

# UC San Diego

## UC San Diego Previously Published Works

### Title

Research Octane Numbers of Primary and Mixed Alcohols from Biomass-Based Syngas

### Permalink

<https://escholarship.org/uc/item/24q0n8x8>

### Journal

Energy & Fuels, 28(5)

### ISSN

0887-0624

### Authors

Rapp, Vi H  
Mack, J Hunter  
Tschann, Philipp  
[et al.](#)

### Publication Date

2014-05-15

### DOI

10.1021/ef5001453

Peer reviewed

# Research Octane Number of Primary and Mixed Alcohols from Biomass Based Syngas

*Vi H. Rapp†\*<sup>a</sup>, J. Hunter Mack†, Philipp Tschann‡, Wolfgang Hable¶, Robert J. Cattolica§,*

*Robert W. Dibble†*

†Department of Mechanical Engineering, University of California, Berkeley, Berkeley,  
California 94720, United States

‡Institute for Internal Combustion Engines and Thermodynamics, Graz University of  
Technology, Rechbauerstraße 12, 8010 Graz, Austria

¶Institute for Internal Combustion Engines and Automotive Engineering, Vienna University of  
Technology, Karlsplatz 13, 1040 Vienna, Austria

§Department of Mechanical and Aerospace Engineering, University of California San Diego, La  
Jolla, California 92093, United States

**Published in Energy and Fuels, 28(5), 3185–3191, 2014**  
**DOI: 10.1021/ef5001453**

## ABSTRACT

Primary alcohols (ethanol, 1-propanol, 1-butanol, and 1-pentanol) derived from biomass offer a sustainable fuel source that can improve efficiency while reducing carbon dioxide (CO<sub>2</sub>) emissions. However, the performance of these primary alcohols in spark-ignited engines is relatively unknown. In this paper, the performance of primary alcohols was experimentally determined using the Research Octane Number (RON) and the Blending Research Octane Number (BRON). The primary alcohol mixture, or “AlcoMix,” consists of 75% ethanol, 11% 1-propanol, 8% 1-butanol, and 6% 1-pentanol, and was approved by the U.S. EPA for use with blending in gasoline. This mixture is the probable outcome of thermochemical conversion of biomass using Fischer-Tropsch chemistry with synthesis gas. The purpose of this research is to determine if AlcoMix is a suitable replacement for Ethanol in fuel blending as an anti-knock blending component for spark-ignited engines. As an indicative measure for knock resistance, the RON of AlcoMix and ethanol were estimated using a modified, validated method in a CFR engine. The anti-knock properties of the AlcoMix as a blending component in gasoline were determined by estimating the BRON. The results show that the measured RON values of the individual primary alcohols closely match published values. Additionally, the RON and BRON of the primary alcohol mixture nearly match those of ethanol. These results indicate that the primary alcohol mixture produced by thermochemical processes could be used as a substitute for ethanol as a primary fuel or as an anti-knock blending component.

## 1. INTRODUCTION

Worldwide, a considerable amount of research has been conducted to develop alternative fuel sources that mitigate climate change by reducing the amount of climate-forcing pollutants, produced by combustion.<sup>1-6</sup> Biofuels made from agricultural products, which are oxygenated by nature, are advantageous because they are renewable and reduce climate-forcing combustion pollutants.<sup>1,2,7,8</sup> Additionally, biofuels reduce the dependence on importing oil, as they can be created from lignocellulosic biomass, offering sustainability without threatening food supplies.<sup>6,9</sup>

Two methods are commonly used to produce biofuels from biomass. The first method is fermenting sugars with yeasts or bacteria to produce ethanol, butanol, acetic acid, and other products. Sugars used in this process can be derived from corn, sugar cane, or wood (lignocellulosic).<sup>10,11</sup> The second method requires a thermochemical conversion process that converts biomass to a synthesis gas (or syngas) composed primarily of hydrogen (H<sub>2</sub>) and carbon monoxide (CO). Using the Fischer-Tropsch (F-T) process followed by an isomerization process, syngas can be synthesized to a straight chain hydrocarbon with a distribution of chain lengths.<sup>12-13</sup> Competing reactions in the F-T process can be used to produce a mixture of straight chain alcohols (R-OH), which generally have a high octane number.<sup>12-16</sup> These high-octane mixed alcohols can be used directly as a transportation fuel in spark-ignited combustion engines or as an anti-knock blending component in gasoline, as is currently done with ethanol.<sup>17</sup>

The thermochemical conversion of biomass to a mixed alcohol is based on a three-step chemical process that includes: gasification of biomass to producer gas, reforming of producer gas into syngas, and synthesis of syngas to produce the final product, a mixed alcohol fuel. The conversion of syngas to mixed alcohols is based on the modern extension of the first synthesis process developed by Fischer-Tropsch over iron catalysts in 1922.<sup>16</sup> In 1989, the Dow Chemical Company<sup>18</sup> developed a process that allows selection of the mixed alcohol composition by

controlling the extent of intimate contact among the catalytic components during synthesis. The synthesis catalyst used in this process is composed of a mixture of MoS<sub>2</sub>, CoS<sub>2</sub>, and K<sub>2</sub>CO<sub>3</sub> in ratio of 3:2:1.5 on a mass basis. Mixed alcohols generated from the 1989 Dow Chemical Company process can be used as a blending component in gasoline or diesel.<sup>18</sup>

The basic alcohol mixture composition using a MoS<sub>2</sub> based catalyst described in the Dow Chemical Company patent<sup>18</sup> contains 30% methanol. Because methanol substantially raises the Reid vapor pressure of gasoline, regulations often limit methanol content in gasoline.<sup>19</sup> In order to create an alcohol mixture that has less of an effect on the Reid vapor pressure of gasoline, methanol can be recycled through the catalyst to produce more, higher order alcohols such as ethanol. Combining mixed alcohols with non-oxygenated gasoline has the potential to enhance octane number and reduce non-methane hydrocarbons, particulate matter, carbon monoxide, and nitrogen oxide emissions.<sup>20-22</sup> Table 1 shows potential mixed alcohol compositions using a MoS<sub>2</sub> based catalyst with and without methanol recycling.

