm-based mould scanned at infrared region of 4000 -

TABLE 1. PREPARATION OF MINERAL STOCK SOLUTIONS

Solution	Chemical	Amount (g)
A	Potassium dihydrogen orthophosphate, KH_2PO_4	8.50
	Dipotassium hydrogen orthophosphate, K_2HPO_4	21.75
	Disodium hydrogen orthophosphate dodecahydrate, $Na_2HPO_4.12H_2O$	44.60
	Ammonium chloride, NH_4Cl	
	All reagents were dissolved in water and made up to 1 litre	1.70
	The solution was adjusted to pH 7.2	
B	Magnesium sulphate heptahydrate, $MgS0_4.7H_20$	22.50
	Dissolved in water and made up to 1 litre	
C	Calcium chloride anhydrous, $CaCl_2$	27.50
	Dissolved in water and made up to 1 litre	
D	Iron (III) chloride hexahydrate, $FeCl_3.6H_20$	0.25
	Dissolved in water and made up to 1 litre	
	The pH of the solution was adjusted to 7.2	

Source: OECD 301 (1992).

TABLE 2. PREPARATION OF BIOCHEMICAL OXYGEN DEMAND (BOD) BOTTLES

Bottle	Preparation
1 and 2	Sample in mineral medium at 100 mg $litre^{-1}$
3 and 4	Reference compound (aniline) in mineral medium at 100 mg $litre^{-1}$
5 and 6	Mineral medium only (blank)

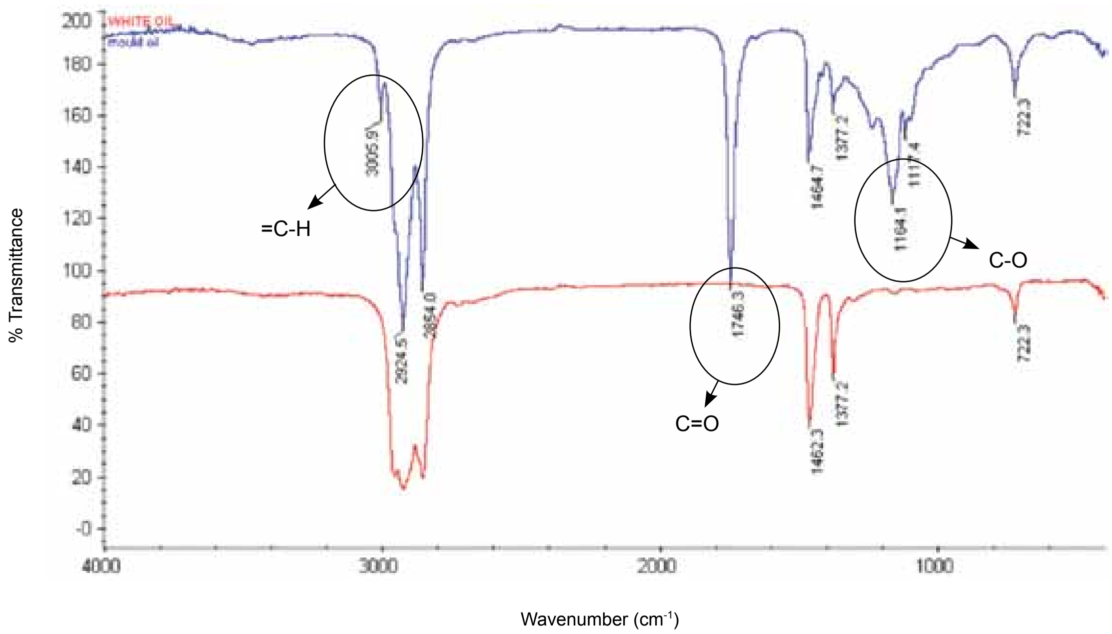

Figure 1. Fourier transforms infrared spectroscopy (FTIR) spectrum of petroleum-based white oil (red line) and palm-based mould oil (blue line).

500 cm^{-1}, respectively. FTIR spectrum of palm-based mould oil shows the presence of C-O stretching (1320 - 1000 cm^{-1}) and C=O stretching (1750 - 1735 cm^{-1}), indicating the presence of ester linkage which were not observed in petroleum-based white oil. Other than that, no aromatic structure (1500 - 1400 cm^{-1}) was detected in both petroleum and palm-based lubricants.

