



A preliminary study for the photolysis behavior of biodiesel and its blends with petroleum oil in simulated freshwater



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HIGHLIGHTS

- For FAMES, higher degree of saturation resulted in lower transformation.
- Water matrices, initial concentration of biodiesel affected degradation slightly.
- Biodiesel source effect can be neglected.
- Presence of biodiesel stabilized the small oil droplets in aqueous phase.
- Biodiesel inhibited the degradation of some heavy hydrocarbons.

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ABSTRACT

With the increasing use of biodiesel and its blends with petroleum fuel, the corresponding environmental issues also occur during its production, application and transportation. The photolysis behavior for biodiesel and the impacts of biodiesel on the photo-oxidation of petroleum hydrocarbons in simulated freshwater was studied by irradiated with ultra violet (UV) and simulated sunlight in the present study. The results indicated that the photolysis rates of fatty acid methyl esters (FAMES) were mainly depended on their degree of saturation, slightly on water matrices and the initial concentration of biodiesel, regardless of biodiesel sources. Similar results were observed for total organic carbon (TOC) removal rates; however, TOC removal rates were slightly dependent on the initial concentration of biodiesel. The presence of humic acid and pyrogallol acid or lake water matrices slightly inhibited the removal rates of TOC. The photolysis rates of individual petroleum hydrocarbons with and without the presence of biodiesel followed similar rules. In brief, alkanes with light molecular weights were transformed faster than those with heavy molecules, the removal of polycyclic aromatic hydrocarbons (PAHs) were more significantly than alkanes, and the removal of alkylated PAHs (APAHs) increased concurrently with the alkylation level in each family. The presence of biodiesel only inhibited the photolysis of some heavy alkanes and PAHs, not for all other petroleum hydrocarbons. Biodiesel, as a surfactant-like material, could stabilize small oil droplets initially formed by agitation, therefore, these droplets experience longer lifetimes in the water phase before re-aggregating into larger globules and rising to the surface. The apparent solubility of petroleum hydrocarbons, especially for those with heavier molecular weights, has been enhanced in the presence of FAMES. In this scenario, light needs to penetrate water phase to degrade these targets compared with diesel alone. The direct contacting opportunities between UV light and targets, and radicals produced to attack targets were reduced, which finally resulted in the inhibited photolysis rates of some heavy molecular weight hydrocarbons.

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1. Introduction

Biodiesel consists of a mixture of long-chain fatty acid alkyl esters processed from biological triglycerides. It has received intensive attention as one of the most significant supplement fuels

and alternatives to petroleum diesel fuel, because of its comparable engine performance and environmental characteristics.

Spill accidents happen more often than ever with the increasing use of biodiesel and its blends with petroleum fuel. Biodiesel spills tend to spread and form a sheer thick layer of clear to light milky white color on top of sea water, and fatty acid methyl esters (FAMES) can be easily broken down to generate free fatty acids and methanol after spillage [1,2]. Corresponding adverse effects will occur to ecosystems and human health. Therefore, it is necessary to understand the fate of biodiesel exposed to the environment, and the dominant degradation mechanisms, for developing suitable remedial action and identifying the source in the case of a fuel spill.

Once biodiesel/its blend with petroleum oil spills into the environment, various weathering processes, for example, biodegradation, photo-oxidation, dissolution and evaporation, will occur. Because biodiesel components are more readily biodegraded than fossil fuels, many studies have focused on microbial degradation for remediation purposes [3–8]. Among them, a remediation study has shown that fatty acid methyl esters in biodiesel are degraded much faster than most components in fossil diesel [4]. This corresponds very well with the fact that biodiesel is more readily biodegradable compared with fossil diesel [3].

The contribution of biodiesel to the physical property of diesel has been investigated by several researchers [4,9]. It was found that the evaporation rate of fossil diesel components was not affected by the presence of FAMES in simulated seawater [4]. However, the physical mobility of heavy oil mixtures was enhanced by FAMES amendment in sand column [5]. Recently, one of our research has reported that the evaporation process and stability of diesel would not alter with the presence of biodiesel in a simulated ambient condition [10].

The contribution of biodiesel to the biodegradation of diesel suggested that the presence of biodiesel could facilitate the biodegradation of some petroleum hydrocarbons due to microbial growth promotion [5,9] and increase bioavailability (emulsion) [11]. Other researchers, however, have found that the presence of biodiesel did not accelerate the biodegradation of hydrocarbons [4,12,13]. For example, the degradation of benzene and toluene in anoxic and hypoxic conditions was hindered by the presence of biodiesel [12]. It seemed that the relatively high viscosity of biodiesel limited the migration potential of target hydrocarbons, resulting in their relatively slow natural attenuation process.