**Table 1.** Mixed alcohol composition for MoS<sub>2</sub> based catalyst with and without methanol recycling<sup>18</sup>

Alcohols	Mixed Alcohol Baseline Composition	Mixed Alcohol Composition after Recycling Methanol
Methanol	28%	0%
Ethanol	50%	75%
1-Propanol	16%	11%
1-Butanol	4%	8%
1-Pentanol	2%	6%

In this paper, we investigate the anti-knock properties of an alcohol mixture produced using a MoS<sub>2</sub> based catalyst described in the Dow Chemical Company patent<sup>18</sup> with methanol recycling. This alcohol mixture, here on referred to as the “AlcoMix”, contains 75% ethanol, 11% 1-propanol, 8% 1-butanol, and 6% 1-pentanol (as shown in Table 1). We chose to investigate this specific blend of alcohols because the U.S. EPA has already approved it for blending with gasoline.<sup>23</sup> Additionally, the AlcoMix can be separated by distillation to individual alcohols and sold into the marketplace. The benefits of using AlcoMix in comparison to pure ethanol are the following:

- Eliminates the need for additional distillation and decreases production cost both in terms of energy consumption and capital costs
- Offers a higher energy content on a volume basis and reduced hygroscopic properties
- Reduces the effect on the Reid vapor pressure of gasoline, enabling higher alcohol concentrations when blending with gasoline without increasing volatile organic compounds

The purpose of this research is to determine if AlcoMix is a suitable replacement for Ethanol in fuel blending. As an indicative measure for knock resistance, the ASTM standard Research Octane Number (RON) of AlcoMix and ethanol were estimated using a modified method. This method can be applied to any engine to estimate the ASTM standard for RON and has been validated by previous research.<sup>20,24,25</sup> The anti-knock properties of the AlcoMix as a blending component in gasoline were determined by measuring the Blending Research Octane Number (BRON). BRON was estimated by measuring the RON using the modified method, here on denoted as “RON”, of blends containing the AlcoMix and non-oxygenated gasoline (RON = 82). Blends of AlcoMix and non-oxygenated gasoline included 0% (no AlcoMix), 5%, 10%, 15%,

and 100% (pure AlcoMix). This method was also used to estimate the BRON for ethanol. The RON of each alcohol (ethanol, 1-propanol, 1-butanol, and 1-pentanol) used to create AlcoMix was also estimated. The suitability of the AlcoMix as an anti-knock blending component was estimated by comparing the BRON of the AlcoMix with the BRON of ethanol. Because gasoline composition has been shown to affect the BRON of alcohol-gasoline fuel blends,<sup>26</sup> the same non-oxygenated gasoline was used for AlcoMix blends and ethanol blends.

## 2. MATERIALS AND METHODS

### 2.1 Experimental Setup

All experiments were conducted in a Waukesha Cooperative Fuel Research (CFR) F-4 research engine. The CFR F-4 is a spark-ignited, single-cylinder, variable compression ratio engine. Selected specifications for the CFR F-4 engine used in this study are shown in Table 2. The CFR F-4 engine was modified from its original specifications (built in 1950) to increase flexibility and control of the operating parameters. Modifications included enabling knock testing and operation with pure alcohols and gasoline-alcohol blends.<sup>27</sup> Additionally, the original coolant system, intake air system, and fuel system were replaced.