NMR Analysis of Lubricant Sample

The presence of ester group in palm-based lubricant (mould oil) was further confirmed by NMR analysis where a carbonyl carbon (C=O) was detected at 174.97 ppm (*Figure 2*). In contrast, the ^{13}C-NMR spectrum of petroleum-based lubricant (white oil) did not show the present of this C=O carbon (*Figure 3*). Peaks associated with =CH (130.11 ppm) and C-O (64.05 ppm) were also observed in palm-based lubricant (mould oil) (*Figure 2*).

Determination of Lubricants' Kinematic Viscosity

In lubricating system, viscosity is an important parameter to characterise the lubricating oil. The viscosity of the oil must be suitable to create and maintain a lubrication film between two moving metal surfaces. The kinematic viscosity of the tested lubricants is shown in *Table 3*.

Viability of Inoculum

The viability of the collected and pre-conditioned inoculum was measured by doing plate counts for

TABLE 3. KINEMATIC VISCOSITY OF PALM AND PETROLEUM-BASED LUBRICANTS

Source	Sample	Kinematic viscosity (cSt)
Petroleum	Mineral oil	95.76
	White oil	13.47
	Motor oil	Too viscous
Palm	Mould oil	50.56
	BO-20	34.02
	BO-18	87.95

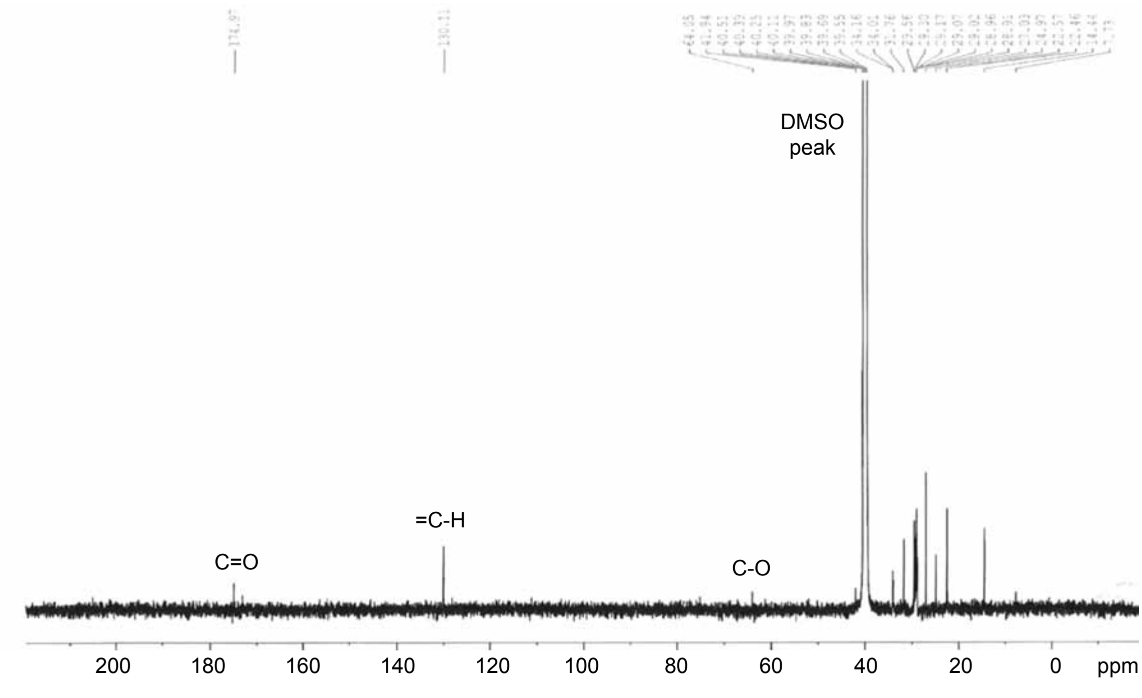

Figure 2. The ^{13}C-NMR spectrum of palm-based lubricant (mould oil).

