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^{1}H low field nuclear magnetic resonance relaxometry for probing biodiesel autoxidation

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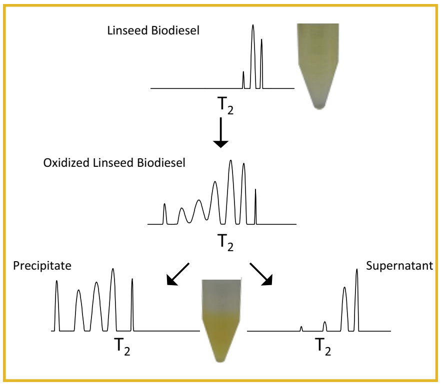
HIGHLIGHTS

- We study the oxidation stability of biodiesel and how it impairs fuel characteristics.
- New oxidative molecular structures affect physico-chemical properties of biodiesel.
- Oxidized products of biodiesel have different secondary interactions.
- Characterization of molecular interactions is a major application of ^{1}H LF-NMR relaxometry.

GRAPHICAL ABSTRACT



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ABSTRACT

The oxidation stability of biodiesel composed of fatty acid esters derived from vegetable oils, is one of the major issues challenging its wide-spread use as an alternative fuel. The poor oxidative stability of biodiesel compared to petrodiesel, is due to its high content of unsaturated fatty acid methyl esters that negatively affects fuel properties such as storage lifetime. Moreover, the relationship between new molecules formed by oxidation and their new solution morphologies is a complex subject that affects physico-chemical properties of the fuel. The goal of this work was to understand how the oxidized unsaturated fatty acid methyl esters and the non-oxidized components of the biodiesel interact and affect the final properties of multi component biodiesel mixtures. Towards this objective standard pure fatty acid methyl esters and biodiesel mixtures were heated for different time periods with constant stirring to induce autoxidation, and then analyzed by ^{1}H low field nuclear magnetic resonance (LF-NMR) relaxometry. To further define the molecular consequence of autoxidation and appearance of autoxidation products, a combination of supporting methods, including, gas chromatography, Fourier transform infrared, ^{1}H high field NMR, and thermogravimetric analysis were used.

^{1}H LF-NMR relaxometry was proven to be an advantageous tool to study autoxidation of biodiesel. It is a direct, rapid, non-destructive method that can be used to study the underlying structural and compositional mechanisms that contribute to changes in the fuel's physico-chemical properties. For example we describe in this paper the interactive effect of new oxidative products and stable non-oxidized components upon each other's molecular movement and morphology during the process of oxidation. One

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Abbreviations: CPMG, Carr–Purcell–Meiboom–Gill; DTG, derivative thermogravimetric; FA, fatty acid; FAME, fatty acid methyl ester; FTIR, Fourier transform infrared; GC, gas chromatography; HF-NMR, high field nuclear magnetic resonance; LF-NMR, low field nuclear magnetic resonance; PV, peroxide value; RC, relative contribution; TG, thermogravimetric; TGA, thermogravimetric analysis.

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major result was to show that the oxidized products of fatty acid methyl esters have different secondary interactions between themselves and the biodiesel components which were not oxidized but are mutually affected by each other. Characterizing these changes in molecular interactions and how they affect biodiesel properties is one of the major contributions of ^{1}H LF-NMR relaxometry. Also, the possibility of ^{1}H LF-NMR to analyze heterogeneous and at times heterophasic whole samples directly, including their physicochemical state, is of great value when studying the effect of different antioxidants on the oxidation stability of fuels and other food and biological systems.

1. Introduction

Air quality deterioration, global warming and acid rain are just some of the negative impact consequences that the widespread use of fossil fuels is generating on the planet. One alternative to conventional petroleum products are biofuels. These include liquid or gaseous fuels produced by plant material. Biodiesel is one such biofuel that offers a sustainable alternative to petrodiesel. It is biodegradable, nontoxic and its combustion results in a decrease in particulate, hydrocarbon, and carbon monoxide emissions compared to petrodiesel. It is safer to handle and store, and has excellent lubricating qualities that lead to improved performance and extension of the engine's life.

Biodiesel consists of mono alkyl esters of long chain fatty acids (FAs), with different lengths and degrees of unsaturation, as a function of the parent oil. Biodiesel is most commonly produced using methanol transesterification of glycerol esters, and therefore is referred as fatty acid methyl esters (FAMEs). The properties of the various individual fatty esters that comprise biodiesel determine the overall properties of the biodiesel fuel, including ignition quality, heat of combustion, cold flow, storage life time via oxidative stability, viscosity, and lubricity [1].

