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Polycyclic aromatic hydrocarbon (PAH) formation in a diesel engine fueled with diesel, biodiesel and biodiesel/n-butanol blends

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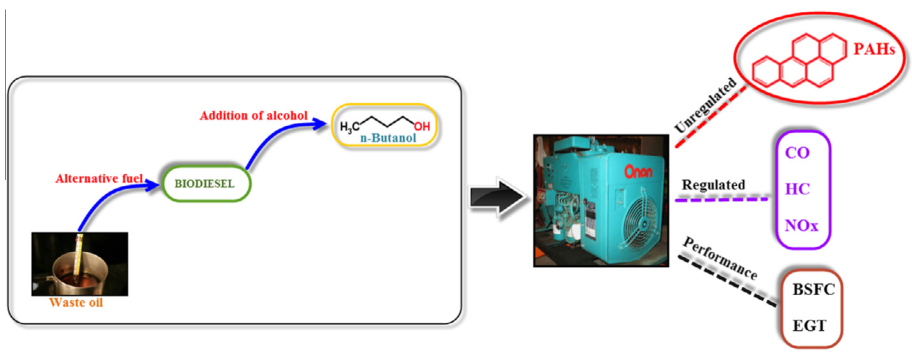
HIGHLIGHTS

- Biodiesel–n-butanol blends were tested in a diesel engine for blends up to 40% n-butanol.
- Exhaust gas emissions and PAHs were extensively determined and analyzed.
- Most of the PAHs were emitted as semi-volatile compounds and not bound to particulate matter.
- Blending more than 20% n-butanol with biodiesel also increased the toxicity of PAH emission.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), described as unregulated emissions, are harmful to the environment, human health and engines, and need to be controlled and reduced. Two of the most common alternative fuel types are biodiesel and alcohols, and their effects on PAH formation are not well-known, currently. Since biodiesel (B) fuels do not contain aromatic components and are suitable for use in diesel engines, the use of biodiesel as the base fuel for studying the effect of n-butanol (Bu) on PAH formation is natural.

With this purpose in mind, waste oil methyl ester, which is a compatible alternative fuel with diesel engines, was blended with 10%, 20% and 40% of n-butanol by volume, and BBu10, BBu20 and BBu40 blends were created. After determining fuel properties, these blends were tested in an ONAN diesel generator under four engine loads at 1800 rpm to quantify PAHs and to determined engine performance characteristics and regulated emissions. Separately, in order to quantify PAHs under the same engine conditions, GC–MS PAH speciation method was applied to real samples obtained from the engine. Cold flow properties were improved by adding n-butanol to biodiesel. For PAHs, it was shown that most of the aromatic hydrocarbons were emitted as semi-volatile compounds and were not bound to particulate matter. Blending more than 20% n-butanol into biodiesel also increased the toxicity of PAHs. No significant change in the aromaticity of the PAH emissions was found between blends.

1. Introduction

Demand for more diesel engines in the transportation sector causes increase of pollutants, which are harmful to humans, the environment and engines. Thus, as reported and emphasized in countless research, alternative fuels need to be used in order to

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control and reduce these emissions [1,2]. Evaluating blends of biodiesel and alcohols in diesel engines is a common approach to investigate effects of these alternative fuels on emissions and engine performance characteristics [3].

Typically, effects of these alternative fuels on fuel consumption and exhaust emissions are studied by blending the novel fuel with diesel [4,5]. The effect biodiesel has on emissions is often unclear due to several factors including: source of diesel, biodiesel origin, and engine parameters. Overall, most studies show an increase in NOx with biodiesel content, and a reduction in CO, HC and particulate matter (PM) emissions [6–8]. Fuel consumption and NOx emissions tend to increase with increased biodiesel fraction, which may be attributed to the lower energy content of biodiesel compared to diesel, and increased oxygen content, and therefore higher flame temperatures in-cylinder [9]. Under low load conditions and high biodiesel fraction, CO may increase compared to diesel, though the increase is small compared to the reduction seen at idle [3]. However, the biodiesel source has significant effects on emissions. As seen in specific research investigations in literature, coconut oil methyl ester, (a type of biodiesel) blending more than 50 vol% into diesel increases CO emissions at high loads, and typically increases NOx [7]. Rapeseed oil methyl ester, on the other hand showed a reduction of CO relative to diesel for all loads [6].

Alcohols are also important alternatives for diesel engines [2], and diesel–alcohol blends (diesohol) have gained attention as a way to control emissions. Diesel–lower alcohol (methanol and ethanol) blends described in literature are shown to reduce both PM emissions and NOx emissions [10]. A few investigations blending biodiesel, or diesel–biodiesel with methanol and ethanol show similar results, with methanol being more effective at controlling PM and NOx than ethanol [7,8,11–13]. Conversely, blends of diesel or biodiesel with methanol or ethanol cause an increase in HC emissions for blends greater than 5 vol% alcohol [12–14]. In recent years, n-butanol has been getting more attention due to its better fuel properties as compared to ethanol and methanol [2,15]. n-Butanol is a longer-chain alcohol compared to methanol or ethanol, resulting in a lower specific heat of vaporization and greater enthalpy of combustion, while lowering water susceptibility [15].

