Evaluation of Anti-Knock Quality of Dicyclopentadiene-Gasoline Blends

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Abstract

Increasing the anti-knock quality of gasoline fuels can enable higher efficiency in spark ignition engines. In this study, the blending anti-knock quality of dicyclopentadiene (DCPD), a by-product of ethylene production from naphtha cracking, with various gasoline fuels is explored. The blends were tested in an ignition quality tester (IQT) and a modified cooperative fuel research (CFR) engine operating under homogenous charge compression ignition (HCCI) and knock limited spark advance (KLSA) conditions. Due to current fuel regulations, ethanol is widely used as a gasoline blending component in many markets. In addition, ethanol is widely used as a fuel and literature verifying its performance. Moreover, because ethanol exhibits synergistic effects, the test results of DCPD-gasoline blends were compared to those of ethanol-gasoline blends. The experiments conducted in this work enabled the screening of DCPD auto-ignition characteristics across a range of combustion modes. The synergistic blending nature of DCPD was apparent and appeared to be greater than that of ethanol. The data presented suggests that DCPD has the potential to be a high octane blending component in gasoline; one which can substitute alkylates, isomerates, reformates, and oxygenates.

Introduction

Carbon mitigation has motivated the development of downsized spark-ignited light duty engines while simultaneously turbocharging them. The energy requirement from light duty vehicle fleets is expected to decrease by almost 10% from 2014 to 2040 [1], due to engine efficiency gains and increased hybridization. The efficiency of spark ignited engines is connected to the fuel octane index (OI = RON - K*S), where RON is the research octane number, S is the octane sensitivity, and K is an empirical constant that depends on engine operating conditions [2]. Increasing the OI of a fuel would maximize tank-to-wheel carbon reductions [3]. However, refinery processes associated with increasing the fuel's anti-knock quality may have an adverse effect on well-to-tank efficiency and cost, depending on the composition of the blend stocks [4]. The use of renewable cellulosic-derived

high octane gasoline blending components, such as ethanol, butanol, furans, or lignin-derived aromatics [5, 6, 7] are a potential solution to achieving high well-to-wheel efficiency, but significant technical, economical, and environmental challenges are slowing their progress to market.

Another possible solution is to optimize the use of petroleum refinery-derived components to increase the anti-knock quality of gasoline. The present gasoline refining process consists of multiple processes - including cracking, alkylation, isomerization, and reformation - to modify the chemical composition of the light and heavy naphtha streams obtained from fractional distillation. The alkylation unit converts low value light compounds, such as isobutane, to higher octane gasoline compounds, mainly C7 and C8 compounds, such as 2,4-dimethylpentane and isooctane. In this unit, sulfuric or hydrofluoric acids are used to catalyze the conversion reactions. In the isomerization unit, low octane straight chain paraffins are converted to high octane isoparaffins. The effluent isoparaffins can also be fed into the alkylation unit. In the reforming unit, low octane straight-run naphtha comprising straight chain paraffins is converted to isoparaffins and naphthenes (cyclic paraffins), which are then dehydrogenized to produce high octane aromatics [8]. These components generally increase the auto-ignition characteristics in non-linearly proportions when blended with base gasoline. Other refinery components also blend non-linearly and synergistically, leading to a substantial increase in reactivity, which is the auto-ignition behavior, for a fuel that is volumetrically blended. The blending research octane number (BRON) and blending motor octane number (BMON) of the blend is defined as follows:

$$RON_{base} . C_{base} + BON . C_{booster} = RON_{mix}$$

(1a)

$$MON_{base} . C_{base} + BON . C_{booster} = MON_{mix}$$

(1b)

