

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.

Keywords

Octane, blending, knock, spark ignition, biofuel

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 0-20%) 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 one cyclic terpene (limonene). These four molecules have recently been shown for microbial production in engineered *E. 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].

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

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 0-20%) 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.

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

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 Equation 1 where p_i is the in-cylinder pressure data for a given cycle, i , and θ is the crank angle degree.

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

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. Figure 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.

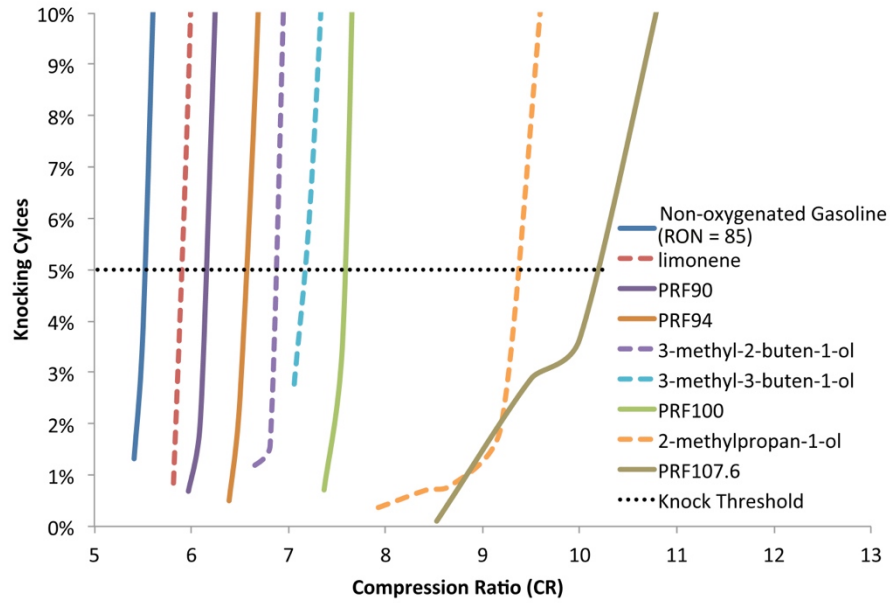


Fig. 1. Knocking frequency of fuels over a range of compression ratios. Note that the 5% threshold for knock occurrence, as indicated by the dotted line, is used for determining the octane number.

Knocking frequency traces like Figure 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 Equation 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].

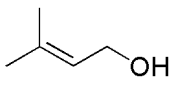
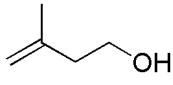
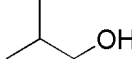
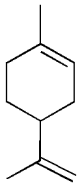
$$BRON = RON_{ref} + \frac{1}{f} (RON_{bl} - RON_{ref}) \quad (2)$$

2.3. Testing Methodology

2.3.1. Fuels

The fuels considered in this study were acquired from commercial vendors (Sigma-Aldrich in St. Louis, MO, Fisher Scientific in Pittsburgh, PA, or VWR in West Chester, PA) and refineries that produce biofuels using conventional methods since the production of fuel from microbial metabolism is not commercially available. Table 3 lists the biofuels and reference fuels investigated in this study. All fuels were available at purities of at least 98%.

Table 3
Investigated Fuels

Sample Fuels	3-methyl-2-buten-1-ol	prenol	
	3-methyl-3-buten-1-ol	isoprenol	
	2-methylpropan-1-ol	isobutanol	
	1-methyl-4-(1-methylethenyl)-cyclohexene	limonene	
Reference Fuels	Non-oxygenated gasoline (RON = 85) PRF 86 PRF 88 PRF 90 PRF 92 PRF 94 PRF 96 PRF 98 PRF 100 PRF 107.6		

RON for each biofuel was determined using the method described in Section 2.2. By definition, the RON of the primary reference fuel is the percent isooctane. Therefore, PRF 86 indicates 86% isooctane and thus a RON of 86. In order to determine BRON, the biofuels were blended with non-oxygenated gasoline at mixtures of 5%, 10%, and 20% biofuel balanced by non-oxygenated gasoline. The blend compositions were chosen to reflect the non-linear increase in RON with compression ratio, as the non-linear effect at higher blend compositions is significantly less [17].

2.3.2. Operating Procedure

Before data is taken for a fuel blend, the air/fuel ratio is adjusted to maximize knock intensity and the engine is operated for five minutes under knocking conditions in order to approximate ASTM2699 procedures [27].