An investigation by Karabektas and Hosoz [16] blended up to 20 vol% iso-butanol into diesel and showed an increase in BSFC and subsequently, a reduction in brake thermal efficiency (BTE). NOx and CO emissions decreased with increasing n-butanol fraction, while HC emissions increased [16]. Blending n-butanol with diesel produced similar trends in other studies [16–22]. However, blending n-butanol into diesel may also cause a slight increase in NOx according to Chen et al. and Merola et al. [19,22]. In a high load and large n-butanol fraction (40 vol%), an increase in NOx and CO was seen as compared to neat diesel. At idle on the other hand, a greater magnitude decrease in NOx and CO emissions compared to neat diesel was noted [19]. Consistently, across those studies which investigated particulate matter, it is reported that there is a decrease in PM with increasing n-butanol fraction [20,22].

The importance and necessity of using biodiesel blends in diesel engines are explained in similar research studies [12,14]. However, there is a gap in terms of the investigation of unregulated emissions such as PAHs formed due to combustion of biodiesel in diesel engines [23]. Due to some of the poor fuel properties of biodiesel, there is limited use of neat biodiesel in diesel engines. In order to improve fuel properties such as density, viscosity and cold flow properties, literature shows investigations of biodiesel blends with alcohols, but these studies focused only on regulated emissions [2,19,21]. In addition, it is important to note that the European Union (EU) aims to use 10% biodiesel in diesel fuel by 2020. And, it is anticipated that biodiesel will be used in diesel engines extensively in the near future. Thus, it is important to understand the effect of biodiesel and biodiesel/alcohol blends on the formation of PAHs from the perspectives of human health, the environment and its influence on engine failure called "wetstacking" [8,24,25].

Polycyclic aromatic hydrocarbons (PAHs), also known as PNA (polynuclear aromatic hydrocarbons) are a class of organic chemical compounds containing several fused benzene rings. While there are an infinite number of possible PAH compounds, ranging in size and complexity from naphthalene (two fused benzene rings) up to graphitic compounds and other macromolecules, of primary concern are the compounds: naphthalene, acenaphthene, acenaphthylene, anthracene, fluorene, fluoranthene, phenanthrene, benzo[a]anthracene, pyrene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, and benzo[g,h,i]perylene according to the US Environmental Protection Agency (EPA) [23]. Generally, PAHs are toxic compounds and with the exception of acenaphthylene, they are known to the International Agency for Research on Cancer (IARC) as probable or possible carcinogens [23,26]. The EPA recognizes benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-c,d]pyrene as the most probable carcinogenic PAHs [23].

Among several other sources, PAHs are well-known to be emitted as a result of incomplete combustion and high pressure processes [23–27]. Combustion of an organic fuel resulting in a cool flame, such as in a diesel engine running at idle (having a very fuel-lean mixture) will not reach the ideal flame temperature and produce sooty emissions [27]. Under low load and at idle, PAH production within an engine is greater than the production at high loads for the same reason [27]. This problem is exacerbated in cold climates, where diesel engines are run at low load for long periods of time to prevent freezing of the fuel and where cold intake air further reduces flame temperature and leads to greater PAH production [27,28]. Because PAHs are semi-volatile, they may condense on surfaces within the engine and lead to engine failure through 'wetstacking' [24,25,29].

Generally, a neat diesel fuel containing a lower fraction of aromatic compounds will produce a smaller mass of PAH than a higher aromatic content fuel [30–34]. Blending biodiesel (a collection of methyl esters derived from various organic oils) has shown contradicting effects on the formation of PAHs in diesel engines. Biodiesel fuels derived from rapeseed oil, palm oil, animal fat, and soy oil have been shown to reduce PAH production in diesel blends [35–38]. On the contrary, methyl esters derived from used fry oil and olive oil may increase PAHs compared to diesel, as will coconut oil [38,39]. With the exception of coconut oil and used fry oil biodiesels, the biodiesel–diesel blends often show a reduction in the BaPeq (benzo[a]pyrene equivalence) which is a measure of PAH toxicity even if the total PAH content of the exhaust has increased [35–39].

Because diesel engines inject their fuel as a spray, the center of the fuel spray may not mix well with the surrounding oxygen, and thus it may be fuel rich. Adding an oxygen-containing compound to the fuel is thought to improve the local oxygen balance resulting in fewer PAHs. Diesel contains no fuel-borne oxygen, whereas methyl decanoate (a biodiesel surrogate) contains 17 wt% oxygen, and alcohols may contain even more (methanol $\sim$ 50 wt%, ethanol $\sim$ 35%, and n-butanol $\sim$ 21.6%). Because n-butanol is more miscible in diesel, with lower susceptibility to water contamination than ethanol, it has garnered significant attention [2,15]. Blending into diesel with biodiesel and/or ethanol, reductions in PAH emissions of 24% and BaPeq by 43% have been reported [40]. Similar trends have been observed for particulate matter (PM) emissions, which are reduced with diesel–n-butanol blending as a result of the reduction of aromatic content of fuels and increased oxygen content [40–43].