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Castor oil biodiesel and its blends as alternative fuel

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ABSTRACT

Intensive production and commercialization of biodiesel from edible-grade sources have raised some critical environmental concerns. In order to mitigate these environmental consequences, alternative oilseeds are being investigated as biodiesel feedstocks. Castor (*Ricinus communis L.*) is one of the most promising non-edible oil crops, due to its high annual seed production and yield, and since it can be grown on marginal land and in semi-arid climate. Still, few studies are available regarding its fuel-related properties in its pure form or as a blend with petrodiesel, many of which are due to its extremely high content of ricinoleic acid. In this study, the specifications in ASTM D6751 and D7467 which are related to the fatty acid composition of pure castor methyl esters (B100) and its blend with petrodiesel in a 10% vol ratio (B10) were investigated. Kinematic viscosity and distillation temperature of B100 (15.17 $mm^2 s^{-1}$ and 398.7 °C respectively) were the only two properties which did not meet the appropriate standard limits. In contrast, B10 met all the specifications. Still, ASTM D7467 requires that the pure biodiesel meets the requirements of ASTM D6751. This can limit the use of a wide range of feedstocks, including castor, as alternative fuel, especially due to the fact that in practice vehicles normally use low level blends of biodiesel and petrodiesel. These issues are discussed in depth in the present study.

1. Introduction

From 2001 to 2007, global biodiesel production increased from 0.8 to almost 4 h m^3, where edible-grade vegetable oils (soy, rapeseed, sunflower and mustard) are currently the major biodiesel feedstocks [1]. This intensive production and commercialization of biodiesel have raised some critical environmental concerns. Its large-scale production can lead to imbalance in the global food market by drastically increasing consumption oil prices, which mainly affect developing countries. Land availability, and in particular competition for acreage with food crops, is also considered a core limitation [2]. In order to mitigate these environmental consequences, unconventional oilseeds are being investigated as alternative feedstocks.

Biodiesel can be used in its neat form (B100) or blended at any level with petrodiesel to create a blend. Blends are denoted as "BXX", where "XX" represents the biodiesel fraction (i.e., B20 is 20% biodiesel and 80% petrodiesel). To ensure proper vehicle performance, official standards were established. ASTM D6751 [3] is a widespread international standard of pure biodiesel (B100). In practice, BXX blends are more common, and have been legislated in Europe and US. For example, France has advanced the use of B5, and in the US blend levels

Abbreviations: FA, Fatty Acid; CaME, Castor Methyl Esters; ULSD, Ultra Low Sulfur Diesel; CN, Cetane Number; CP, Cloud Point; OS, Oxidative Stability; KV, Kinematic Viscosity; DT, Distillation Temperature.

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are mandated at the state level [4]. As a result, ASTM D7467 [5] was recently introduced for fuel blend grades of B6–B20.

The various parameters specified in ASTM D6751 and ASTM D7467 can be divided into process- and oil/petrodiesel-related parameters. The first category can be controlled by changing the reaction conditions, including: water and sediment, sulfated ash, carbon residue, glycerin content, copper strip corrosion and content of metals. The second category, which is the main interest of this study, comprises of parameters that largely depend on the Fatty Acid (FA) composition of the chosen oil or quality of the petrodiesel fuel, including: Cetane Number (CN), Cloud Point (CP), Oxidative Stability (OS), Kinematic Viscosity (KV), Distillation Temperature (DT) and lubricity. Several other parameters depend also on the quality of the oil, though not directly linked to the FA composition, including: flash point, acid number and phosphorous content.

CN is a dimensionless descriptor of biodiesel ignition quality, which decreases with decreasing chain length and increasing branching and unsaturation. CN is a measure of the biodiesel's ignition delay, with higher CNs indicating shorter time between initiation of fuel injection and ignition [6]. High CN values have been correlated with reduced NO_x emissions and improved engine performance [7,8]. Biodiesels usually hold higher, thus improved CN compared to diesel fuels. CP is a low temperature property of biodiesel, and one of the major problems associated with its use. CP is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates, causing clogging of fuel lines. Biodiesel derived from oils which contain significant amounts of saturated FAs will display unfavorably higher CP [7,9]. ASTM does not specify a CP limit. Rather a report is required, due to the differing weather conditions present in each geographic area, affecting its value [7].

