



## Full Length Article

# Synthesis, characterization and antioxidant properties of 2,4,6-tris-isopropylbenzoic acid hydrazide in biodiesel



Ferdinand Bär<sup>a,\*</sup>, Henning Hopf<sup>b</sup>, Markus Knorr<sup>a</sup>, Jürgen Krahl<sup>c,d</sup>

<sup>a</sup> Coburg University of Applied Sciences and Arts, Coburg, Germany

<sup>b</sup> Technical University of Braunschweig, Germany

<sup>c</sup> OWL University of Applied Sciences, Lemgo, Germany

<sup>d</sup> Fuels Joint Research Group, Germany

## ARTICLE INFO

## Keywords:

Biodiesel

Additives

Antioxidant

FAME

Oxidation stability

## ABSTRACT

The use of biodiesel as fuel for diesel engines can reduce emissions of hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM). Unfortunately, however, biodiesel tends to increase emissions of nitrogen oxides (NO<sub>x</sub>) (EPA, 2002) [1]. Previous studies demonstrated that additives can lower this biodiesel NO<sub>x</sub> effect. Krahl et al. (2010) reduced NO<sub>x</sub> formation of rapeseed oil methyl ester (RME) to ca. 45% by the addition of 2.0 wt% of octadecanoic hydrazide. However, 2.0 wt% of a solubilizer were needed to dissolve the hydrazide in RME. Bär et al. (2014) modified these hydrazides to get a better solubility and found that hydrazides can be used as antioxidants. In this work, we present the synthesis, the characterization and antioxidant properties of 2,4,6-tris-isopropylbenzoic acid hydrazide. It was found that the solubility of 2,4,6-tris-isopropylbenzoic acid hydrazide in RME at 25 °C amounts 0.45 wt%. In addition it was shown that 4.5 mmol/kg 2,4,6-tris-isopropylbenzoic acid hydrazide increases the oxidation stability of distilled RME from 8.08 min to 10.25 min in PetroOxy tests and from zero hours to 2.27 h in Rancimat tests.

## 1. Introduction

Fossil fuels are still one of the world's major sources of energy supply. Because of their limited availability, however, renewable fuels like biodiesel provide an attractive contribution to meet the growing demand for energy. Challenges associated with the use of biodiesel in diesel engines are higher NO<sub>x</sub> emission [1] and lower oxidation stability compared to fossil diesel fuel. It is known that antioxidants can not only prevent oxidation but mitigate NO<sub>x</sub> emissions from biodiesel and biodiesel blends as well [4–11]. Krahl et al. [2] demonstrated that 2 wt% of *cis*-9-octadecenoic hydrazide in combination with a solubilizer reduces NO<sub>x</sub> emissions from biodiesel combusted in an ignition bomb to ca. 45%.

Krahl et al. [2] suggested a reduction mechanism for NO<sub>x</sub> by a thermal decomposition process of hydrazides and the release of hydrazine by thermal stripping. Miller et al. [12] and Fenimore and Jones [13] showed that hydrazine acts much like ammonia in flames and is a potent reducing agent (Eqs. (1)–(3)).



In addition, Bär and Krahl [3,14] showed that some hydrazides can inhibit the oxidation of biodiesel and biodiesel blends. Timmins and Deretic [15] reported that hydrazides can abstract hydrogen atoms from the hydrazide group breaking the chain reaction of autoxidation (Fig. 1). The α-N–H bond dissociation energy (BDE) of benzoic hydrazide (339 kJ/mol [16]) is similar to the BDE values of tocopherols (330.0–341.5 kJ/mol [17]) and BHT (339 kJ/mol [18]). The weak N–H bond of hydrazides will imply the scavenging of a peroxy radical (ROO·). The resulting hydrazide radical is thermodynamically more favorable and, therefore, it increases the antioxidant efficiency of the compound [19].

