



Storage and oxidation stabilities of biodiesel derived from waste cooking oil



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HIGHLIGHTS

- Storage and oxidation stabilities of B100 derived from waste cooking oil are reported.
- Waste cooking oil derived B100 contained over 60% unsaturated esters.
- DSC was used to study the impact of oxidation on B100's low-temperature quality.
- Three oxidation stages were identified during modified ASTM D2274 testing of B100.
- The effects of oxidation on B100's physicochemical properties are reported.

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ABSTRACT

The present work investigates the storage and oxidation stabilities of 100% biodiesel (B100) derived from waste cooking oil. Physical properties and chemical composition of B100, including viscosity, density, peroxide value, heat of combustion, acid number, and phase behavior, were measured. The analysis showed that this B100 contains over 60% unsaturated esters. The long-term storage stability was studied based on ASTM D4625 which simulates up to two years storage by holding samples at 43 °C. Modified ASTM D5304 and D2274 tests were conducted to investigate oxidation processes of B100. An extended ASTM D2274 method was also employed to investigate the influence of oxidation time on stability. The influence of long-term storage and oxidation reactions on physicochemical properties and phase behavior was investigated using ASTM methods. The existence of three stages of B100 oxidation was identified based on the property changes after the modified ASTM D5304 and D2274 tests.

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1. Introduction

Biodiesel is defined as “a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100” by the American Society for Testing and Materials (ASTM) [1]. Generally, biodiesel is produced by a transesterification process in which triglycerides from the vegetable- and animal-derived feedstocks are alcoholized with methanol in the presence of catalyst to obtain fatty acid methyl esters (FAME) and glycerol as a byproduct. The fatty acid composition of the feedstock is not altered by the transesterification reaction. Table 1 lists the five most common compounds in biodiesel [2]. Interest in biodiesel is continuously increasing worldwide motivated by its renewable and environmental benefits. In the U.S., the most common feedstocks for biodiesel are soybean oil, canola oil, used

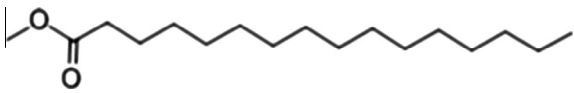
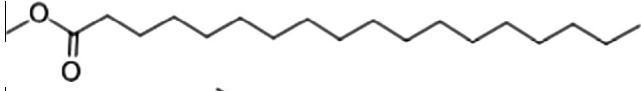
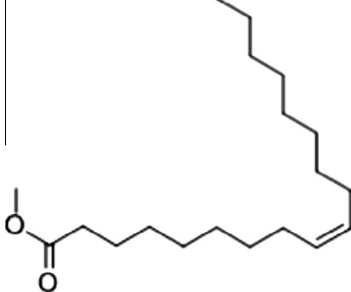
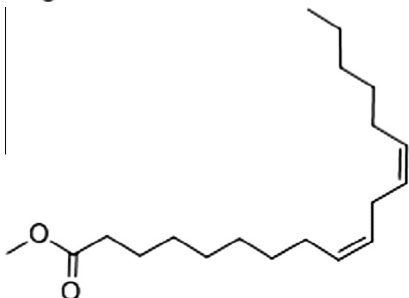
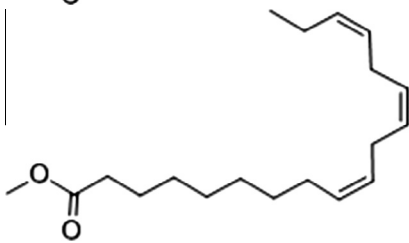
cooking oil, waste grease and tallow. It is commonly used for ground transportation in pure form (B100) or as 5% or 20% blends with petroleum diesel, B5 and B20, respectively. In 2012, approximately 991 million gallons of biodiesel were produced in U.S., and this value increased to over 1200 million gallon in 2014 [3]. As of January, 2015, there were 97 biodiesel plants in the U.S. with capacity of over 2.0 billion gallons per year [3].

