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Investigation of biofuels from microorganism metabolism for use as anti-knock additives

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ABSTRACT

This paper investigates the anti-knock properties of biofuels that can be produced from microorganism metabolic processes. The biofuels are rated using Research Octane Number (RON) and Blending Research Octane Number (BRON), which determine their potential as additives for fuel in spark ignition (SI) engines. Tests were conducted using a single-cylinder Cooperative Fuel Research (CFR) engine and performance of the biofuels was compared to primary reference fuels (PRFs). The investigated fuels include 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, 2-methylpropan-1-ol (isobutanol), and limonene. Results show that 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, and 2-methylpropan-1-ol (isobutanol) sufficiently improve the anti-knock properties of gasoline.

1. Introduction

Fuel production from biomass has gained increased attention due to concerns with greenhouse gas emissions and shrinking global fuel reserves. A large number processes that convert biomass into combustible fuels are available, but many rely on resources such as simple sugars derived from corn [1,2]. Although potential sources of biomass are numerous, conventional feedstocks often come from places where they compete with food for cultivable land and other resources [3]. Therefore, further research is required assess other potential biomass sources that do not disrupt the food supply. A promising source of sustainable biomass for second-generation biofuels is lignocellulose, the most abundant biopolymer on earth [4,5]. Research in the conversion of sugars derived from the breakdown of lignocellulose to alcohols and other biofuels is currently being conducted [6–8]. Recent advances in synthetic biology have allowed the engineering of new microbes that are able to convert this complex lignocellulosic biomass efficiently into liquid biofuels [9–12]. However, the variety of biofuels that can be produced by this method is restricted and the combustion properties of these potential fuels have not been sufficiently investigated.

A property that impacts a fuel's suitability for spark-ignited (SI) internal combustion engines is knock resistance, which increases thermal efficiency [14]. Knock resistant fuels, such as alcohols, generally have high octane numbers and can be used as anti-knock fuel additives which, when added to non-oxygenated gasoline, increases the octane number [13]. The octane boost of an anti-knock fuel additive can be determined using the blending octane number [15]. The blending octane number is defined as the theoretical octane number for a pure compound and is determined using a linear extrapolation from the octane number of mixtures (between 0% and 20%) of the anti-knock fuel additives and non-oxygenated gasoline. This method represents the effect of a fuel's ability to increase the octane number at low blend compositions and is therefore useful in determining a fuel's potential as an anti-knock additive. The improvement in octane number that anti-knock fuel additives give to the resulting fuel blend depends on the both the anti-knock fuel additive and the blend composition [16]. One should note that many fuel components in anti-knock fuel additives contribute a non-linear effect when boosting the octane number, especially at low blend compositions [17].

The objective of this study is to rate the suitability of selected biofuels as anti-knock fuel additives for SI internal combustion engines. The biofuels investigated include three alcohols (3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, and 2-methylpropan-1-ol) and

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one cyclic terpene (limonene). These four molecules have recently been shown for microbial production in engineered *Escherichia coli* strains [10–12]. While fully saturated limonene (through hydrogenation) has been investigated in combustion engines [18], it has not been investigated as an additive. C5 alcohols and isobutanol are also of interest to the biofuel community and have been investigated as potential fuels in combustion engines [19,20], though their effect on knock resistance has not been fully explored. Table 1 lists the investigated fuels and selected properties [21–24].

As an indicative measure for knock resistance, the Research Octane Number (RON) is measured for each biofuel. In order to assess suitability as an anti-knock additive, the Blending Research Octane Number (BRON) for each biofuel is measured using mixtures (between 0% and 20%) of each biofuel and non-oxygenated gasoline (RON = 85).

2. Materials and methods

2.1. Experimental setup

All tests were conducted in a Waukesha Cooperative Fuel Research (CFR) F-4 single cylinder research engine. The engine was modified in order to enable knock testing and operation with pure alcohols and gasoline–alcohol blends [25]. A variable needle fuel jet was installed to allow increasing fuel flow rate and to overcome the higher latent heat of alcohols. Three pressurized fuel tanks were added to allow for fast fuel switching and to prevent mixing while transitioning between fuels. The cooling system was also redesigned to deal with the thermal stress on engine components [26]. Selected specifications for the Waukesha CFR F-4 engine used in this study are shown in Table 2.

In-cylinder pressure was measured using a 6052B Kistler piezoelectric pressure transducer in conjunction with a 5044A Kistler charge amplifier and was recorded every 0.1 crank angle degree (CAD). The cylinder pressure transducer was mounted in the cylinder head. Intake pressure was measured using a 4045A5 Kistler piezoresistive pressure transducer in conjunction with a 4643 Kistler amplifier module. Crank angle position was determined using an optical encoder, while an electric motor, controlled by an ABB variable speed frequency drive, controlled the engine speed. A Motec M4 engine control unit (ECU) controlled spark timing, injection timing, injection pulse width, and injection duty cycle.