A problem in the usage of hydrazides is their poor solubility in diesel fuel, biodiesel and biodiesel blends which is caused by strong hydrogen bridges the hydrazide group is able to form [20,21] (Fig. 2).

Bär and Krahl [14] have shown that those hydrogen bridges can be weakened by the introduction of bulky fatty acid residues such as aromatic and substituted aromatic rings into the hydrazide or by an electron releasing inductive effect of the fatty acid residue.

This work aims to synthesize, characterize and investigate the

\* Corresponding author.

E-mail address: [ferdinand.baer@tac-coburg.de](mailto:ferdinand.baer@tac-coburg.de) (F. Bär).

URL: <http://www.fuels-jrg.de> (J. Krahl).

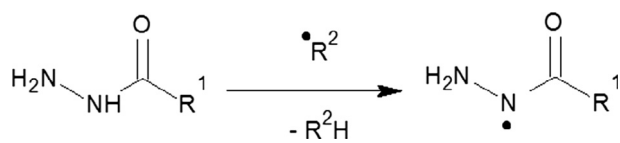


Fig. 1. Antioxidative action of hydrazides.

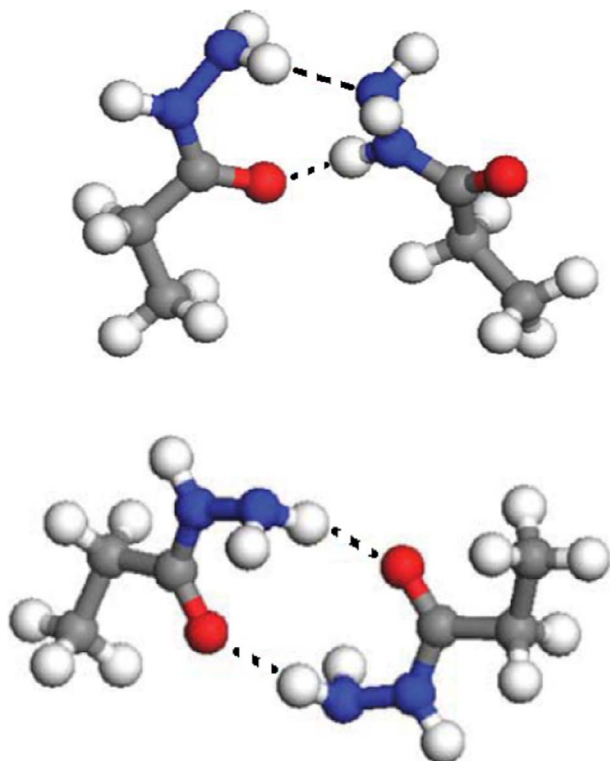


Fig. 2. Computer models of geometry-optimized dimers for propanohydrazide: parallel orientation (top) and anti-parallel orientation (bottom) [20].

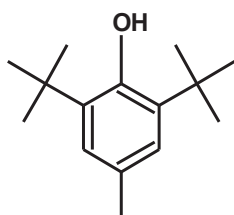


Fig. 3. 3,5-Bis(1,1-dimethylethyl)-4-hydroxytoluol (BHT).

antioxidative potential of a hydrazide that is soluble in biodiesel without requiring the addition of a solubilizer. In addition the antioxidative effect should be increased compared to hydrazides like benzoic acid hydrazide used in previous studies [3,14,22].

On the basis of sterically hindered phenol antioxidants like 3,5-bis(1,1-dimethylethyl)-4-hydroxytoluol (BHT) (Fig. 3) our plan was to synthesize a hydrazide with a sterically hindered hydrazide group to prevent the formation of strong hydrogen bridges and to stabilize the radical that is formed by its antioxidant activity (Fig. 1).