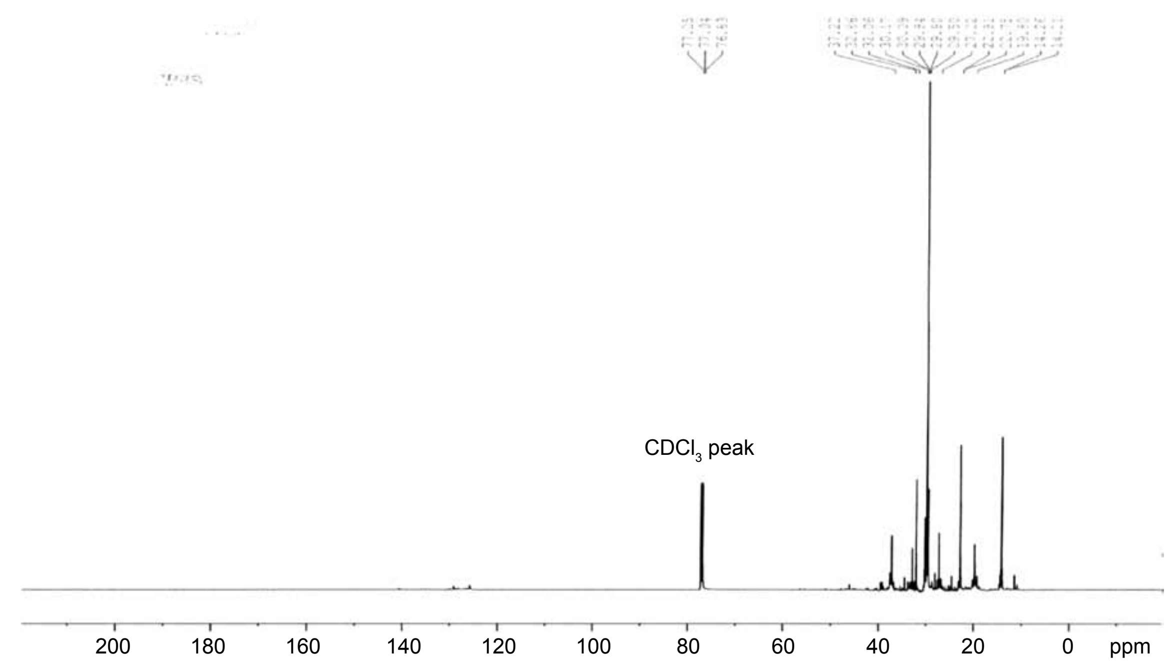

Figure 3. The ^{13}C-NMR spectrum of petroleum-based lubricant (white oil).

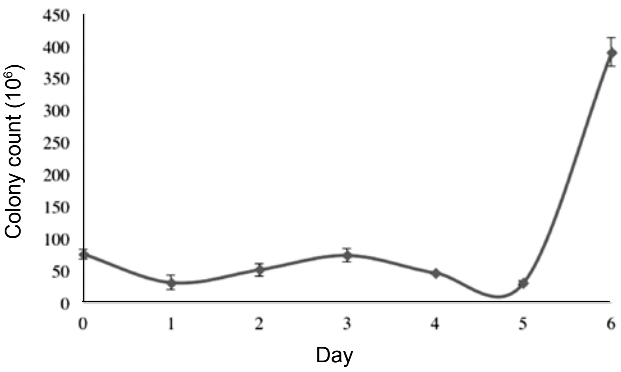

Figure 4. Colony counts of inoculums received from Indah Water Konsortium (IWK), Putrajaya, Malaysia.

six days. The number of colony count increased from 75 x 10^6 colony forming unit (cfu) on Day 0 to 389 x 10^6 cfu on Day 6 (*Figure 4*). Thus, the pre-conditioned inoculum was well maintained at the test conditions.

Theoretical Oxygen Demand (ThOD)

The ThOD of lubricants was calculated using their elemental composition as described by Gerike (1984). The elemental analysis of palm-based and petroleum-based lubricants is as shown in *Table 4*. From the table, the composition of oxygen was higher for palm-based lubricants compared to petroleum-based lubricants. The palm-based lubricants have slightly lower ThOD values than the petroleum-based lubricants due to the high oxygen content.

Biodegradability of Reference Substance

The biodegradability of the reference substance (aniline) was determined specifically within 14 days from the start of test to check the validity of the test and the suitability of the inoculum used. According to the standard method, the biodegradability of aniline should be at least 60% after 14 days. It was observed that its biodegradability reached 100% within 14 days (*Figure 5*). The validity of this study and the suitability of the inoculum are thus confirmed.

Biodegradability of Lubricants

The biodegradability of palm-based and petroleum-based lubricants is presented in *Figure 6*. In principle, any substance meeting the OECD ready

TABLE 4. THEORETICAL OXYGEN DEMAND (ThOD) OF THE LUBRICANTS

Test substance	% C	% H	% O	ThOD
Mineral oil	81	12	6	3.08
White oil	80	14	5	3.23
Motor oil	85	8	5	2.91
Mould oil	74	12	13	2.82
BO-20	67	11	21	2.47
BO-18	75	11	13	2.76

Note: C - carbon, H - hydrogen, O - oxygen.
The %N value of the lubricants will not be included in ThOD calculation since it is less than 0.05% and this will not affect the final ThOD value.