Although biodiesel has many prominent advantages over petroleum diesel, it is more prone to oxidation than conventional petroleum diesel owing to the presence of unsaturated bonds in the molecules inherited from its parent feedstock. This susceptibility to oxidation has significant impact on the diesel quality during long-term storage and handling. The general oxidation mechanism of unsaturated FAME is reasonably well understood [4,5], and the reaction generally involves two types: autoxidation and photo-oxidation [4]. Autoxidation is the major cause of biodiesel degradation, and it generally comprises four steps: (i) release of hydrogen radicals by radical initiators; (ii) formation of peroxide and carbon

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Table 1
Five most common fatty acid methyl ester compounds in the biodiesel [2].

Common name	Formal name	CAS. no.	Molecular formula	Molecular weight	Molecular structure
Methyl palmitate	Hexadecanoic acid, methyl ester	112-39-0	C ₁₇ H ₃₄ O ₂	270.45	
Methyl stearate	Octadecanoic acid, methyl ester	112-61-8	C ₁₉ H ₃₈ O ₂	298.50	
Methyl oleate	9-Octadecenoic acid (9Z)-, methyl ester	112-62-9	C ₁₉ H ₃₆ O ₂	296.49	
Methyl linoleate	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	112-63-0	C ₁₉ H ₃₄ O ₂	294.47	
Methyl linolenate	9,12,15-Octadecatrienoic acid (Z,Z,Z)-, methyl ester	301-00-8	C ₁₉ H ₃₂ O ₂	292.45	

radicals when hydrogen radicals interact with oxygen, (iii) further reaction of carbon radicals with oxygen; (iv) formation of stable oxidized product [4]. Temperature also impacts the oxidation reaction of biodiesel. Highly-stable, conjugated structures are formed by the Diels–Alder reaction of polyunsaturated methyl esters [4]. In general, the oxidation process of commercial biodiesel has three stages: (i) induction stage, in which free radicals react with antioxidant compounds preferentially rather than FAME; (ii) exponential stage, in which ~80–90% antioxidants have been consumed and FAMEs start to rapidly react with oxygen; (iii) termination stage, in which the rate of peroxide degradation exceeds the rate of peroxide formation and the fuel quality is significantly changed [5].

The storage and oxidation stabilities of biodiesel derived from various feedstocks have been investigated [4–27]. The oxidation stability concerns the tendency of fuels to react with oxygen, while the storage stability concerns the general stability of the fuel under long-term storage. Both types of biodiesel stability depend on its susceptibility to degradation by oxidation reactions, which are highly influenced by the makeup of unsaturated esters. Generally, the oxidation rate of FAME depends on the number of double bonds and their position [28,29], and is mainly affected by the number of bis-allylic methylene groups adjacent to the double bond compared to the allylic methylene groups, e.g. methyl

linoleate is more susceptible to oxidation than the methyl oleate, and methyl linolenate is more susceptible to oxidation than methyl linoleate owing to the presence of additional bis-allylic methylene configuration [4,13].

In this article, the physicochemical properties and chemical composition of commercial biodiesel derived from waste cooking oil produced by Pacific Biodiesel are reported. Method ASTM D4625 [30] was employed to investigate the long-term storage stability of biodiesel. Modified methods ASTM D5304 [31] and ASTM D2274 [32] were used to study oxidation processes of biodiesel under various conditions. Additionally, the influence of oxidation on fuel physicochemical properties and low-temperature qualities, such as density, viscosity, peroxide value, acid number, heat of combustion, fusion and crystallization temperature and enthalpies, were also investigated using ASTM methods.

2. Materials and methods

2.1. Materials

Biodiesel produced by Pacific Biodiesel was purchased from Carl's Jr. 76 Station in Honolulu, HI. The biodiesel purchased is defined as B99.99 with <0.01% impurity and approximately 0.04%

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