Where,

RON_{base} = *Research octane number of the base fuel*

C_{base} = Concentration of the base fuel

$C_{booster}$ = Concentration of the booster

RON_{mix} = RON of the mixture

MON_{base} = Motor octane number of the base fuel

MON_{mix} = MON of the mixture

The blending octane number (BON) is defined as the octane response of a fuel to the addition of a certain octane booster. A review of Ref. [9] shows that dicyclopentadiene (DCPD) has one of the highest blending octane indexes (BOI), with a BRON of 229, and a BMON of 167. The BRON and BMON reported were linear extrapolations from the RON and motor octane number (MON) measurements of primary reference fuel (PRF) 60 blended with 20% DCPD (vol.). The BRON and BMON of toluene (a fair representation of aromatics present in gasoline) are 124 and 112, respectively. Nevertheless, the RON and MON of pure DCPD was reported to be lower than that of toluene [9].
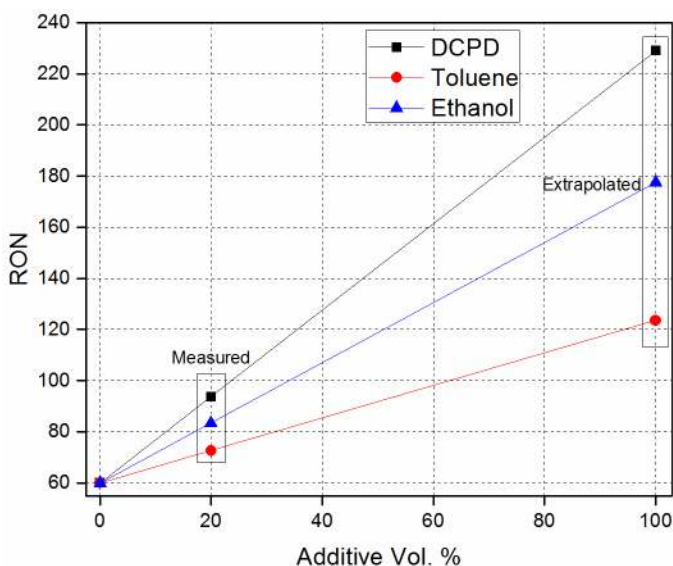

Figure 1. RON values of DCPD, toluene, and ethanol with PRF 60 (values at 100% are extrapolated) [9] [11]

The blending characteristic of ethanol, a common antiknock improver, with various gasoline fuels has been widely explored. The blending octane quality of ethanol was thoroughly explored by Anderson et al. [10] and Foong et al. [11]. The BRON of ethanol was calculated using extrapolation and found to be 177.5 (Fig. 1). The calculation was based on ASTM method, in which, the blending octane number is obtained through the extrapolation of the 20% concentration to the 100% concentration of the specific hydrocarbon, in our case it is ethanol. The obtained value is only applicable for this specific base fuel and cannot be use to predict BRON values in other fuel mixtures. This is because of the highly variable BRON of every hydrocarbon and its dependence on the fuel mixture type in the fuel it is blended in [9]. A comparison of BRON of DCPD, toluene, and ethanol is presented in Figure 1.

Because of its high knock resistivity under variable compression conditions [12], ethanol was also tested in boosted engines to evaluate its performance. Bromberg et al. [13] tested ethanol in a supercharged engine; the intake charge pressure was set at 2 bar to achieve improved efficiency without engine knock. Blending ethanol with gasoline also allows more advance ignition timing to improve engine performance [14]. For these reasons, ethanol was chosen as a benchmark for judging the anti-knock performance of DCPD.
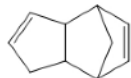
The present work extensively explores the blending octane quality of DCPD with various base gasoline compositions for the first time, using various experimental techniques that cover a wide range of operating conditions. DCPD exhibited synergistic effects with all the base gasolines tested. The composition of the base gasoline also appears to have an effect on DCPD's BRON and BMON. The chemical kinetic nature of DCPD oxidation is elucidated to rationalize the observed improvements in anti-knock quality compared to other fuels.

Fuels

Dicyclopentadiene

DCPD is a byproduct of steam cracking naphtha during the production of ethylene. It is solid at room temperature; and it is formed by the dimerization of the unstable product cyclopentadiene (CPD). In addition, DCPD is produced in small quantities from coal tar distillation process. The produced amount of DCPD depends on the feedstock to the cracker. Usually, the amount of CPD and DCPD in pyrolysis gasoline is between 15-25 wt%. DCPD is separated from the stream using fractionation. The yielding DCPD stream has 82-90% purity.

