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Effect of hydrazides as fuel additives for biodiesel and biodiesel blends on NOx formation

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ABSTRACT

Fossil fuels are still one of the worlds major sources of energy. Because of their limited natural availability, however, renewable resources like biodiesel provide an attractive contribution to meet the growing demand for energy supply. A significant problem associated with the use of biodiesel as fuel for diesel engines is a higher NOx emission tendency. It is known that additives can mitigate NOx emissions from biodiesel and biodiesel blends. Therefore, this study investigated the effect of the additives benzoic and pivalic hydrazide using an ignition bomb (Advanced Fuel Ignition Delay Analyser – AFIDA (ASG Analytik-Service Gesellschaft). In addition, the hydrazides were tested with a Farymann single cylinder four-stroke diesel engine. In contrast to results reported elsewhere previously, it was found that the tested hydrazides did not show any significant influence on NOx emissions under the test conditions.

1. Introduction

Due to the limited availability of fossil fuels, alternative sources of energy are needed to secure the worlds energy supply in the future. Transesterification of vegetable oils can be used to yield fatty acid methyl esters (FAME) as a suitable fuel for diesel engines, commonly called biodiesel. However, biodiesel and the blending of biodiesel into fossil fuel often results in an increase in NOx emissions relative to conventional diesel fuel [1].

NOx is formed during combustion via three main mechanisms. High combustion temperature (>1700 K) breaks the double bond of oxygen, which can disassociate molecular nitrogen (N_2), leading to thermal NOx formation. The prompt NOx formation mechanism is based on free radicals in the flame front of hydrocarbon flames that react with N_2. The third source of NOx originates from fuel bound nitrogen, which is converted to NOx during combustion. As diesel fuel contains a low fraction of bound nitrogen, thermal and prompt NOx predominate in diesel fueled engines.

Compared to conventional diesel fuel, biodiesel is generally characterized by a reduced emission of hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM) [2,3]. In many cases, however, the use of biodiesel leads to an increase of NOx formation [1].

Various reasons have been proposed for this increase. A challenge in explaining the biodiesel effect is provided by the non-uniform dependence on numerous factors like biodiesel concentration, engine type, chosen test cycle, emissions control strategy, exhaust gas recirculation and injection strategy [2,4,5]. Mueller et al. [6], Cheng et al. [7] and Ban-Weiss et al. [8] introduced summaries of these theories.

A common theory for the NOx effect of biodiesel in pump-line-nozzle fuel injection systems interferes with speed of sound and bulk modulus of compressibility of biodiesel and fossil diesel fuel. Biodiesel is less compressible than fossil fuel, which leads to premature fuel injection. This results in an earlier combustion, higher peak in-cylinder temperature and increasing thermal NOx formation [9,10]. However, Cheng et al. [7] showed, that a fixed start of combustion timing leads to a load-averaged NOx increase of about 10% for soy-based biodiesel relative to fossil diesel fuel.

Due to the fact that bulk-modulus effect does not occur in common rail injection systems, a number of other theories were developed. It is known that biodiesel combustion produces less soot than the combustion of fossil diesel fuel. Mueller et al. [6] and Cheng et al. [7] investigated the radiative heat transfer of soot particles within the combustion chamber and found evidence that soot from fossil diesel fuel combustion lowers the combustion temperature by radiative heat transfer and therefore produces less

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thermal NOx. Another theory, presented by Hoekman and Robbins [2], considers the higher cetane number of biodiesel, which results in a shorter ignition delay and therefore a longer residence time at elevated temperature. However, this theory stands in contrast to observations of McCormick et al. [12], who reduced NOx emissions by cetane number enhancers. They conclude that a higher cetane number leads to less premixed air/fuel-mixture at the moment of combustion and this could lead to a lower peak in-cylinder temperature.

Hoekman and Robbins [2] summarize that, due to the complexity of combustion processes, one single theory cannot explain the NOx effect of biodiesel usage.

To prevent the increase of NOx emissions, several strategies can be employed. With a known concentration of biodiesel blend in diesel fuel, the engine management system can adjust the injection timing to an optimum as reported in [13–15].

However, Ye and Boehman [11] showed that a variation of injection pressure and injection timing does not influence the difference between NOx emissions of biodiesel and fossil diesel fuel. They concluded that the dominant mechanism leading to the NOx increase comprises higher local temperatures and earlier maximum cylinder temperatures due to leaner combustion in the premixed and mixing controlled combustion phases.

Another way to reduce NOx emissions is the usage of additives such as antioxidants, [12,16–20] which can quench radicals during combustion and thus decrease the formation of prompt NOx.

İleri and Koçar [18,19] used the common antioxidant BHT in a concentration of 0.1 wt.% to reduce NOx emissions from a B20 in the range of 5%. Fattah et al. [20] reduced NOx emissions from B20 by a mean of 9.8–12.6% with 0.1 wt.% of butylhydroxyanisole and BHT. Varatharajan et al. [17] reduced NOx emissions from a neat jatropha biodiesel fueled diesel engine in the range of 14% by addition of 0.025 wt.% of BHT.