Several technical problems exist in using biodiesel, including increased NO_x exhaust emissions, cold flow and oxidative stability [2]. Oxidation of unsaturated fatty esters is due to atmospheric oxygen. Oxidized fuel can block filters and injectors, leading to fuel starvation and poor combustion; cause fuel injection equipment failure due to production of an acidic, corrosive environment within the fuel delivery system; and be the basis of other serious operational problems [3]. To overcome these problems there is an intensive effort to understand the changes in biodiesel solution properties upon oxidation, and the conditions that can be altered to modify the oxidation stability of the fuel.

The poor oxidative stability of biodiesel compared to petrodiesel originates from the larger number of double bonds in its alkyl chain components. Oxidation of unsaturated fatty compounds proceeds at different rates depending on the number and position of double bonds, where bisallylic carbons are especially susceptible to oxidation. Thus, if methyl oleate (mono unsaturated) is assigned a relative oxidative rate of 1, then methyl linoleate and methyl linolenate (di and tri unsaturated respectively) exhibit relative oxidation rates of 41 and 98, respectively [2].

Autoxidation is considered the primary mechanism of biodiesel degradation [3]. This is a radical chain process that involves an initiation step, a propagation sequence and one or more termination steps (Fig. 1). Its initiation is promoted by elevated temperature, light exposure or extraneous materials such as metals or initiators [4,5]. Initiation precedes with the formation of a radical hydrocarbon species on the allylic carbon ($R^{\cdot}$) via the removal of hydrogen from a carbon atom, followed by isomerization of the double bonds into a conjugated structure. The structure of $R^{\cdot}$ depends on the FAME being oxidized, and influences both the composition of the product and the rate of reaction. This radical can then react with atmospheric oxygen to form peroxide species ($ROO^{\cdot}$) propagating the reaction. $ROO^{\cdot}$ is not as reactive compared to $R^{\cdot}$, but is sufficiently reactive to quickly abstract hydrogen from a carbon to form another $R^{\cdot}$ and a hydroperoxide (ROOH) [5,6]. This chain reaction terminates when two free radicals react with each other to yield stable products.

(1) Initiation^a: $RH \rightarrow R\bullet$

(2) Propagation: $R\bullet + O_2 \rightarrow ROO\bullet$

$ROO\bullet + RH \rightarrow ROOH + R\bullet$

(3) Termination: $ROO\bullet + ROO\bullet \rightarrow$

$ROO\bullet + R\bullet \rightarrow$ Stable products

$R\bullet + R\bullet \rightarrow$

Fig. 1. Reactions in the autoxidation of FAMEs. RH in the initiation step represents a FAME with a hydrogen attached to an allylic carbon. ^{a}Initiation is promoted by elevated temperature, light exposure or extraneous materials such as metals or initiators.

The hydroperoxides, which are highly reactive species, may undergo further decomposition into oxygenated intermediates that additionally degrade into small chain acids, ketones, alkenes and aldehydes. The hydroperoxides and oxygenated derivatives can also form higher molecular weight dimers and oligomers via oxidative polymerization of peroxy (C—O—O—C), ether (C—O—C) or carbon–carbon (C—C) bridges [4]. One of the apparent results of oligomer and polymer formation is the increase in solution viscosity [6].

The evaluation of lipid autoxidation in general and FAMEs in particular is considered a challenging task, due to the need to use several different analytical methods to obtain a complete picture of the autoxidation process. Traditional test methods include measuring the FAMEs initial composition, primary oxidation products, secondary oxidation products, physical properties, and storage stability [7]. Several methods for determining both primary and secondary lipid oxidation products, along with their characteristics, advantages and limitations are summarized and discussed in a recent review [8]. Autoxidation products of fatty esters have very different chemical compositions and therefore different physical properties, polarities, degrees of solubility, molecular size and more. As a result, they require specific methods for analysis. Similar substrates and experimental conditions may yield opposite results depending on the analytical method used, which generally provide only partial information of the autoxidation state [8,9].

Typically oxidized biodiesel contains a complex mixture of oxidized and non-oxidized components which interact to form very different chemical and morphological properties as compared to the non-oxidized biodiesel. A major goal of this work is to understand how the oxidized products and the non-oxidized