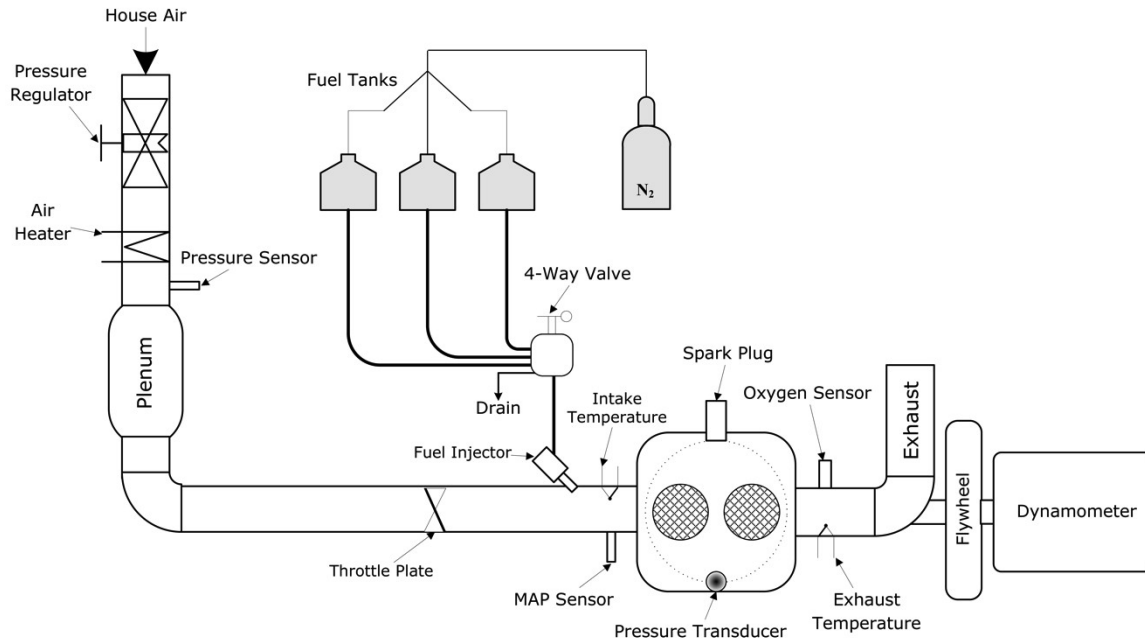
The original coolant system, which operated by natural convection of the coolant through the cylinder jacket, was replaced with a forced convection system that continuously pumps coolant through the jacket. Building water was used to cool the engine coolant in a heat exchanger to maintain a constant engine cylinder temperature. The intake air system was modified from a naturally aspirated system and connected to the house air supply with a heater. This modification allowed for controlling intake air pressure as well as intake air temperature. A 10 L plenum was added prior to the intake manifold to dampen pressure pulses. Intake air temperature was

controlled using a Sylvania Sure Heat Jet (8 kW) resistant heater. Three pressurized fuel tanks were added, allowing for quick fuel switching while minimizing contamination when transitioning between fuels. A schematic of the modified CFR F-4 system is shown in Figure 1.

**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 <sup>3</sup> (37.432 in <sup>3</sup> )
Compression Ratio	4:1 to 17.5:1 (variable)
Combustion Chamber Volume	176.7 cm <sup>3</sup> – 40.8 cm <sup>3</sup> (10.784 in <sup>3</sup> – 2.489 in <sup>3</sup> )
Connecting Rod Length	25.4 cm (10 in)
Piston Material	Aluminum
Piston Rings	3 compression, 2 oil





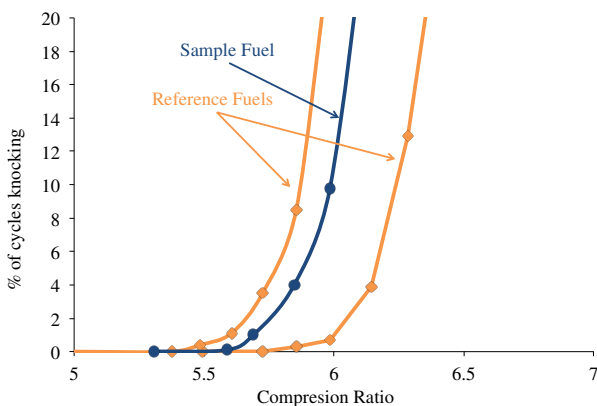
**Figure 1.** Schematic of experimental setup for the Waukesha CFR F-4 research engine.

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 Determining Knock Resistance

The American Society for Testing and Materials developed a standard test for determining the knock resistance of fuels using the Research Octane Number (RON), ASTM2699.<sup>28</sup> The standard

test method requires a Waukesha CFR F-1 engine and derives the octane number by bracketing a test fuel's knocking characteristics with data from Primary Reference Fuels (PRFs). The original CFR F-1 engine determines the octane number using a "detonation meter" (magnetostrictive transducer) to measure the degree of knock intensity. The detonation meter is located in the cylinder head and measures the peak knock intensity over a short period of time. A knock meter is used to display the knocking intensity and measure the frequency of the knocking intensity measured by the detonation meter. At a specified RPM and intake temperature, the compression ratio is steadily increased until the signal from the knock meter surpasses the published standard threshold.<sup>24</sup> The compression ratio is then recorded and compared to data from the PRFs to determine the octane number. Figure 2 provides a graphical representation of bracketing a test fuel using PRFs to determine octane number. For example, if the references fuels have an octane number of 70 and 75, then the sample fuel will have an octane number of about 71, assuming the knock criteria is 5% of the cycles are knocking. One should also note that the percentage of knocking cycles increase with compression ratio.



**Figure 2.** Diagram illustrating the bracketing method used to determine octane number.<sup>28</sup> At a set percent of knocking cycles, the octane number is linearly interpolated using the two reference fuels.

The CFR F-4 engine used for experimental results presented in this paper was not equipped with a detonation meter or knock meter. However, an alternative method for measuring the occurrence of knock and knock intensity was generated due to the nearly identical engine designs between the CFR F-1 and CFR F-4. The in-cylinder pressure was used as a direct and reliable method for measuring knock and knock intensity. Several methods exist for creating a knock indicator using the pressure trace.<sup>29-32</sup> Most methods use a band-pass filter and a rectifier to generate a signal of the relevant pressure oscillations. The rectified signal may be integrated to produce an averaged measure of the oscillations creating a knock indicator.<sup>29,30</sup> Another method uses the first and the third derivative of the pressure trace to create a knock indicator.<sup>32</sup> The use of a pressure trace based knock indicator requires high sampling frequencies in order to measure the pressure oscillations accurately. The location of the in-cylinder pressure transducer also influences the ability to measure the fluctuation of the pressure because of pressure nodes.<sup>32</sup> Using the in-cylinder pressure trace to measure knock intensity assumes that under set operating conditions, combustion in both Waukesha CFR engines is similar. Section 3 provides details on the theoretical basis for the knock detection method.