Table 1. Physical properties of dicyclopentadiene (adapted from Ref [15])

Molecular Structure	
Molecular formula	$C_{10}H_{12}$
Molecular weight	132.2
Density (Kg/L)	0.98
Boiling Point, °C, at 101.3 kPa,	170
Melting Point, °C	32
Physical form	Colorless solid
Odor	Camphoraceous
Heat of combustion, kJ/mol	5767
Heat of vaporization, kJ/mol	39
Specific heat, kJ/(kg·K)	0.406
Heat of cracking, kJ/mol	24.59
Spontaneous ignition point, °C	
In oxygen	510
In air	680
RON	108 [9]

DCPD has high energy content in addition to high anti-knock characteristics. For storing purposes, DCPD is stabilized with 100-200 ppm of antioxidants like tert-butyl catechol or butylated hydroxytoluene (BHT) to inhibit gum deposits formation during storage. DCPD is slightly toxic with a lethal dose of 353 mg/kg. DCPD has no known compatibility issues with other materials since it is just a cyclic olefin [15].

Some of the important physical properties of DCPD are listed in Table 1. It is an intermediate in the manufacturing of many chemicals because it is very reactive due to the presence of two double bonds [15]. Many of the reactions that DCPD undergoes were extensively studied. Because it is an important intermediate in the oxidation chemistry of aromatic molecules and PAH formation pathways, the chemistry of the cyclopentadienyl radical in combustion systems has also been studied [16]. However, it has not been investigated as a possible transportation fuel component, or as an additive [17]. The DCPD was obtained from Sigma-Aldrich with BHT added in small amount (150 to 200 ppm) as an anti-oxidant.

Table 2. Properties and compositions of FACE and PRF fuels

	FACE A	FACE J	FACE I	PRF 70	PRF 84
RON	83.9	73.8	70.15	70	84
MON	83.5	70.1	69.5	70	84
S	0.4	3.7	0.65	0	0
N-paraffins %	11.65	31.64	14.39	30	16
Iso-paraffins %	85.99	33.64	74.54	70	84
Cyclo-paraffins %	1.61	2.29	3.30	0	0
Aromatics %	0.38	31.69	1.15	0	0
Olefins %	0.21	0.60	6.35	0	0
Carbon wt.%	83.99	86.24	84.14	84.2	84.2
Hydrogen wt.%	16.01	13.76	15.86	15.8	15.8

Fuel Blends

DCPD and ethanol were blended with fuels for advanced combustion engines (FACE) gasoline fuels A, I and J, as well as PRF 70, and 84. PRFs are binary mixtures of iso-octane and n-heptane with the number denoting the volume percentage of iso-octane in the mixture. The blends are listed in Table 3. The properties of FACE gasolines and their blends with ethanol are reported in Ref. [18]. FACE A has a RON of 84 and it is mostly paraffinic with no sensitivity. FACE I and FACE J have similar RON numbers, but different compositions. They also have very low sensitivity. FACE I is highly paraffinic while FACE J is 71% paraffinic, and 28% (vol.) aromatic. These gasoline fuels were chosen to evaluate the effect of both RON and the composition of base gasoline on the blending characteristics of DCPD. The properties and compositions of FACE fuels and PRFs are shown in Table 2.

Since DCPD is solid at room temperature, with a low melting point of 32 °C [15], it was heated in a water bath (with the measuring glassware) to maintain DCPD in its liquid phase. When the DCPD was totally liquefied and ready for blending with a base fuel, it was carefully transferred to avoid solidification (using the warmed graduated cylinder) into one liter bottles. The fuel was measured using a graduated cylinder. Then the DCPD and the fuel were mixed and left for several hours, to ensure the homogeneity of the fuel mixture. No preparation was required for the ethanol and toluene since both chemicals are liquid at room temperature. The ethanol bottle remained closed, except during transfer operations, due to the hydrophilic nature of alcohols.