2.2. Octane number determination

The standard for knock rating of spark-ignition engine fuels, as issued by the American Society for Testing and Materials ASTM2699 [27], is coupled to a Waukesha Model CFR F-1 Motor Method Octane Rating Unit. Due to this particular requirement, a specific testing procedure based on ASTM2699 [27] has been previously designed for the Waukesha CFR F-4 used in these experiments [26,28]. The procedure assumes that combustion in both Waukesha CFR engines is similar. This is due to the corresponding engine design and comparable operation conditions.

A fuel's octane number is derived by bracketing its knocking characteristics with data from primary reference fuels (PRFs) per ASTM2699 [27]. However, in order to bracket knocking characteristics of the fuels tested in our CFR F-4 engine, a criterion that represents knocking operation was established. A Knock Indicator (KI) is introduced to rate knock intensity at the point of comparison. The knock intensity is assessed by analyzing the in-cylinder pressure data [28,29]. In order to establish a KI, the in-cylinder pressure trace is band-pass filtered (4–10 kHz) and rectified. The filtered and rectified pressure data is then integrated over 90 crank angle degrees, starting at 20° before top dead center (BTDC), resulting in the KI as seen in Eq. (1) where p_i is the in-cylinder pressure data for a given cycle, i, and θ is the crank angle degree.

Table 2
Selected engine specifications CFR F-4.

Type	Water cooled four stroke
Bore	8.265 cm (3.254 in.)
Stroke	11.43 cm (4.500 in.)
Cylinder swept volume	613.252 cm^3 (37.432 in^3)
Compression ratio (CR)	4:1 to 17.5:1 (variable)
Combustion chamber volume	176.7 cm^3–40.8 cm^3 (10.784 in^3–2.489 in^3)
Connecting rod length	25.4 cm (10 in.)
Piston material	Aluminum
Piston rings	3 compression, 2 oil

$$KI = \int_{i-20}^{i+70} \left|\tilde{p}_i\right| d\theta \tag{1}$$

Adjusting the engine's compression ratio (CR) varies both the KI and the frequency of knock occurrence. As a first step towards calculating the octane number of a fuel, the compression ratio is increased and then recorded when 5% of all cycles knock. A cycle was defined as knocking if its KI range exceeded the noise level by 50 units. Noise level as a function of compression ratio was determined by comparing the in-cylinder pressure from non-knocking combustion with motoring (no combustion) in-cylinder pressure. A complete sweep from no knock to strong knock (over the 5% frequency threshold) was recorded for every test. Fig. 1 provides a graphical representation of knocking cycles increasing with compression ratio for the biofuels tested in this paper alongside selected reference fuels and a non-oxygenated gasoline.

Knocking frequency traces like Fig. 1 were generated for each biofuel and Primary Reference Fuels (PRFs) – blends of isooctane and *n*-heptane – that bracketed the biofuel (i.e., reached the 5% knocking frequency threshold and lower and higher compression ratios than the fuel of interest). Because RON is assumed to vary linearly with compression ratio, the RON of each biofuel was determined by linearly interpolating between the RON of the PRFs and the corresponding 5% knocking threshold compression ratios. Even though ASTM2699 [27] has not fully been applied in this study, this method of predicting RON using our CFR F-4 has been previously validated [26].

After determining the RON of each biofuel mixture, the blending RON (or BRON) can be calculated using Eq. (2) where RON_{ref} is the Research Octane Number of the base fuel (i.e., non-oxygenated gasoline), RON_{bl} is the octane number of the mixture, and f is the fraction of the anti-knock fuel additive on a volumetric basis [15].

Table 1
Selected properties of investigated fuels.

Fuel	3-Methyl-2-buten-1-ol	3-Methyl-3-buten-1-ol	2-Methylpropan-1-ol	Limonene
Molar mass (g/mol)	86.13	86.13	74.12	136.23
Density (g/cm^3)	0.848 (@ 20 °C)	0.853 (@ 25 °C)	0.803 (@ 25 °C)	0.842 (@ 25 °C)
Solubility in water (g/L)	170 (@ 20 °C)	90 (@ 20 °C)	85 (@ 25 °C)	13.8 (@ 20 °C)
Vapor pressure (hPa)	1.9 (@ 20 °C)	38.66 (@ 56.7 °C)	8 (@ 20 °C)	<4 (@ 14.4 °C)
Boiling point (°C)	140	130–132	108	176–177