Initial experiments showed that the steric hindrance of the three *tert*-butyl groups of 1,3,5-tris-*tert*butylbenzene is too strong to be used as a precursor for subsequent synthetic steps. Furthermore, references from the literature suggest that the specific synthesis of highly hindered carbonyl compounds is often more difficult than one might anticipate [23]. Therefore 1,3,5-tris-isopropylbenzene was chosen to yield 2,4,6-tris-isopropylbenzoic acid hydrazide as a model substance for the

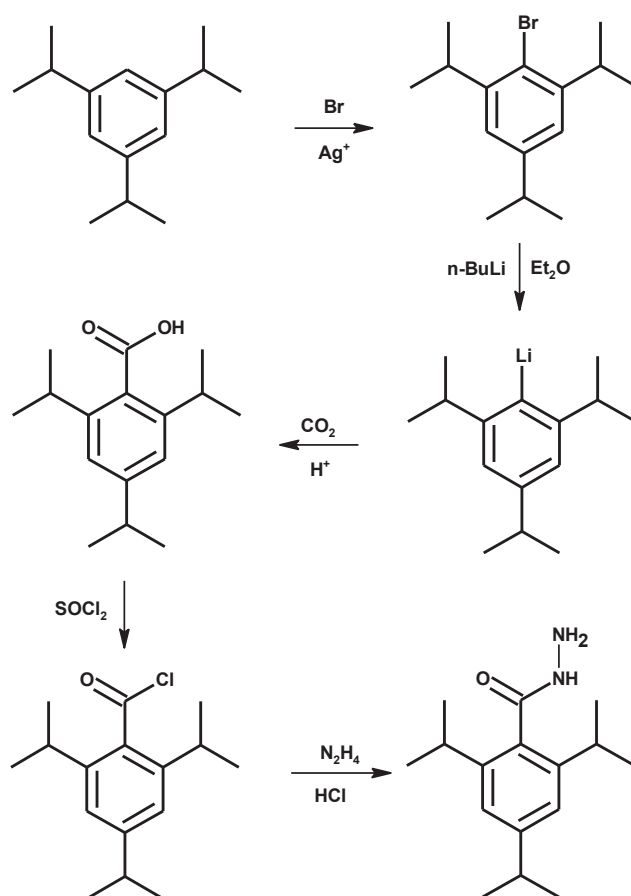


Fig. 4. Preparation route of 2,4,6-tris-isopropylbenzoic acid hydrazide.

Table 1

Fatty acid pattern of distilled rapeseed oil methyl ester.

FAME	Content [% (m/m)]
Hexadecanoic acid methyl ester	4.8
9-Hexadecenoic acid methyl ester	0.2
Octadecanoic acid methyl ester	1.4
9-Octadecenoic acid methyl ester	65.0
9,12-Octadecadienoic acid methyl ester	19.4
9,12,15-Octadecatrienoic acid methyl ester	8.2
Eicosanoic acid methyl ester	0.2
11-Eicosenoic acid methyl ester	0.8

Table 2

Induction periods with 4.5 mmol/kg additive in distilled RME.

Additive	PetroOxy [min]	Rancimat [h]
Neat distilled RME	8.08	0.0
2,4,6-Tris-isopropylbenzoic acid hydrazide	10.25	2.3
Benzoic acid hydrazide	9.51	1.7
BHT	23.01	6.2

investigation of solubility and antioxidant potential of sterically hindered hydrazides.

2,4,6-Tris-isopropylbenzoic acid hydrazide was obtained by a five step synthesis (Fig. 4). Thus, 1,3,5-tris-isopropylbenzene was halogenated with bromine and the subsequent lithiation step was performed by a halogen metal exchange with *n*-butyllithium. The intermediate was quenched with carbon dioxide to yield 2,4,6-tris-isopropylbenzoic acid. After reacting 2,4,6-tris-isopropylbenzoic acid with thionyl

Download English Version:

<https://daneshyari.com/en/article/6632300>

Download Persian Version:

<https://daneshyari.com/article/6632300>

[Daneshyari.com](https://daneshyari.com)