### 2.3 Suitability as an Anti-Knock Blending Component

The Blending Research Octane Number (or BRON) represents a fuel's ability to increase the octane number at low blend compositions. Therefore, BRON is a useful tool for assess a fuel's

potential as an anti-knock blending component in gasoline. The BRON is determined using a linear extrapolation from the octane number of mixtures (between 0-20%, either on a volumetric or molar basis) of the anti-knock blending components and non-oxygenated gasoline. The BRON of a fuel blend can be calculated using Equation 1 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 fuel blend, and  $f$  is the fraction of the anti-knock blending component on a volumetric basis.<sup>33</sup>

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

The improvement in octane number that anti-knock blending components give to the resulting fuel blend depends on the both the anti-knock blending component and the blend composition.<sup>33</sup> Many fuel components in anti-knock blending components contribute a non-linear effect when increasing the octane number, especially at low blend compositions.<sup>34</sup>

## 2.4 Fuel Blends

The “AlcoMix” created for this study was made from a mixture containing several alcohols of at least 98% purity. The AlcoMix (75% ethanol, 11% 1-propanol, 8% 1-butanol, and 6% 1-pentanol) represents a potential alcohol mixture composition using a  $MoS_2$  based catalyst described in the Dow Chemical Company patent<sup>18</sup> with methanol recycling. The RON of each alcohol (ethanol, 1-propanol, 1-butanol, and 1-pentanol) in the AlcoMix was estimated using the method described in Section 2.2. The anti-knock properties of the AlcoMix are evaluated using BRON. BRON was estimated by blending the AlcoMix with non-oxygenated gasoline at mixtures of 0% (pure non-oxygenated gasoline), 5%, 10%, 15%, and 100% (pure AlcoMix).

Blend compositions less than 15% were chosen to capture the non-linear increase in RON with compression ratio, as the non-linear effect at higher blend compositions is significantly less.<sup>35</sup> The BRON of ethanol was also estimated using blends of 0% (no ethanol), 6%, and 100% ethanol balanced by non-oxygenated gasoline. An exact composition of the non-oxygenated gasoline used in this study could not be obtained. However, the non-oxygenated gasoline used in this study was a California reformulated gasoline blendstock for oxygenate blending. The California CaRFG3 standards stipulate that this gasoline can have a RON ranging from 82 to 88, and this gasoline cannot contain more than 1.22 vol% Benzene, 38.7 vol% Aromatics, and 11.1 vol% Olefins.<sup>36</sup>

Primary Reference Fuels (PRFs) were used for bracketing the knocking characteristics of fuels and determining RON. As defined in the ASTM2699 standard,<sup>28</sup> PRFs are blends of n-heptane (RON=0) and isooctane (RON=100). The RON of a PRF is the percent volume isooctane. For example, PRF 75 indicates 75% isooctane and thus a RON of 75. Using PRFs, a fuel with any RON between 0 and 100 can be created. The PRFs were tested in the same procedure as the Test Fuels and used as references for RON less than or equal to 100. When the Test Fuel had a RON greater than 100, the PRFs were extended using toluene standardization fuels (TSF).<sup>37</sup> The reference fuel blends used in this study are summarized in Table 3.

**Table 3.** The composition of reference fuels used in this study as defined in the ASTM D 2699<sup>28</sup> standard and the ASTM Manual for Rating Motor, Diesel and Aviation Fuels, 1973/74<sup>37</sup>

RON (x)	n-Heptane	iso-Octane	Toluene
---------	-----------	------------	---------

70-100	(100-x)%	x%	0%
103.3	11%	15%	74%
107.6	6%	20%	74%
113	0%	26%	74%

## 2.5 Test Operating Procedure

The conditions described in the ASTM D2699 standard for determining RON<sup>28</sup> were approximated using a modified knock indication method described Section 3 and a modified injection method. As described in Section 2.1, the CFR F4 engine used for our experiments is port fuel injected, while the CFR F-1 required in the ASTM standard for RON is carbureted. As shown in previous research, port fuel injection captures more of the latent heat from the alcohol fuel blend.<sup>38</sup> In order to minimize the latent heat gained by port fuel injection and mimic carbureted conditions, a closed-valve fueling strategy where the injector was aimed at the intake valve and the fuel was injected at top dead center (TDC) when the intake and exhaust valves are closed (i.e., during combustion of the previous charge). This method attempts to maximize the vaporization time, better simulating a carburetor.

Before data was taken for a fuel blend, the air/fuel ratio was adjusted to stoichiometric and the engine was operated for five minutes under knocking conditions in order to approximate ASTM 2699 procedures.<sup>28</sup> When knocking operation was stable, the compression ratio was gradually decreased until almost no knock occurred. Starting from this point, the compression ratio was increased incrementally until 30% of all cycles knocked. The percent knocking cycles was determined from 1000 consecutive knocking cycles at a set compression ratio. At a knocking threshold less than 30%, the percent knocking cycles varied significantly between engine cycles.

At a knocking threshold greater than 30%, the engine knock was severe. Therefore, to minimize the risk of damaging the engine as well as ensure repeatability for measuring RON, we chose a knocking threshold of 30%. At each compression ratio, 1000 consecutive pressure cycles were recorded. Table 4 lists selected engine operation conditions for knock testing.