OS of biodiesel has been the subject of considerable research, primarily in regard to oxidation during extended storage periods. This is one of the major issues affecting the use of biodiesel because of its content of unsaturates, which are especially susceptible to oxidation [10]. Factors such as presence of air, elevated temperatures and presence of metals were found to promote oxidation. Increase in the number of double bonds also enhances oxidation [11]. KV affects the atomization of a fuel upon injection into the combustion chamber, and thereby ultimately the formation of engine deposits [7]. Reducing KV is the main reason for transesterifying oils, since biodiesel viscosity is approximately an order of magnitude less than that of the parent oil [12]. DT determines the distillation curve of a fuel, as an indication for the fuel composition, which is normally difficult to obtain for petrodiesel, and specifies the maximum temperature of distillation for 90% of its components. The presence of high boiling point components in fuels can significantly affect the degree of formation of solid combustion deposits. As mixtures of a few relatively similar compounds, biodiesels exhibit a narrow boiling range relative to petrodiesel, which is near the high end of the range reported for the fuel [6]. Lubricity is an essential property of the fuel for proper functioning of engine components such as fuel pumps and injectors. Due to strict environmental regulations, sulfur content in petrodiesel has been significantly reduced over the past few years. This has led to reduced fuel lubricity, which can cause severe damage to the engine [13]. Many have reported on the inherently greater lubricity of biodiesel, compared to petrodiesel, even at low blend levels [[13–17] and others].

Castor (*Ricinus communis L.*) is an important non-edible oil crop, considered a vital industrial raw material. Castor seeds are poisonous to humans and animals since they contain the toxic protein ricin, although absent from the oil itself [18]. Worldwide, castor is cultivated on 12 600 km^2 with an annual seed production of 1.14 Mt and an average seed yield of 902 kg ha^{-1} [19]. It is available at low cost and the plant is known to tolerate diverse weather conditions. In addition, castor can be grown on marginal lands, usually unsuitable for food crops. All these features make it an attractive alternative biodiesel feedstock. Castor oil consists mainly of ricinoleic acid (12-hydroxy-*cis*-9-octadecenoic acid). The high level of this hydroxylated FA imparts unique properties to the oil and biodiesel produced from it.

Although Castor Methyl Esters (CaME) had recently gained global interest, few studies are available regarding its fuel-related properties, most of which denote only part of the specifications. Among these studies there is an agreement in regards to several of the physical properties of CaME including, favorably high flash point and improved lubricity. The extremely high KV, exceeding by far the international standard specifications and high density (which is not specified in the ASTM methods), have been known to limit its use and commercialization as an alternative fuel. Other physical properties are not as definite.

Based on the properties of methyl ricinoleate, the use of CaME as biodiesel was dismissed [20], not only due to its extremely high KV, but also for its relatively high melting point, and low CN and OS. Nonetheless, several authors have examined the physical properties of CaME itself, and have come up with contradicting results. Cvengros et al. [21] reported of excellent OS, low temperature properties and poor CN. Scholtz and da Silva [22] stated that CaME consists of high CN and OS, and low temperature stability. Sanford et al. [23] measured as part of a large-scale survey of different biodiesel feedstocks, excellent CP but high cold filter plugging point (denoted in EN 14214), and poor OS. None of these authors, however, have looked at the DT of CaME.

In this study, the specifications which are related to the FA composition of pure CaME (B100) and its blend with petrodiesel in a 10% vol ratio (B10) were investigated according to ASTM D6751 and D7467. To the best of the authors' knowledge, full properties of CaME and its blends, according to the aforementioned standards have not been reported yet in the literature.

2. Material and methods

2.1. Material and reagents

All chemicals and reagents used in this study were analytical grade. Castor seeds were obtained through an Israeli seed company, Evogene Ltd. The seeds well represent the local Israeli castor genetic population as previously characterized [24]. Prior to oil extraction, seeds were oven dried at 70 °C for 72 h to remove excess moisture. Castor oil was attained by either cold-pressing castor seeds with an industrial extruder