Fuel 218 (2018) 375–384

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

A comparative study on the fuel properties of biodiesel from woody essential oil depending on terpene composition

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A R T I C L E I N F O

Keywords:
Woody essential oil
Alternative biodiesel
Terpene composition
Fuel properties

A B S T R A C T

The essential oils from four Korean domestic gymnosperm species (red pine, white pine, cypress, and cedar) were examined in this study to understand the fuel characteristics based on their terpene compositions. The elemental composition, heating value, density at 20 °C, energy density, flash point, and kinematic viscosity at 40 °C of each woody essential oil were analyzed based on their terpene composition. The major elements in all woody essential oils investigated in this study were carbon, hydrogen, and oxygen. The woody essential oils were composed of more than 80% carbon and less than 10% oxygen due to the presence of terpene derivatives (terpene alcohols and terpene acetates). With respect to minor elements, sulfur contents did not satisfy the quality standard (10 ppm). Among the four woody essential oils, both red pine oil and white pine oil showed slightly lower higher heating values (HHVs; 44.09 MJ/kg and 44.13 MJ/kg, respectively) than diesel fuel. There was a negative correlation between oxygen content and HHV. Density was raised by an increase in the average number of carbon atoms and/or the terpene derivative contents and ranged from 0.875 g/mL for red pine oil to 0.924 g/mL for cedar oil. Based on their higher densities than diesel fuel and although they had lower HHVs, higher energy densities (38.59–39.18 MJ/L) were observed, with the exception of cypress oil. All the woody essential oils satisfied the quality standard for flash point (> 40 °C). These flash points should consider both the average number of carbon atoms and terpene derivatives. In contrast, the kinematic viscosity of the essential oils was only affected by the number of carbon atoms. Cedar oil (6.1 mm^2/s) had the largest kinematic viscosity followed by cypress oil (2.7 mm^2/s), white pine oil (1.6 mm^2/s), and red pine oil (1.4 mm^2/s). By considering all assessed properties, a terpene mixture similar to the essential oil from red pine oil or white pine oil was deemed the most appropriate alternative biodiesel candidate though its viscosity and sulfur content must be improved.

1. Introduction

The global population has doubled over the past 50 years. Simultaneously, demands for a high standard of living and aspirations for continuous economic development have induced ever-increasing amounts of global primary energy consumption. World petroleum consumption amounted to 9.5 million barrels per day in 2015 [1]. In compliance with the concerns over energy security, energy source diversification, oil crisis management, greenhouse gas reduction, and environmental regulation policy, research on alternative fuel has been vigorously supported. It is urgent to develop alternatives to diesel fuel due to its versatility as a transportation fuel for vessels, automobiles, rolling stock, construction equipment and agricultural machines.

The first attempt to apply vegetable oil as an alternative for diesel fuel utilized untreated vegetable oil to operate conventional diesel engines [2]. However, it has been deemed an inappropriate biofuel for direct injection diesel engines. Its kinematic viscosity is 10 times higher than diesel fuel, which causes meager atomization performance accelerating vaporization and combustion. The incomplete combustion of fuel and carbon deposits in engine injectors or engine valve sheets were also reported as problems when untreated vegetable oil was directly used as biofuel [3,4]. To improve the fuel suitability of vegetable oil, research has been focused on blending it with diesel fuel [4–6], emulsification [7,8], pyrolysis [9–11] and transesterification [12–15].

A fatty acid alkyl ester (FAAE) mixture manufactured by the transesterification of vegetable oil and alcohols has been known to be

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https://doi.org/10.1016/j.fuel.2018.01.021
Received 16 August 2017; Received in revised form 21 November 2017; Accepted 5 January 2018
Available online 02 February 2018
0016-2361/

Nomenclature

ANC	average number of carbon atoms
C_{KF}	concentration of Karl-Fischer reagent (mg/mL)
D	density of the sample at 20 °C (mg/μL or g/mL)
e	heat from the fuse wire and acid production (J)
EE	water equivalent (J/°C)
G	weight of sulfur in the sample (μg)
HHV	higher heating value of the sample (J/g)
HHV_S	higher heating value of the gelatin capsule (J/g)
K	viscometer constant (0.014 mm^2/s^2)
LHV	lower heating value of the sample (J/g)
m	weight of the sample (mg or g)
m_S	weight of the gelatin capsule (g)
S	sulfur content of the sample (ppm)
T_e	efflux time (s)
U	energy density of the sample (J/mL)
V	volume of the sample (μL)
υ	kinematic viscosity at 40 °C (mm^2/s)
V_{KF}	volume of the Karl-Fischer reagent (mL)
ΔT	temperature increase (°C)
$\%Di$	diterpene composition of the sample (%)
$\%H$	hydrogen content of the sample (%)
$\%H_2O$	moisture content of the sample (%)
$\%Mono$	monoterpene composition of the sample (%)
$\%Sesqui$	sesquiterpene composition of the sample (%)

the most popular biodiesel to date. Major sources of FAAE biodiesel are rape seed oil and soybean oil, of which the mass production and supply are possible. Glycerides or fatty acids derived from animal fats, used cooking oils and waste greases can also be utilized for FAAE biodiesel production [16–19]. Furthermore, FAAE biodiesel from microalgae has been recently studied with significant effort [20–22]. This is because microalgae can be cultivated on non-arable land and enable the simultaneous production of high value-added co-products from a microalgae biorefinery [23,24].