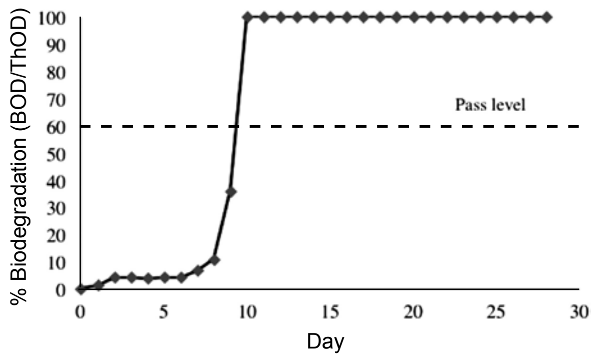

Figure 5. Biodegradation curve of reference substance (Aniline).

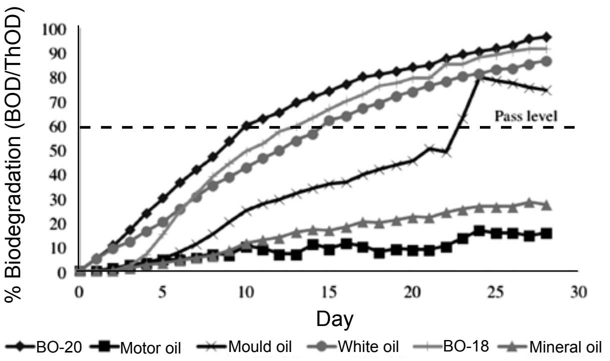

Figure 6. Biodegradation curves of palm-based and petroleum-based lubricant.

biodegradability pass levels (60% CO_2 evolution, 60% BOD / ThOD or 70% DOC removal within 28 days test period) in one of the biodegradability screening tests are considered as 'readily biodegradable' (OECD, 1992). *Figure 6* shows that palm-based lubricants can be considered as readily biodegradable where the percentage of biodegradability of mould oil reached 62.7% within 23 days, BO-20 reached 62.8% within 11 days and BO-18 reached 63% within 14 days. The petroleum-based lubricants, *i.e.* mineral oil and motor oil, were not readily biodegraded when tested according to standard method OECD 301F where their biodegradability did not achieve the 60% pass level within the 28 days test period. Palm-based lubricant is readily biodegradable compared to petroleum-based lubricant due to presence of ester linkage in an ester group. This ester linkage provides a vulnerable site for microbes to initiate the biodegradation process of the ester molecule. This translates into very high biodegradability rates for ester lubricants and allows more environmental-friendly products to be formed. Study done by Eisentraeger *et al*. (2002) also demonstrated that generally, the ester-based lubricants were more biodegradable in comparison with the substances present in mineral oils.

The biodegradability of a lubricant can also be correlated with its viscosity. The inverse relationship between lubricant's biodegradability and its viscosity has already been reported by Frederique (2000). This inverse relationship was due to the fact that all degrading organisms grew without adaptation phase or lag phase on oils with low viscosity, while in the highly viscous lubricating oil the degrading organisms grew with pronounced lag phases (Carpenter, 1994). The petroleum-based white oil has a low viscosity at 13.47 cSt and its biodegradability reached 61.8% within 15 days. Therefore, this petroleum-based white oil can be considered as readily biodegradable.

Since mineral oil and motor oil were not readily biodegradable, they may take a longer time to degrade in the environment or may not degrade at all, and this may pose environmental problems when they are released into the environment.

CONCLUSION

The palm-based lubricants; mould oil, BO-18 and BO-20, readily biodegraded in the OECD 301F Manometric Respirometry Standard Test Method where their biodegradability surpassed the 60% pass level as stated in the standard method. The biodegradability of petroleum-based lubricants; mineral oil and motor oil, did not surpass the 60% pass level and therefore cannot be considered as readily biodegradable in the test. Petroleum-based lubricants showed high tendencies to persist in the environment for a long time. The viscosity of the lubricant may also be used as an indicator in predicting the biodegradability of a lubricant. The petroleum-based white oil for example, has a low viscosity and it is readily biodegradable. The use of palm-based lubricants is more environmental-friendly and is one of the alternatives to reduce adverse environmental effects of lubricants on ecosystem.

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