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Comparative study of NOx emissions of biodiesel-diesel blends from soybean, palm and waste frying oils using methyl and ethyl transesterification routes

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HIGHLIGHTS

- 20% soybean methyl ester presented lowest emissions compared to the reference fuel.
- Blends with palm ethyl ester were amongst blends with best emissions at all loads.
- 20% palm methyl ester had the highest NOx emissions.
- Waste frying oils increase NOx emissions comparing to diesel.
- Ethyl esters blends showed lower NOx emissions than methyl esters blends.

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ABSTRACT

The research for renewable and less polluting fuels has focused on biodiesel. This fuel can derive from vegetable, animal or waste oils, and despite its potential to decrease atmospheric pollutants and greenhouse gases, its influence on NOx emissions is still uncertain. It is believed that biodiesel emissions, especially NOx vary depending on the feedstock, blend percentage and transesterification route. A better understanding of these factors can help choosing the best blend. In this context, this article aims at evaluating how the variation of these factors affects NOx emissions. Tests are carried out in a stationary internal combustion engine with 20% and 50% blends of methyl and ethyl esters made from soybean oil, palm oil and waste frying oil (collected in the University Campus). The analysis of the results with Tukey's test compare their means and lead to the conclusion that, when considering the route, ethyl blends have lower NOx emissions, and palm ethyl ester blends had the best results. Also when all factors are taken into account, B20 from soybean methyl ester has the lowest emissions of NOx. We recommend that future studies test the effect of antioxidants in NOx emissions, as well as test higher blend ratios.

1. Introduction

Concerns with the exhaustion of oil resources and environmental issues linked to the combustion of its products have motivated research for alternative and cleaner fuels from renewable sources [1]. Oil products account for 40% of the total energy consumed worldwide and, among them, diesel fuel is the most used. Its combustion is responsible for emitting air pollutants and greenhouse gases (GHG), prejudicial to human health and the environment [2,3].

Biodiesel, as an alternative diesel, is obtained from the transesterification of vegetable oils, such as soy, palm, and sunflower, and from animal fats, such as pork lard, beef tallow and fish oil. The use of biodiesel is interesting since it is highly biodegradable, has low toxicity and can replace diesel in many applications such as boilers and internal combustion engines without major modifications to the engine or losses in performances. Moreover, in comparison with regular diesel, biodiesel is capable of reducing hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM) emissions and practically eliminating the emission of sulfates and CO_2 (when its entire life cycle is considered) [1,4].

However, international literature does not agree on the effects of biodiesel on nitrogen oxides (NOx) emissions, which vary

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depending on the feedstock, blend percentage, transesterification route (depending on the alcohol used in the reaction) and engine load [1,5–9]. On that note, it is important to comprehend how this factors influence emissions in order to determine which combination constitutes the best alternative to diesel fuel.

Considering the hypothesis that these factors influence biodiesel NOx emissions, this article aims to evaluate how varying feedstock, transesterification routes, blend percentage and engine load affect these emissions. With that purpose, we conducted tests with biodiesel produced from soybean oil, palm oil and waste frying oil (collected from restaurants in the university's campus), using methyl and ethyl transesterification routes, to generate electrical energy using stationary internal combustion engines.

It will be possible to see in the bibliographical review section that, among the papers selected in this research, the majority focused only in testing methyl esters and very few conducted tests with ethyl esters. Furthermore, the number of papers that compares both transesterification routes is also limited. In light of this, by studying more than one route, and comparing them, this paper contributes with this existing research gap.

Starting from this introduction, the current work is divided into six sections. The second section provides a bibliographical review about biodiesel, its feedstock and NOx emissions. The third section presents the materials and methods used in this study. The obtained results are described in the fourth section and analyzed in the following section. Lastly, the sixth section presents the conclusions, limitations and suggestions for new studies.

2. Bibliographical review

Biodiesel is a fuel composed of long-chain fatty acid alkyl esters, from vegetable oils or animal fats. Among the methods for obtaining biodiesel, the transesterification process is commonly used due to its simplicity and low cost [1,10].

This method promotes a reaction between oils or fats with an alcohol, forming esters (biodiesel) and glycerol, which is a byproduct that can be burned for heating purposes or used as raw material in the cosmetics industry. Methanol and ethanol are the alcohols most used in the process, forming methyl esters or ethyl esters, respectively. However, methanol is used more frequently due to its lower costs and physicochemical advantages, since its shorter chain allows for an easier separation process between esters and glycerol [1,10].