Among the various weathering processes, photolysis behavior of fuel is one of the important factors to control their transformation and fate in the environment. It is well known that the photolysis behavior of organic compounds in aquatic phase is based on the ability of solar/UV radiation to attack the target compounds. As a consequence, photochemical processes may take place, in which different transient species are generated: e.g., photo-ionization, radicals generated by bond homolysis or bond heterolysis, as well as a number of photo-physical processes (fluorescence, phosphorescence, etc.) [14]. The photo-oxidation behavior of petroleum in water has attracted much attention in the past years [15–18]. Generally, the photolysis rates of petroleum hydrocarbons depend on the composition and physical properties of the exposed parent oil, wavelength, turbidity levels of sample, suspended particulate matter concentration, and water matrices [17,19,20]. Till yet, different mechanisms for the photo-oxidation of petroleum and FAMES have been described, including free-radical oxidation in the presence of oxygen, singlet oxygen initiation of hydro peroxide formation, and ground state triplet oxygen combining with free radicals to form peroxides [17,18,21]. Recently, the photochemical process of crude oil has also become better characterized due to the development of analytical technologies [16,22].

Biodiesel, produced from different feedstocks, is generally spiked with different antioxidants to extend its storage stability [23]. The environmental factors affecting the fate of biodiesel and its blends with diesel at spillage site may vary with the physical and chemical properties of the spilled contaminants, the environmental matrices, climate, weather, topography and hydrology. Unfortunately, the impacts of environment matrices and physico-chemical properties of biodiesel on the photolytic behavior of biodiesel have not been extensively studied till yet. The photolytic behavior for individual petroleum hydrocarbons in biodiesel and diesel blends has not been fully understood either.

The purpose of the present study is to investigate the effect of physico-chemical properties of biodiesel and environmental matrices on the photolysis of biodiesel. The impact of biodiesel on the photolytic behavior of individual petroleum hydrocarbons would also be discussed. Biodiesel samples with different sources and initial concentration spiked into ultrapure (UP) water, and several simulated freshwater matrices (UP water, UP water with humic acid (HA) or pyrogallol acid (PY), and lake water) were irradiated by UV and simulated sunlight firstly. The removal rates of main FAMES and total organic carbon (TOC) were measured and compared to evaluate the significant contributors to the photolysis of biodiesel in freshwater. Similarly, the depletion rates of petroleum hydrocarbons with and without the presence of biodiesel after irradiated by UV light were measured and compared to investigate the influence of the presence of biodiesel on the photolytic behavior of petroleum hydrocarbons.

2. Experimental procedures

2.1. Chemicals and materials

Solvents including hexane, dichloromethane (DCM) and acetone were supplied by Spectrum Chemicals (Gardena, CA, USA) at the highest purity and used without further purification. Silica gel (100–200 meshes), humic acid and pyrogallol acid were purchased from Tianjin Chemical Co., Ltd. (Tianjin, China).

Normal alkane calibration standards from $n\text{-C}_9$ to $n\text{-C}_{40}$, 5α -androsterane, and polycyclic aromatic hydrocarbon (PAH) calibration certified standard mixtures were purchased from Restek (Bellefonte, PA, USA) and the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), respectively. Deuterated internal and surrogate standards including [$^2\text{H}_{14}$] terphenyl (terphenyl- d_{14}), [$^2\text{H}_{50}$] $n\text{-C}_{24}$ ($\text{C}_{24}\text{D}_{50}$), and PAH surrogate standards including [$^2\text{H}_8$] naphthalene (naphthalene- d_8), [$^2\text{H}_{10}$] acenaphthene (acenaphthene- d_{10}), [$^2\text{H}_{10}$] phenanthrene (phenanthrene- d_{10}), [$^2\text{H}_{12}$] benz[a]anthracene (benz[a]anthracene- d_{12}), and [$^2\text{H}_{12}$] perylene (perylene- d_{12}), were supplied by Supelco (Bellefonte, PA, USA).

FAME mixtures, including 14 FAME standards ranged from C_6 to C_{24} with different saturated degree, surrogate of 13-methyl, methyl myristate (13-methyl, $\text{C}_{14:0}$), and internal standard of methyl heptadecanoate ($\text{C}_{17:0}$) purchased from Sigma-Aldrich (Bellefonte, PA, USA) were employed for identifying and quantifying FAMES. Detailed chemical information for FAME standards used for calibration and identification are shown in Ref. [24].

2.2. Preparing fuel mixtures

Diesel purchased from a gas station in Wuhan, China, was used in this study as the reference oil to be blended with biodiesel. Three pure biodiesel samples sourced from soybean oil, canola oil and animal fat was designated as B_{soy} , B_{ca} and B_{an} , respectively. All samples were diluted with hexane to stock solution with a final concentration of 80 mg/mL.

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