When a knocking operation is stable, the compression ratio is gradually decreased until almost no knock occurs. Starting from this point, the compression ratio increased incrementally until more than 30% of all cycles knock. At each compression ratio, 700 consecutive cycles are recorded. Table 4 lists selected engine operation conditions for knock testing.

Table 4
Selected Operation Conditions during Knock Testing

Engine Speed	600 +/- 6 rpm
Intake Air Temperature	52 +/- 1° C
Intake Pressure	1.015 bar (14.72 psi)
Injection Timing	360° BTDC
Spark Timing	13° BTDC
Throttle Position	100% (Wide Open)
Fuel Pressure	2.75 bar (40 psi)
Oil Temperature	40° C
Cylinder Jacket Temperature	81 +/- 2° C
Initial Warm-Up Time	45 minutes
Fuel Transition Time	15 minutes
Equivalence Ratio	Adjusted to maximum knock (typically 0.93-0.95)

When changing fuels, the spark plug is turned off and the engine is allowed to motor (no combustion) using the dynamometer. When the fuel is changed, the engine is warmed back up to temperature using gasoline for 15 minutes to ensure that any residual fuel is flushed from the system and the engine is operating at steady-state temperatures.

3. Results and Discussion

The Research Octane Number (RON) and Blending Research Octane Number (BRON) were determined for four biofuels: 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, 2-methylpropan-1-ol (isobutanol), and limonene. The figures below show the RON of the pure biofuels and biofuel mixtures in relation to the blend composition. The blend composition represents the volume percent of biofuel blended with non-oxygenated gasoline. Multiple tests were conducted for each blend. RON and BRON values for each biofuel are indicated by the dashed lines.

As shown in Figure 2, 3-methyl-2-buten-1-ol has a BRON of 117.9 and a RON of 96.5. The trendline indicates the extrapolation of BRON using the measured RON at the lower blend compositions. A BRON value of 117.9 indicates that 3-methyl-2-buten-1-ol could be a candidate for use as an anti-knock additive since ethanol, a common anti-knock additive, has a BRON ranging from 112-120 [30].

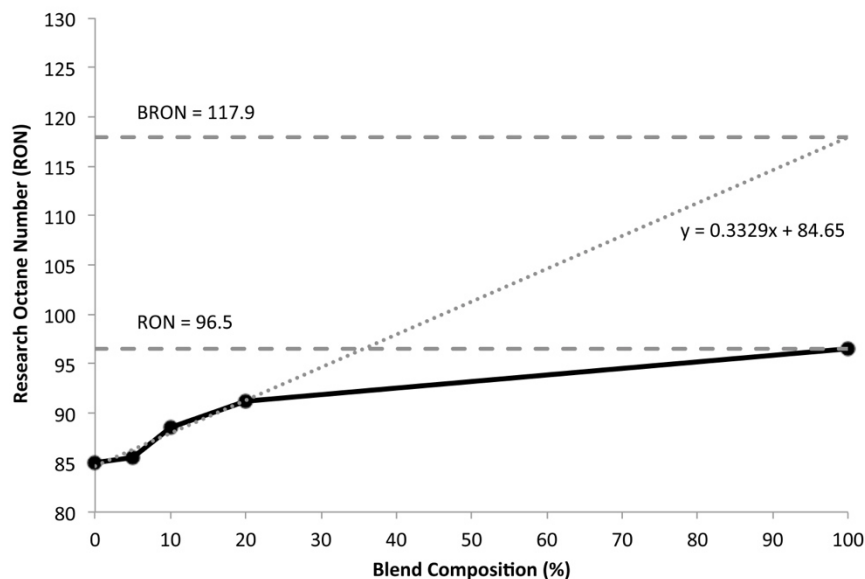


Fig. 2. BRON and RON for 3-methyl-2-buten-1-ol as a function of blend composition.

3-Methyl-3-buten-1-ol has a BRON of 125.7 and a RON of 98, as shown in Figure 3. The BRON exceeds the published BRON of ethanol (112-120) [30], also indicating 3-methyl-3-buten-1-ol is a good candidate for use as an anti-knock additive.