The oils and fats used to obtain biodiesel can come from different feedstocks and can be classified as [1,8,11]:

- Edible vegetable oil: sunflower, rapeseed, rice bran, soybean, coconut, corn, palm, olive, canola, almond, etc.
- Non-edible vegetable oil: jatropha, karanja, polanga, tobacco seed, cotton seed, linseed, mahua, rubber seed, etc.
- Waste or recycled oil: waste frying oil and sewage sludge.
- Animal fats: chicken fat, pork lard, beef tallow and fish oil.

Table 1 lists the main feedstocks used in the six largest biodiesel producing countries in the world [1,3]. Brazil, the fourth largest producer, uses as its feedstock 76.9% of soybean oil, 19.8% of animal fats and 2.2% of cotton seed oil. The remaining 1.1% refers to palm oil, peanut oil, oilseed radish oil, sunflower oil, castor oil, sesame oil, waste frying oil and other oily products [12].

Biodiesel has similar properties to diesel and can be used in internal combustion engines without major modification to its characteristics. It can replace diesel entirely or blended to it in any proportion, with minor losses in performance [1,8,10].

According to Hoekman and Robbins [13], the interest in biodiesel arises mainly from its domestic origin and renewable origin,

Table 1
Largest biodiesel producers and its main feedstocks. *Source:* [1,3,11].

	Country	Feedstock
1	United States	Soybeans/waste oil/peanut
2	Germany	Rapeseed
3	Argentina	Soybeans
4	Brazil	Soybeans/cotton oil/animal fat/palm oil
5	Indonesia	Palm oil/jatropha/coconut
6	France	Rapeseed/sunflower

which potentially decreases GHG when considering the whole life cycle (including cultivation, production of oil, conversion to biodiesel and transportation), since the CO_2 produced by the fuels combustion, will be consumed by the crops via photosynthesis. As it is a renewable energy source, its role in providing energy requirements for transportation is expected to increase significantly [1,9].

Compared to diesel, using biodiesel (net or blended with diesel) lowers the emissions of HC, CO and PM. Moreover, it is highly biodegradable and non-toxic, has no aromatic compounds and a lower sulfur content. However, using biodiesel may lead to higher emissions of NOx, a local pollutant that causes respiratory problems [1,8,10,13].

NOx emissions are worrisome as they represent a group of reactive gases containing nitric oxide (NO) and nitrogen dioxide (NO_2), which are harmful to human health, contribute to acid rain, causing damages in structures and increasing the acidity of water resources [14].

To further comprehend biodiesel's NOx emissions, we conducted a bibliographical review with 35 papers, published from 2003 to 2017, with experimental results for NOx emissions. Papers that only contemplated bibliographical reviews were not included. The review results are shown in Table 2, where it can be seen which feedstock, blend, load and transesterification routes were used.

Among the gathered papers, only 1 [15] tested biodiesel made from both ethyl and methyl transesterification routes. 33 papers tested methyl esters while 1 tested only ethyl esters. This validates the contribution of this study that carries out experiments with both routes.

Amidst the papers that studied ethyl esters, the only feedstocks used in these were mahua oil [29] and rapeseed oil [15]. All found reductions in NOx, except when testing B75 and B100 of rapeseed biodiesel [15]. Regarding the papers that tested methyl esters, 75% reported an increase in NOx emissions.

Among the papers contemplated in this bibliographical review, 71% showed an increase in NOx emissions when using biodiesel, while 23% presented decreases in emissions. The remaining 2% had results that increased and decreased emissions when varying blend percentage. Makareviciene and Janulis [15] tested biodiesel made from rapeseed oil and found lower emissions for with blends ratios of 25% and 50% while higher emissions for 75% and 100%. Serrano et al. [35] tested biodiesel made from a mixture of soybean and palm oils and identified lower percentages for B20 and higher emissions for B7.

Considering the feedstocks used in this study we gathered six [6,7,23,24,37,45] papers that studied palm methyl ester, in which all of them detected higher emissions, except for Abu-Hamdeh and Alnefaie [6] and Ng et al. [24]. Abu-Hamdeh and Alnefaie [6] discovered that at constant engine speed and various torques, B10, B30 and B50 had lower emissions than diesel; and Ng et al. [24] identified 5% reductions in NOx emission for B100, under reduced steady-state emissions test cycle, representative of on-road driving condition, with constant speed and load values.

As for soybean methyl ester, four papers testing this fuel were found [14,22,31,41] and only one [31] reported reducing in NOx emissions by 7% for B100.