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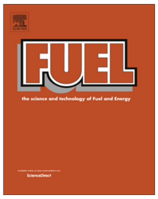

An environmentally friendly approach to treat oil spill: Investigating the biodegradation of petrodiesel in the presence of different biodiesels

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HIGHLIGHTS

- Biodiesels were used as an environmental-friendly method for treating oil spills.
- Biodegradation rate of biodiesel and petrodiesel mixtures was effectively enhanced.
- Increased biodegradation rate could be due to cometabolism and solvation effects.

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ABSTRACT

Petroleum oil spills constitute a major source of contamination for the ecosystem and can cause serious human health problems. In this work, therefore, biodiesels were used as cost effective and sustainable means in treating oil spills. A comparative study was conducted on the biodegradation of petrodiesel mixed with *Jatropha*, palm and soybean biodiesels at different ratios (20%, 50% and 80% by carbon mass). The experimental results showed positive synergistic effects for all cases. The biodegradation of the mixtures was enhanced by as much as 12.8%, 19.4% and 17.5% for the *Jatropha*, palm and soybean biodiesel blends, respectively (when the blend ratio was *Jatropha* 50%, palm 80% and soybean 20%). The enhancements could be caused by the effects of cometabolism and solvation. Maximum mixing ratios where the biodegradation enhancement was the highest under the experimental conditions (*Jatropha* 50%, palm 80% and soybean 20%) were attributed to the solvation properties of the surfactant-like fatty acid esters of the biodiesels.

1. Introduction

In 2010, the world was transfixed to the *Deepwater Horizon* oil spill which could be potentially the worst oil spill disaster in history [1]. Even after three years, tar balls still could be found on the Mississippi coast [2]. Obviously, oil spills destroy wildlife, taint seafood and dampen socioeconomic activities such as tourism and fisheries [3]. In the sea, the oil spill undergoes weathering over time, making treatment much more difficult [4]. Conventional oil spill treatment methods, including using booms, skimmers, sorbents (big sponges), *in-situ* burning and chemical dispersants have many harmful ecological effects and can cause serious environmental problems [5–7]. While, sorbents can be widely used either independently or in coordination with other remediation methods under various oil spill conditions, which can provide substrate for natural microbes to attenuate oil and thus speed up oil degradation. One major disadvantage of adsorbents is the erosion of sorbents by the moving waves and limited information on its effectiveness and prior use in a wide application area. Besides, natural biodegradation is also a less viable option, as it is a very long-term remediation process. For example, the *Florida* oil spill in Massachusetts was still detectable 30 years after the incident [8]. Therefore, it is necessary to develop environmental-friendly and efficient methods for treating oil spills.

Recently, biodiesel has been reported to be able to enhance the biodegradation of petrodiesel, and thus it could be an attractive and environmental-friendly method for treating oil spills [9,10].

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Generally, biodiesels act in treating oil spills via two mechanisms. One involves solvating weathered oil spills for easier recovery and the other involves enhancing the biodegradation of petrodiesel when mixed together. Solvating oil spills with biodiesels can render the oil ease of dispersion, therefore preventing it from incorporating into sediments and facilitating recovery [11]. It also increased the surface area of the oil which subsequently enhances microbial degradation [12]. The enhancement of microbial degradation occurred through cometabolism. Under normal circumstances, microorganisms cannot degrade petroleum oil spill as they are unable to use the hydrocarbon compounds as their carbon sources. However, when a readily biodegradable substrate is added to serve as the energy source, it is possible for the microorganisms to degrade the resilient oil substances through cometabolic activities.

Biodiesels differ in their fatty acids and minor chemical constituents may lead to different enhancement in biodegradation. So far, only limited work has investigated on the potential of biodiesel in oil spill bioremediation. Furthermore, only a limited range of biofuels was tested in those studies, which mostly used rapeseed and soybean oil derived biodiesels [13–15]. This might not fully uncover the potential of biofuels for this purpose, as different biofuels from various sources have different chemical properties which could affect their interaction with petroleum. Hence, a comparative study on the biodegradation enhancement effects of different biodiesels is needed in order to gain more understanding in the mechanisms of the interaction.