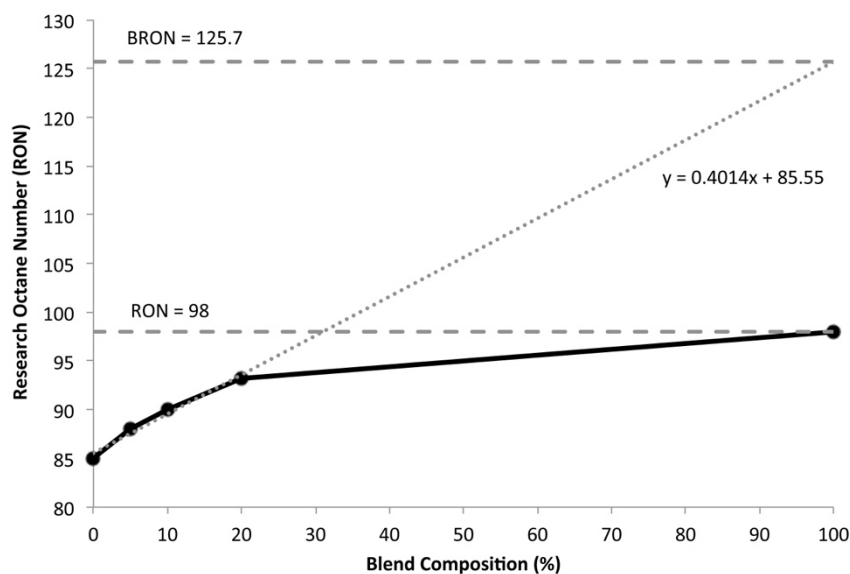


Fig. 3. BRON and RON for 3-methyl-3-buten-1-ol as a function of blend composition.

Figure 4 shows 2-methylpropan-1-ol (isobutanol) has a BRON of 120.7 and a RON of 105.5. The measured RON shows good agreement with previously published RON data for isobutanol, suggesting a RON value of 106.3 on a similarly modified CFR engine [25]. Unlike the results for 3-methyl-2-buten-1-ol and 3-methyl-3-buten-1-ol, the measured RON for isobutanol mixtures do not level off. Instead, at the 20% blend composition, the data indicates a continuing trend upward. Therefore, additional tests are recommended at the higher blend compositions

to further understand the potential of isobutanol as an anti-knock additive. However, the high BRON value calculated using the existing results indicates isobutanol is a good candidate for use as an anti-knock additive.

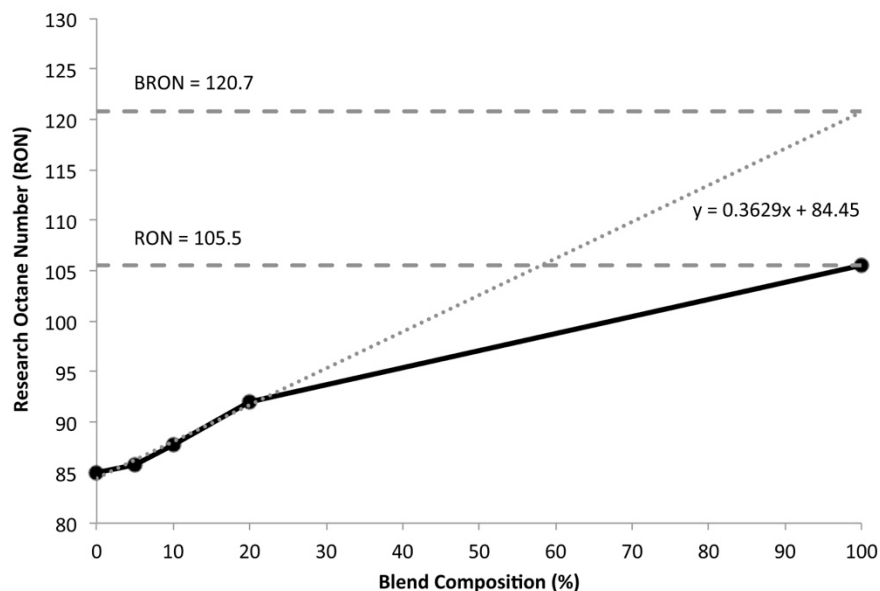


Fig. 4. BRON and RON for 2-methylpropan-1-ol (isobutanol) as a function of blend composition.

As shown in Figure 5, the BRON and RON for limonene are 98.8 and 87.5, respectively. The results show limonene has a relatively low RON, despite its ring-shaped structure, which would initially imply a high RON due to strong intermolecular binding forces. Limonene also does not show any significant effects on RON for higher blend compositions, resulting in a low BRON and indicating limonene would not make a good candidate for use as an anti-knock additive.