Table 3. Fuel matrix (Vol. %)

FACE A	FACE A + 5% EtOH	FACE A + 5% DCPD	FACE A + 15% EtOH	FACE A + 15% DCPD
FACE J	FACE J + 5% EtOH	FACE J + 5% DCPD	FACE J + 15% EtOH	FACE J + 15% DCPD
FACE I	FACE I + 5% EtOH	FACE I + 5% DCPD	FACE I + 15% EtOH	FACE I + 15% DCPD
PRF 70	PRF 70 + 5% EtOH	PRF 70 + 5% DCPD	PRF 70 + 15% EtOH	PRF 70 + 15% DCPD
PRF 84	PRF 84 + 5% EtOH	PRF 84 + 5% DCPD	PRF 84 + 15% EtOH	PRF 84 + 15% DCPD

Experimental

Table 4. Key conditions of different testing methods

	IQT	HCCI	KLSA
Air/fuel ratio	2	0.3	1
Temperature	545°C	52 and 149°C	52°C
Intake Pressure	21.37 bar	1 atm	1 atm
Ignition type	Compression	Compression	Spark

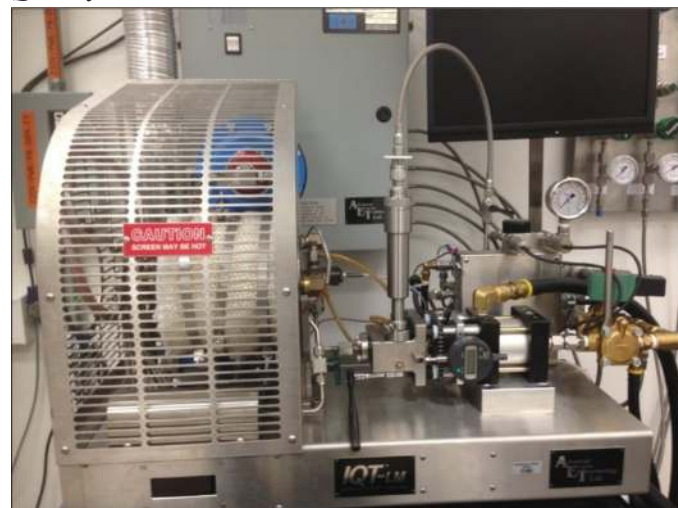### *Ignition Delay Time Measurements in Ignition Quality Tester*

Figure 2. Ignition quality tester (IQT)

As this testing requires very low quantities of fuel and little experimental time, and in order to rapidly screen the fuel blends, the ignition quality tester (IQT) shown in Figure 2 was used to measure the ignition delay times of DCPD fuel blends, according to ASTM D6890 [19]. The IQT is a constant volume combustion chamber with a single-hole S-type pintle nozzle [20]. The fuel is injected into zero air (air with a trace amount of hydrocarbon < 0.1 ppm) at a pressure of 21.3 bar. The chamber temperature is fixed to a temperature obtained with a calibration method, using *n*-heptane ignition delay measurements; this method allows for faster screening. The physics of fuel spray and mixing makes this combustion mode quite complex compared to a gasoline engine. Nevertheless, the method has been demonstrated to have a good correlation with the RON of a fuel [21].

The total ignition delay (ID) is defined as the time difference between the start of injection to the start of ignition. Ignition is identified by a rapid change in the pressure of the chamber obtained with the gradient method as described in [20,22] The IQT was initially designed to measure ID, and the derived cetane number (DCN) of diesel-like fuels. Therefore, in order to test gasoline-like fuels, the IQT was modified according to [20,22] The DCN was computed from the ID using equation (2a). Derived RON (DRON) was correlated to DCN by using equation (2b) [21].

$$DCN = 83.99[(\tau_{id}-1.512)]^{-0.658} + 3.547$$

$$(2a)$$

$$DRON = -293(DCN/100)^2 - 52(DCN/100) + 114.1$$

$$(2b)$$

Where,

DCN = Derived cetane number

τ_{id} = Ignition delay time (in ms)