When changing fuels, the spark plug was turned off and the engine was allowed to motor (no combustion) using the dynamometer. After changing fuels, the engine was operated for at least 15 minutes to ensure that any residual fuel was flushed from the system and the engine was operating at steady-state temperatures.

**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	Stoichiometric

---

### 3. KNOCK DETECTION THEORY

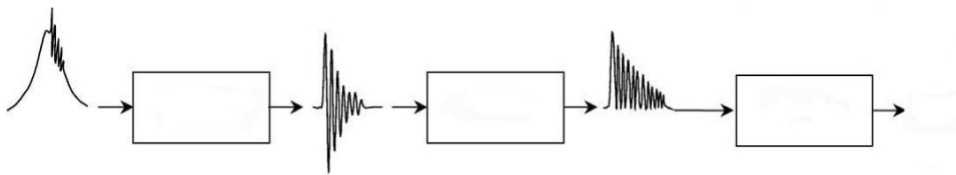
As stated in the previous section, the CFR F-4 engine used for experimental results presented in this paper was not equipped with a detonation meter or knock meter. Therefore, an alternative method for measuring the occurrence of knock and knock intensity was generated due to the nearly identical engine designs between the CFR F-1 and CFR F-4. Knock was detected using a modified version of the Integral of Modulus of Pressure Oscillation (IMPO) published by Brecq et al.<sup>31</sup> In this method, the in-cylinder pressure data is high pass filtered, rectified, and then integrated to yield the IMPO value. For our CFR F-4 engine, the IMPO value was used as the knock indicator (KI), but we applied a band-pass filter (4-10 kHz) instead of a high-pass filter in order to remove pressure oscillations not caused by engine knock. The range of frequencies in which knock occurs was determined using a Fourier transformation on the in-cylinder pressure data while the engine was knocking. Multiple experiments with different fuels and operating conditions confirmed that the natural frequency range for the band-pass filter was from 4 kHz to 10 kHz. Previous research conducted by Millo et al.<sup>29</sup> agree well with our results as they give a natural frequency range of 4-9 kHz for combustion chambers similar to the CFR F-4.



After being filtered and rectified pressure data was then integrated over 200 crank angle degrees, starting at 20° before top dead center (BTDC). Integrating the filtered and rectified pressure data yields the *KI* shown in Equation 2, where  $|p_i|$  is the band-pass filtered and rectified in-cylinder pressure data for a given cycle,  $i$ , and  $\theta$  is the crank angle degree.<sup>31</sup>

$$KI = \int_{i-20}^{180} |p_i| d\theta \quad (2)$$

A schematic of the *KI* developed for our CFR F-4 engine that was implemented into LABVIEW is shown in Figure 3.

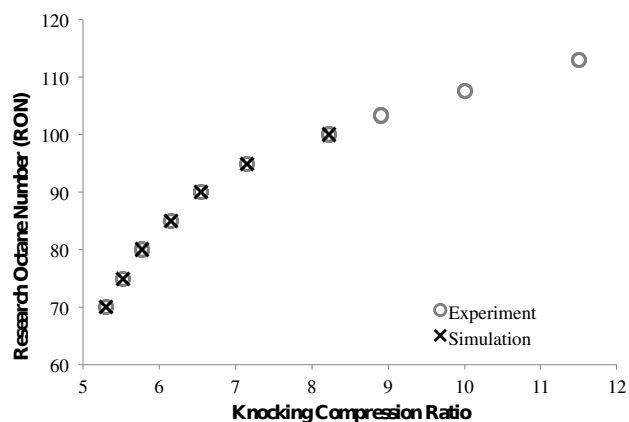


**Figure 3.** Schematic for developing a knock indicator using the in-cylinder pressure as described by Brecq et al.<sup>31</sup>

Adjusting the engine’s compression ratio varies both the *KI* and the frequency of knock occurrence. When determining octane number of a fuel, the compression ratio was increased and then recorded when 5% of all cycles knock. The high cycle-to-cycle variation in the CFR F-4 engine set the 5% knocking threshold. For the CFR F-4 engine, a cycle was defined as knocking if the *KI* range exceeded the “noise level” by 50 units (bar-CAD). The “noise level,” which is a function of compression ratio, was determined by comparing the in-cylinder pressure from non-knocking combustion with motoring (no combustion) in-cylinder pressure for 1000 consecutive cycles. A complete sweep from no knock to strong knock (over the 5% frequency threshold) was

recorded for every experiment. Although the ASTM2699<sup>28</sup> has not fully been applied in this study, this method of predicting RON using our CFR F-4 has been previously validated.<sup>20,24,25</sup>

For example, Figure 4 shows that our measured RON results for PRFs are consistent with simulated results using a detailed mechanism.<sup>20</sup>



**Figure 4.** RON as a function of knocking compression ratio for Primary Reference Fuel (PRF) blends. By definition, the number following the PRF blend is equal to the RON. For example, PRF 70 has a RON of 70. Therefore, each data point represents a different PRF blend. The knocking compression ratio is the compression ratio at which knocking first occurs in the CFR engine. The simulated results, using the detailed mechanism from DeFilippo et al.,<sup>20</sup> are consistent with the experimental data.