Cetane number enhancer additives were used by McCormick [12] and Xing-cai [21] to control combustion phasing. These studies aimed at an earlier ignition and lower peak in-cylinder temperature for a reduction of thermal NOx.

Krahl et al. [22] reduced NOx formation of rapeseed oil methyl ester (RME) to a range of 45% by addition of 2.0 wt.% of octadecanoic hydrazide (Fig. 1). However, these experiments were carried out in an ignition bomb and not in an engine and by additional use of 2.0 wt.% of a solubilizer (2,2-dimethyl-(4-diethylaminomethoxy methy)-1,3-dioxolane) due to the poor solubility of the additive. In a supporting test Tanugula [23] showed that the solubilizer has no influence on NOx emissions.

The reduction of NOx was explained by thermal decomposition processes of hydrazides and the release of hydrazine by thermal stripping. Miller and Bowman [24] and Fenimore and Jones [25] showed that hydrazine acts much like ammonia in flames and is a potent reducing agent (Eqs. (1)–(3)).

$$N_2H_2 + O \rightarrow NO + NH_2 \quad (1)$$

$$N_2H_2 + NO \rightarrow NH_2 + N_2O \quad (2)$$

$$NH_2 + NO \rightarrow N_2 + H_2O \quad (3)$$

The poor solubility of hydrazides is caused by strong hydrogen bridges formed by the hydrazide group [26,27]. Bär and Krahl [28] have shown that those hydrogen bridges can be weakened by the introduction of bulky fatty acid residues like aromatic and substituted aromatic rings into the hydrazide or by an electron releasing inductive effect of the fatty acid residue provided by a *tert*-butyl group.

The aim of this study was to evaluate the effects of hydrazides on NOx emissions of ignition bomb tests with an Advanced Fuel Ignition Delay Analyser (AFIDA) (ASG Analytik-Service Gesellschaft) and the comparison of these results with emissions from engine tests. For a realistic application, hydrazides must be soluble without a solubilizer in a concentration comparable to other additives (<0.12 wt.%).

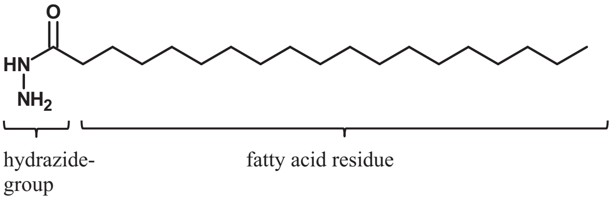

Fig. 1. Octadecanoic hydrazide.

2. Experimental details

2.1. Additives

The hydrazides used in this present study are shown in Fig. 2. Benzoic hydrazide (BH) was delivered by Merck KGaA. Pivalic hydrazide (PivH) was synthesized from methyl pivalate [29]. Both hydrazides are soluble at a concentration of at least 0.1 wt.% in RME at room temperature without additional solubilizers.

To be enable to compare our results with those obtained by Varatharajan et al. [17] and İleri and Koçar [18,19], who used BHT (Fig. 3) for NOx reduction, the combustion chamber experiments and the engine tests were performed with BHT as well.

2.2. Synthesis of pivalic hydrazide

A mixture of methyl pivalate (23 mL, 172.8 mmol) and hydrazine hydrate 80% (12.6 mL) was refluxed for 28 h. After cooling to room temperature, the reaction mixture was evaporated under reduced pressure, dried by azeotropic removal of the solvent with toluene and the residue was dissolved in $CHCl_3$. The mixture was washed with brine. The aqueous layer was extracted three times with $CHCl_3$. The combined organic layers were dried with anhydrous Na_2SO_4, and concentrated to afford pivalic hydrazide as white crystals. (9.6 g, 48%) (M.P. 64 °C; ^1H NMR (200 MHz, $CDCl_3$) δ: 7.3 (br s, 1H), 3.9 (br s, 2H), 1.2 (s, 9H))

2.3. Fuels

According to the common nomenclature, the amount of biodiesel added to conventional fossil diesel fuel determines the blend name (e.g. 7% biodiesel = B7).

The B100 used was made of rapeseed oil, which gives rapeseed oil methyl ester (RME) delivered by ASG – Analytik Service Gesellschaft.

B7 used in this study was Diesel R33 diesel fuel containing 7% used cooking oil methyl ester (UCOME, delivered by Tecosol GmbH, Germany), 26% hydrotreated vegetable oil (HVO, delivered by Neste Oil, Finland), 67% conventional fossil diesel fuel (delivered by Mabanaft GmbH & Co. KG, Germany) and a high-performance additive package (ERC Emissions-Reduzierungs-Concepte GmbH, Germany). Diesel R33 was purchased at the Walther filling station (Coburg, Raststraße 13, Germany).

For the engine tests, conventional fossil diesel fuel, Aral Ultimate Diesel™ (B0) was purchased at the Aral filling station (Coburg, Rodacher Straße 69, Germany).

2.4. Advanced Fuel Ignition Delay Analyser (AFIDA)

The combustion chamber experiments were performed in an Advanced Fuel Ignition Delay Analyser (AFIDA) at ASG – Analytik