RON = Research octane number

Homogenous Charge Compression Ignition (HCCI) Number

Figure 3. Cooperative fuel research (CFR) engine

HCCI numbers were introduced by Lund-Chevron to quantify the auto-ignition behavior of fuels under engine conditions without transport, or flame propagation effects [23]. The detailed procedure for calculating HCCI numbers is presented in detail in Ref. [23]. The HCCI number is the volumetric percentage of isooctane in a PRF mixture with the same ignition behavior as the fuel at a given engine operating condition, similar to standard RON and MON test procedures [24,25]. Engine speed and intake conditions are presented in Table 6. The test was conducted in a modified cooperative fuel research (CFR) engine (Figure 3). The experimental model is detailed in Ref. [26]. Engine specifications and operating conditions are presented in Table 6.

Table 5. HCCI test engine conditions

HCCI fuel numbers	Engine speed (rpm)	Intake air Temperature (°C)
HCCI (RON)	600	52
HCCI (MON)	900	149

Table 6. Engine specifications and operating conditions

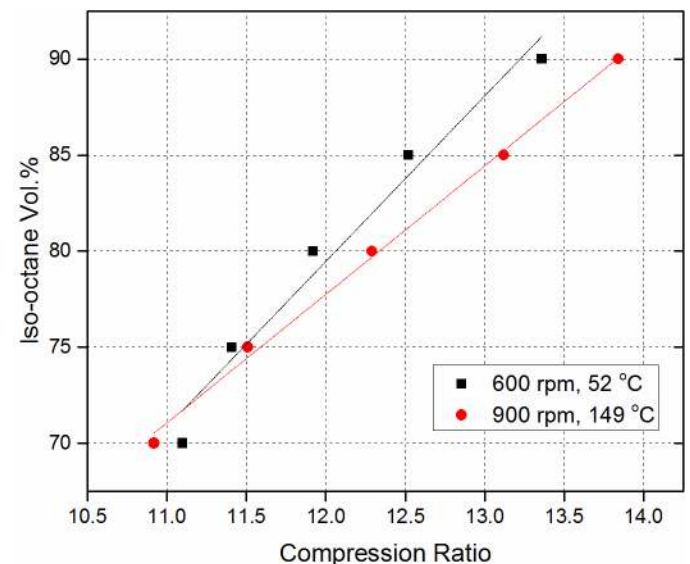|	
Engine Type	CFR single cylinder
Bore	82.55 mm
Stroke	114.3 mm
Connecting rod	254 mm
Injection system	Port fuel injector
Speed	600 and 900 rpm
Compression ratio	4:1 to 15:1
Spark timing	-13 CAD (Crank Angle Degree) ATDC
Lambda (λ)	3
Intake air temperature	52 ± 2 °C and 149 ± 2 °C

Figure 4. Transfer function plot

The engine was operated at lambda 3, and at each operating point the compression ratio (CR) required to obtain a CA50 at 3° ATDC (crank angle at which 50% of heat is released) was determined. The

compression ratio was then translated to a HCCI number, based on a transfer function plot. The transfer function was generated by testing PRF mixtures with 70% isooctane to 90% isooctane, at intervals of 5%, under the same experimental conditions [23]. The plot could not be extended beyond 90 since the compression ratio of the engine was limited. The transfer function plots are shown in Figure 4 adopted from Waqas *et al.* [27] CR values. From the best line fit, equations (3) and (4) were obtained and used to calculate the HCCI numbers for the fuels investigated.

$$HCCI (RON) = 8.621(CR) - 23.987$$

(3)

$$HCCI (MON) = 6.6923(CR) - 2.5559$$

(4)

The HCCI numbers, as detailed in Ref. [23], were measured at four operating points; due to the limited quantity of fuel available, tests were confined to two points. The compression ratio response at different conditions showed the effect of different engine operating conditions on reactivity. PRFs are generally more resistant to auto-ignition at higher speed and low intake air temperature conditions. Higher intake air temperature usually increases reactivity for the same engine speed, as shown in Ref. [23]. However, increased speed decreases residence time, which thereby reduces reactivity of the fuel air mixture. The empirical constant K, defined by Kalghatgi [3], for the PRF mixtures greater than RON of 75 would be lower for the engine operating at 900 rpm and 149°C than at 600 rpm and 52°C operating in HCCI mode. This is opposite to the actual RON and MON tests were K is greater at 900 rpm and 149°C. Thus, K in HCCI mode is not independent of the fuel unlike in spark ignition mode. Truedsson *et al.* [23] made a similar observation in their work. Therefore, determination of K for HCCI mode operation needs to be reevaluated.