#### 4. RESULTS AND DISCUSSION

The Research Octane Number (RON) was estimated for the following fuels: non-oxygenated gasoline (RON=82), ethanol, 1-propanol, 1-butanol, 1-pentanol, and AlcoMix (75% ethanol,

11% 1-propanol, 8% 1-butanol, and 6% 1-pentanol) and blends of 0%, 5%, 10%, 15%, and 100% AlcoMix with non-oxygenated gasoline. The volumetric and molar Blending Research Octane Number (BRON) was estimated for ethanol and AlcoMix. Figure 4 and Figure 5 show the RON of AlcoMix and ethanol in relation to the blend composition. The blend composition represents the volume percent of alcohol (ethanol or AlcoMix) blended with non-oxygenated gasoline. A single test was conducted for each blend. The dashed lines in each figure indicate the RON and BRON values for ethanol and AlcoMix. The dotted line in each figure indicates extrapolation of the BRON using the measured RON of blend compositions less than or equal to 15%.

From Figure 4, AlcoMix has a BRON of 130.4 and a RON of 110.8. A BRON of 130.4 indicates that the AlcoMix could be a good candidate for use as an anti-knock blending component, since ethanol has a measured BRON of 134.4, as shown in Figure 5. The measured RON for ethanol is 111.2. Figure 6 compares the RON enhancement of AlcoMix and ethanol at equal volumetric blending concentrations in non-oxygenated gasoline. Although AlcoMix contains 75% ethanol and 25% alcohols with lower octane numbers than ethanol, AlcoMix provides similar RON enhancement as ethanol when blended with gasoline.

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 deviation for RON values of blends containing 15% or less of AlcoMix ranges from 0.1 to 1.5. Error bars for AlcoMix results are omitted to improve clarity in the figure. The standard

deviation for the RON of ethanol was 1.8. RON for blends of ethanol in non-oxygenated gasoline were measured once, so the standard deviation range is not available.

The effects of blending on RON with AlcoMix and ethanol can also be compared using the molar composition instead of the volumetric composition.<sup>39,40</sup> 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, the AlcoMix is 75% ethanol and as expected, the BRON on a molar basis of the AlcoMix and ethanol are almost the same (see Table 5). Values of 750 kg/m<sup>3</sup> and 110 g/mol were assumed for the density and molar mass of the gasoline used in blending when calculating the molar composition.

**Table 5.** Average Measured RON and BRON from AlcoMix and Ethanol\*

Fuel	RON	Standard Deviation	Volumetric BRON	Molar BRON
AlcoMix	110.8	± 0.2	130.4	107.1
Ethanol	111.2	± 1.8	134.3	107.9

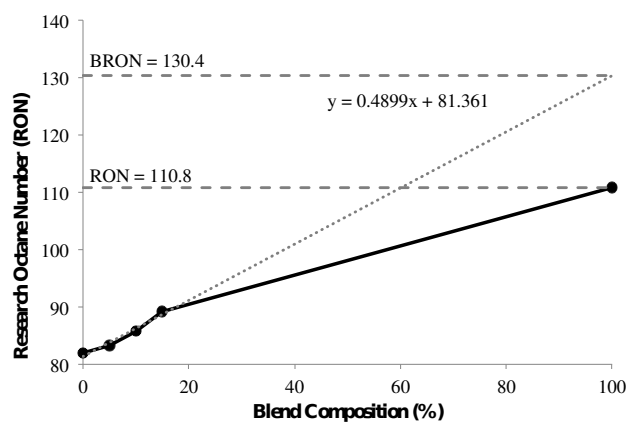
\*Two RON experiments were conducted for AlcoMix and AlcoMix blends. Three RON experiments were conducted for pure ethanol, while one experiment was conducted for ethanol blends.

Table 6 shows the measured RON of primary alcohols agrees well with values in the literature.<sup>26,27,30,41-43</sup> Published values for the RON of 1-propanol and 1-pentanol were not found. One study<sup>17</sup> does state that 1-pentanol is known to decrease the RON when blended with gasoline

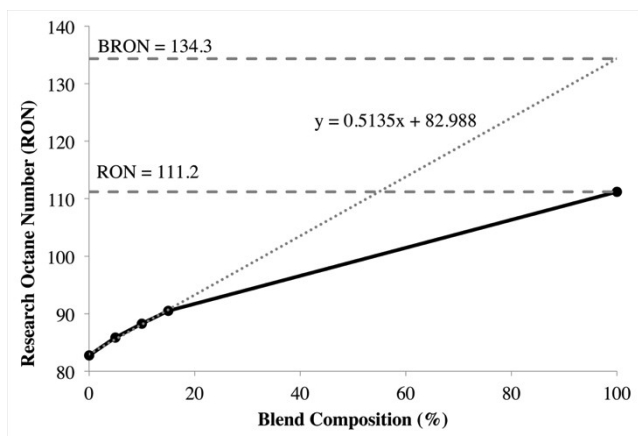
(octane number 66.7), PRF-70, or PRF-92. However, we did not observe this effect because the RON of pure 1-pentanol in gasoline blends was not investigated.