Previous enhancement studies of biodiesels derived from rapeseed, soybean oil and waste cooking oil utilized preconditioned inocula and agitated vessels to increase the efficiency of the biodegradation process [16,17]. The current study adapted the CO_2 evolution test method from British Standard Institution (BS EN ISO 9439:2001/BS 6068-5.12:2001) [18] and aimed to build on previous works by taking a real scenario approach, in which the used inocula were not preconditioned and the used vessels were non-agitated (floating samples). In on-site applications, the petroleum oil and biodiesel samples may not be thoroughly mixed throughout the bioremediation processes. Therefore, our study was designed to mimic the physical conditions of the actual field so as to draw as much insights as possible on the synergistic effects of mixing oil and biodiesels on the overall biodegradation rates.

This study reports on the potential of the biodegradation efficiency of petrodiesel in the presence of three different biofuels, namely *Jatropha curcas* (*Jatropha*), *Elaeis guineensis* (palm) and *Glycine max* (soybean) biodiesels at different ratios. The biodegradation efficiency was evaluated using the CO_2 evaluation test [18]. Of the three biofuels, *Jatropha* biofuel was selected as it is inedible and can be grown on unarable land, and hence does not compete with staple food crops for agricultural land. Thus, its large-scale usage as biofuel is less detrimental to global food supply levels [19]. Palm oil was chosen as it is a popular and readily available crop in the South East Asia and Pacific region. In addition, *Jatropha* and palm biodiesels have not been studied for their effects on biodegradation of petrodiesel. Soybean biodiesel was chosen as a reference as it was previously investigated [16].

2. Materials and methods

2.1. Plant culture condition and oil sample preparation

The *Jatropha curcas* trees were planted on a hill, with about 30° slope in Singapore. The average temperature during the growth period was about 28 °C with maximum irradiation of 2200 μmol (quantua) $m^{-2}\,s^{-1}$ and plants were well maintained and weeded once a week. No extra watering was supplied and plants received water from the regular rains during the experimental period. The plants were supplemented with 60 g of slow-release fertilizer (Osmocote® Plus, Australia, N:P:K: ratio = 18:5:8) once a month.

Jatropha curcas oil was extracted from the matured seeds, while palm and soybean oils were bought from a local supermarket, Singapore. *Jatropha* oil was extracted from seeds obtained from trees grown on a *Jatropha* plot in Singapore. The protocol adopted for extraction was similar to that of BS 4289-4:1999, Section 8.3.4 [20] for seeds using *n*-hexane (Sigma Aldrich) as the solvent. The solvent was removed from the *Jatropha* oil by a rotary evaporator at 50 °C and 335 mbar followed by drying at 103 °C in an oven. The oil obtained was sealed in glass containers and stored in a dry and dark [21,22] environment at room temperature to preserve the oil quality.

2.2. Transesterification

As *Jatropha* oil was reported to have high free fatty acid content (>2 wt%), a two-step acid-base catalysis method was used [23–25]. As palm and soybean oils were evaluated to contain 0.75% and 0.2% free fatty acid content respectively [26], direct base catalysis was conducted according to previous studies [27–29].

2.3. Determination of sample properties and mixing ratio

The densities of biodiesel and petrodiesel were determined from the weight and a known volume of the biodiesel/petrodiesel. Elemental analysis was performed using a Vario EL Elemental Analyzer (Elementar, Germany) to obtain the carbon mass fractions of the biodiesels and petrodiesel (Table 1) [30].

The various test samples were prepared in the following manner:

(i) Since aniline has a known degradation rate, it was used as an additional tracking tool to determine the efficacy of the experimental conditions in degrading the test samples. Therefore, aniline (reference sample), petrodiesel (Euro-4, Shell), Jatropha, Palm and Soybean biodiesels were used as pure samples.
(ii) Various blends for Jatropha, Palm and Soybean biodiesels were 20%, 50% and 80% by carbon mass, respectively.
(iii) A blank sample (inoculum only) was used as control.

There were a total of 15 samples and experiments were conducted in duplicates.

2.4. Evaluation stage – carbon dioxide (CO_2) evolution tests

The biodegradation of biodiesel, petrodiesel and their blends were analyzed and quantified using the CO_2 evolution test adopted from the British Standard Protocol [18]. The biodiesel or petrodiesel would act as the sole organic carbon source for the microorganisms. A test culture medium containing the other basic inorganic

Table 1
Density and carbon mass fractions of samples.

Sample	Density (mg/mL)[a]	Carbon mass fraction (wt C/wt biodiesel)
Petrodiesel	806.6	0.86
Jatropha biodiesel	873.3	0.75
Palm biodiesel	872.2	0.73
Soybean biodiesel	875.6	0.77
Aniline	1022	0.77

[a] Density measured at 298.15 K.