Several attractive advantages of FAAE biodiesel have led to a number of relevant studies [25–31]. Because FAAE biodiesel can be directly applied to conventional diesel engines, it is unnecessary to devise a new type of diesel engine for alternatively developed biofuels. In particular, its outstanding tribological properties give us no apprehension about engine abrasion, and its high flash point assures safety during fuel handling and storage. The reduced emission of smoke, unburned hydrocarbons (HC), carbon monoxide (CO), as well as lower sulfur content and superior biodegradability compared to diesel fuel enable the positive evaluation of FAAE biodiesel in terms of the environment. However, its low level heating value and high freezing point are issues of great concern. It also often suffers from deterioration including oxidation, autoxidation and biodegradation, which could exacerbate substantial corrosion in fuel tanks during storage. Furthermore, the relatively high hygroscopicity of FAAE biodiesel gives rise to increasing water content and the subsequent accumulation of free water, which adversely affects fuel properties [32–38].

Woody essential oil obtained from the water distillation of woody foliage is composed of terpene compounds (hydrocarbons and derivatives thereof), known as secondary metabolites of plants. They are biosynthesized via five-carbon isoprene units and can be classified as monoterpenes (C10), sesquiterpenes (C15), and diterpenes (C20) depending on the number of carbon atoms. Because petroleum diesel fuel is mainly composed of paraffinic, naphthenic, and aromatic hydrocarbons whose number of carbon atoms ranges from 9 to 23 [39], the expected physical and chemical properties of woody essential oil are considered comparable to those of diesel fuel [40]. In this light, many attempts to apply essential oil as biodiesel have been reported. Anand et al. [41] prepared a FAAE biodiesel blend with turpentine oil and Kasiraman et al. [42] mixed cashew nut shell oil and camphor oil in various ratios. These fuels were examined to evaluate engine performance, emission, and combustion characteristics using a direct injection 4-stroke single-cylinder diesel engine. Vallinayagam et al. [43] reported a terpene mixture obtained by the acid-catalyzed hydration of turpentine gum extracted from oleoresin as a suitable alternative biofuel. This biodiesel containing α-terpineol, dipentene, and α-pinene as the major constituents and could be directly used in diesel engines without further processing.

Diesel fuel has various fuel characteristics such as boiling point, freezing point, density, heating value, cetane number, and viscosity depending on whether the diesel constituents are paraffinics, naphthenics or aromatics [44]. These differences in fuel physicochemical properties can be controlled with fuel additives and ultimately affect engine performance characteristics (brake specific fuel consumption, brake thermal efficiency, volumetric efficiency, exhaust gas temperature, etc.), exhaust characteristics (smoke density, NO_X, CO, HC, and CO_2 emission, etc.), and combustion characteristics (heat release rate, ignition delay, pressure rise rate, combustion duration, etc.) in the field [45].

Given the effect of fuel chemical composition on utilization in a diesel engine, there has been a host of studies focused on the relationships between the composition of diesel blend with biofuel, especially FAAE biodiesel, and engine performance, exhaust, and combustion characteristics. For example, it was reported that increasing the FAAE biodiesel blend ratio increased brake-specific fuel consumption [32,46–48]. The blend ratio of hydrated turpentine gum, however, showed the opposite tendency due to its relatively low viscosity compared to diesel fuel, which resulted in faster and more complete combustion [43]. CO and HC emissions are also affected by fuel types. These exhaust characteristics were decreased by increasing the FAAE biodiesel blend ratio [46,48,49]. These relationships were comprehensible based on the (a) combustion efficiency, which were improved by the presence of oxygen atoms in the FAAE biodiesel, and (b) carbon and hydrogen contents. In contrast, this explanation was not perfect for diesel blend with hydrated turpentine gum blend or ethanol. The former displayed effective relationships only under high load conditions [43] and the HC emissions of the latter showed the reverse relationship [50]. Ignition delay, which is a combustion characteristics, also varies in fuel types. While it showed a positive correlation with viscosity in petroleum-derived fuels because of poor atomization and slower mixing with air, the reverse was true for diesel blend with FAAE biodiesel [46]. In this blend fuel, volatile gases derived from the breakdown of FAAE biodiesel molecules at high temperature reduced the delay period in the diesel engine [51].

Although there have been a few studies on the engine performance, exhaust, and combustion characteristics of terpene mixtures, there is currently no comprehensive understanding regarding not only the relationship between fuel properties and the preceding characteristics but also how terpene composition affects fuel properties. With the goal of applying terpene mixtures to alternative biodiesel, we aimed to suggest an appropriate terpene composition through comparative analyses of fuel properties and the terpene composition of essential oils extracted from Korean domestic gymnosperm species including Korean red pine (*Pinus densiflora*), Korean white pine (*Pinus koraiensis*), hinoki cypress (*Chamaecyparis obtusa*), and Japanese cedar (*Chryptomeria japonica*).

2. Experimental

2.1. Materials

Korean red pine was collected from the Seoul National University