**Table 6.** Measured and published RON of pure alcohols

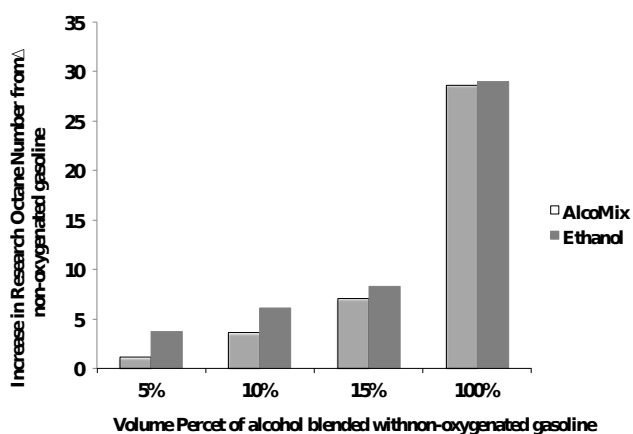
Fuel	Measured RON	Published RON
Ethanol	111.2	108-108.5 <sup>26</sup> 109 <sup>27,41,42</sup> 111 <sup>30</sup>
1-Propanol	102.6	104 <sup>42</sup>
1-Butanol	96.0	96 <sup>43</sup> 98 <sup>42</sup>
1-Pentanol	78.0	-



**Figure 5.** RON for AlcoMix (75% ethanol, 11% 1-propanol, 8% 1-butanol, and 6% 1-pentanol) as a function of volumetric blend composition.



**Figure 6.** RON for ethanol as a function of volumetric blend composition.



**Figure 7.** AlcoMix displays similar anti-knock blending characteristics as ethanol when blended at various concentrations with non-oxygenated gasoline (RON=82).

## 5. CONCLUSIONS

The anti-knock properties of an alcohol mixture produced from the thermochemical conversion of biomass using Fischer-Tropsch chemistry with synthesis gas is investigated in a spark-ignited engine to determine its potential as an anti-knock blending component. The alcohol mixture

(AlcoMix), which contains no methanol as it is recycled back through the catalyst, is comprised of 75% ethanol, 11% 1-propanol, 8% 1-butanol, and 6% 1-pentanol. RON and BRON values for AlcoMix and ethanol were determined experimentally using a single cylinder Cooperative Fuel Research (CFR) engine. The Research Octane Number (RON) of each alcohol (ethanol, 1-propanol, 1-butanol, and 1-pentanol) used to create AlcoMix is also estimated.

A testing procedure that can be applied to any engine was developed to estimate the ASTM standard for RON. This method is based on in-cylinder pressure data was developed and validated to measure the knocking intensity at a set operating point. The values obtained by the modified approach outlined in this paper yielded RON values for ethanol, 1-butanol, and 1-propanol similar to those found in the literature. Additionally, measured RON values for Primary Reference Fuels are consistent with simulated results.

The RON and BRON results for AlcoMix indicate that AlcoMix acts as an octane enhancer (BRON ~ 130) similar to ethanol. The measured RON for AlcoMix is 110.8 and closely matches the measured RON of ethanol, 111.2. Similar RON values for the AlcoMix and ethanol were expected since ethanol is 75% of AlcoMix. These results indicate that the use of AlcoMix produced from syngas is a viable substitute for pure ethanol when blending with gasoline.

## AUTHOR INFORMATION

### **Corresponding Author**

\*E-mail: [vhrapp@berkeley.edu](mailto:vhrapp@berkeley.edu)

### **Present Addresses**

<sup>a</sup> Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States.

## ACKNOWLEDGMENT

This work was part of the UC Discovery - IUCRP Pilot Project titled "An Investigation of a Thermochemical Process for the Production of Mixed Alcohol from Biomass" under agreement number gcp06-10228.

## ABBREVIATIONS

BRON, Blending Research Octane Number; BTDC, before top dead center; CFR, Cooperative Fuel Research; F-T, Fischer Tropsch; IMPO, Integral of Modulus of Pressure Oscillation; PRF, Primary Reference Fuel; RON, Research Octane Number; RPM, revolutions per minute; TSF, toluene standardization fuel.

## REFERENCES

- (0) Rakopoulos, D. C.; Rakopoulos, C. D.; Kakaras, E. C.; Giakoumis, E. G. *Energy Convers. Manage.* 2008, 49, 3155–3162.
- (0) Yan, J.; Lin, T. *Appl. Energy* 2009, 86, S1–S10.
- (0) Miyamoto, N.; Ogawa, H.; Nabi, M. N. *International Journal of Engine Research* 2000, 1, 71-85.
- (0) Choi, C. Y.; Reitz, R. D. *Fuel* 1999, 78, 1303-1317.
- (0) Rakopoulos, C. D.; Michos, C. N.; Giakoumis, E. G. *Proc. IMechE, Part D: J. Automobile Engineering* 2008, 222, 2065-2084.



- (0) Abu-Jrai, A.; Rodriguez-Fernandez, J.; Tsolakis, A.; Megaritis, A.; Theinnoi, K.; Cracknell, R. F.; Clark, R. H. *Fuel* 2009, 88, 1031-1041.
- (0) Hansen, A. C.; Kyritsis, D. C.; C.F., L. Characteristics of biofuels and renewable fuel standards. In *Biomass to biofuels - strategies for global industries*; John Wiley: Chichester, West Sussex, PO19 8SQ, United Kingdom, 2009; pp 1-26.
- (0) Hansen, A. C.; Zhang, Q.; Lyne, P. W. L. *Bioresource Technology* 2005, 96, 277-285.
- (0) Rakopoulos, C. D.; Antonopoulos, K. A.; Rakopoulos, D. C.; Hountalas, D. T.; Giakoumis, E. G. *Energy Conversion and Management* 2006, 47, 3272-3287.
- (0) Bai, F. W.; Anderson, W. A.; Moo-Young, M. *Biotechnology Advances* 2008, 26, 89-105.
- (0) Holtzapple, M. T.; Granda, C. B. *Applied Biochemistry and Biotechnology* 2009, 156, 525-536.
- (0) Schulz, H. *Applied Catalysis A: General* 1999, 186, 3-12.
- (0) Pichler, H.; Schulz, H. *Chemie Ingenieur Technik*, 1970, 42(18), 1162-1174.
- (0) Holtzapple, M. T.; Davison, R. R.; Ross, M. K.; Aldrett-Lee, S.; Nagwani, M.; Lee, C.-M.; Lee, C.; Adelson, S.; Kaar, W.; Gaskin, D.; Shirage, H.; Chang, N.-S.; Chang, V. S.; Loescher, M. E. *Applied Biochemistry and Biotechnology* 1999, 77-79, 609-631.
- (0) Dry, M. E. *Catalysis Today* 2002, 71, 227-241.