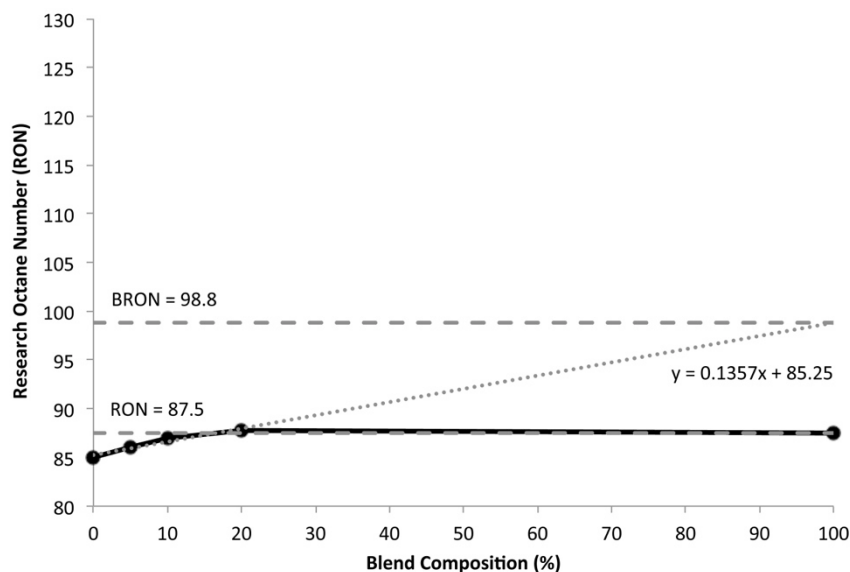


Fig. 5. BRON and RON for limonene as a function of blend composition.

Determination of the RON value of a pure fuel or blend was found to be quite repeatable. For all biofuel blends, the standard deviation in RON ranged from 0.14 to 0.78. Error bars were omitted from the previous figures due to their small scale and to improve clarity in the figures. Possible sources of error when determining RON and BRON include slight fluctuations of the intake air temperature, humidity, and pressure, all of which could impact the combustion event. Because the determination of BRON requires an extrapolation from RON values at low blend compositions, small deviations in the RON values could have a significant effect on BRON. The standard deviations for BRON values of the investigated fuels range from 0.7 to 5.4.

While the results presented above have calculated BRON using volumetric composition of the blend, the effect of blending on RON can also be presented using molar composition [31]. For fuels with smaller molar masses (e.g. methanol and ethanol), the nonlinearity of the volumetric blending curves is effectively eliminated. Thus, the blending octane number can be closely approximated by the octane number of the pure fuel when calculated as a function of the molar composition. However, this effect is less pronounced for fuels with a similar molar mass to gasoline [32], as is seen when calculated the BRON on a molar basis for 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, and limonene. As expected, the BRON for 2-methylpropan-1-ol (isobutanol) based on a molar basis does approach the RON of pure 2-methyl-1-propanol (isobutanol) due to its lower molar mass in comparison with gasoline. Values of 750 kg/m³ and 110 g/mol were assumed for the density and molar mass of the gasoline used in blending when calculating the molar composition. A comprehensive overview of the results is provided in Table 5.

TABLE 5
Summary of Results

	RON	volumetric		molar	
		BRON	Standard deviation	BRON	Standard deviation
3-methyl-2-buten-1-ol	96.5	117.9	+/- 1.7	109.7	+/- 1.3
3-methyl-3-buten-1-ol	98	125.7	+/- 5.4	115.8	+/- 4.2
2-methylpropan-1-ol (isobutanol)	106.5	120.7	+/- 0.7	109.8	+/- 0.5
limonene	88	98.8	+/- 1.7	99.9	+/- 1.9

4. Conclusions

Four prospective biofuels that can be produced from microorganism metabolism were investigated in a spark-ignited engine to determine their potential as anti-knock additives. RON and BRON values for each biofuel were determined experimentally using a single cylinder Cooperative Fuel Research (CFR) engine. The cyclic terpene limonene did only show suitable anti-knock qualities due to a low BRON of 98.8. High BRON values of 117.9, 125.7, and 120.7 for 3-methyl-2-buten-1-ol, 3-methyl-3-buten-1-ol, and 2-methylpropan-1-ol (isobutanol) respectively indicate significant knock resistance, and thus are ideal candidates for use as anti-knock additives in fuels for spark-ignited internal combustion engines.

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