(0) Lloyd, L. Handbook of Industrial Catalysts; Springer: Bath, United Kingdom, 2011; pp 3, 63-65.

(0) Barannik, V. P.; Makarov, V. V.; Petrykin, A. A.; Shamonina, A. Chemistry and Technology of Fuels and Oils 2005, 41, 452-455.

(0) Stevens, R. R.; Conway, M. M. (Dow Chemical Company). Mixed Alcohols Production from Syngas. U. S. Patent 4,831,060, May 16, 1989.

(0) Andersen, V. F.; Anderson, J. E.; Wallington, T. J.; Mueller, S. A.; Nielsen, O. J. Energy and Fuels 2010, 24, 3647-3654.

(0) DeFilippo, A.; Chin, G. T.; Chen, J.-Y. Combustion Science and Technology 2013, 185, 1202-1226.

(0) Ratcliff, M. A.; Jon†Luecke; Williams, A.; Christensen, E.; Yanowitz, J.; Reek, A.; McCormick, R. L. Environmental Science and Technology 2013, 47, 13865–13872.

(0) Gravalos, I.; Moshou, D.; Gialamas, T.; Xyradakis, P.; Kateris, D.; Tsiropoulos, Z. Renewable Energy 2013, 50, 27-32.

(0) Environmental Protection Agency. Title 40 CFR Part 79 – Registration of Fuels and Fuel Additives. March 14, 2014.

(0) Hable, W. Combustion performance of mixed alcohol fuels in a CFR engine. M.S. Thesis, Institute for Internal Combustion Engines and Automotive Engineering, Vienna University of Technology, Austria, October 2009.

(0) Tschann, P. Emission and Performance Studies of Alternative Fuels. M.S. Thesis, Technical University Graz, Austria, October 2009.

(0) Foong, T. M.; Morganti, K. J.; Brear, M. J.; da Silva, G.; Yang, Y.; Dryer, F. L. Fuel 2014, 115, 727-739.

(0) Hunwartzen, I. Society of Automotive Engineers Technical Paper 820002 1982, doi:10.4271/820002.

(0) Standard Test Method for Research Octane Number of Spark-Ignition Engine Fuel; ASTM International: West Conshohocken, PA, 2011; ASTM Standard D2699-11.

(0) Millo, F.; Ferraro, C. Society of Automotive Engineers Technical Paper 982477 1998, doi:10.4271/982477.

(0) Gautam, M.; Martin II, D. Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy 2000, 214, 497-511.

(0) Brecq, G.; Bellettre, J.; Tazerout, M. International Journal of Thermal Sciences 2003, 42, 523-532.

(0) Syrimis, M.; Assanis, D. Journal of Engineering for Gas Turbines and Power 2003, 125, 494-499.

(0) Golombok, M.; De Bruijn, J. Ind. Eng. Chem. Res. 2000, 39, 267-271.

(0) Stone, R. Introduction to internal combustion engines; Society of Automotive Engineers, Inc.: Warrendale, PA, 1999; pp 86-90.

- (0) Johnson, R.; Riley, R. Society of Automotive Engineers Technical Paper 760377 1976,  
doi:10.4271/760377.
- (0) California air Resources Board. Title 13, California code of Regulations, Sections 2250-  
2273.5. October 9, 2012.
- (0) ASTM Manual for Rating Motor, Diesel and Aviation Fuels, 1973/-74; American Society for  
Testing and Materials: Easton, MD., U. S. A., October 1973; pp 15-26.
- (0) Stein, R.; Polovina, D.; Roth, K.; Foster, M. et al. SAE Int. J. Fuels Lubr. 5, 2012, 823-843.
- (0) Anderson, J. E.; Kramer, U.; Mueller, S. A.; Wallington, T. J. Energy and Fuels 2010, 24,  
6576-6585.
- (0) Mack, J. H.; Rapp, V. H.; Broeckelmann, M.; Lee, T. S.; Dibble, R. W. Fuel 2014, 117, 939-  
943.
- (0) Bormann, G.; Ragland, K. Combustion Engineering; McGraw-Hill  
Science/Engineering/Math: Madison, WI, 1998; pp 37.
- (0) Christensen, E.; Yanowitz, J; Ratcliff, M.; McCormick, R. L. Energy and Fuels 2011, 25(10),  
4723-4733.
- (0) Wallner, T.; Miers, S. A.; McConnell, S. J. Eng. Gas Turbines Power 2009, 131(3);  
doi:10.1115/1.3043810.