Knock Limited Spark Advance (KLSA)

KLSA experiments were also conducted in the CFR engine facility. This test method was performed to evaluate DCPD blending in the spark ignition mode. The engine was near RON conditions (52 °C - intake air temperature, 600 RPM - engine speed, lambda 1). The fuel's resistance to auto-ignition with advancing spark timing was measured in the form of peak knock pressure derived from in-cylinder pressure measurements. Peak knock pressure is defined as the maximum positive amplitude of pressure oscillations occurring due to auto-ignition of end gas at a certain compression ratio [28]. AVL GH14 D transducer was used to measure pressure with a resolution of 0.1 CAD. The transducer is located on top of the cylinder. In order to control intake conditions, multiple thermocouples were used to maintain the air intake temperature. They are located upstream of the port fuel injectors. The fuel intake was controlled by AVL controlled system and equivalence ratio is measure at the exhaust using an ETAS oxygen sensor.

The knocking cycles have cycle-to-cycle variability, and the values presented are averages of 190 cycles. The compression ratio was chosen so that the fuel would have a peak knock average of around 1.5 bar at 13° CAD BTDC. DCPD gasoline mixtures were compared to ethanol-gasoline mixtures

Results and Discussions

Derived RON (DRON) from IQT

Table 7. Ignition delay times for pure and blends

Fuel	Ignition Delay (ms)	DCN	DRON
Toluene	213.17	6.0	109.9
Isooctane	16.95	17.4	96.2
Ethanol	93.10	8.0	108.1
Isooctane + DCPD (1:1)	42.06	10.9	105.0
Toluene + DCPD (1:1)	56.6	9.6	106.4

Ignition delay times from the IQT for DCPD and other high octane components - toluene, ethanol, and isooctane - presented in Table 7 along with their derived cetane numbers (DCN). Ignition delay of pure DCPD could not be measured since it is solid at room temperature; therefore, it was blended with isooctane, and toluene (50% vol.) separately. The results present the relative reactivity of these components. Toluene has the highest resistance to auto-ignition, followed by ethanol. The reactivity of DCPD can be inferred from the ignition delay of its blends. Its reactivity is between isooctane on the lower end and ethanol on the upper end. This is consistent with the RON reported in Ref. [9].
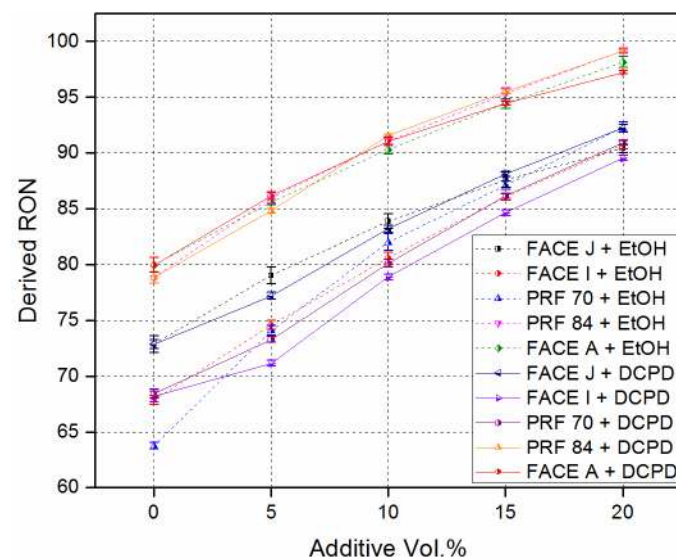

Figure 5. Derived RON of gasoline with varying % vol. of DCPD and ethanol

The DRON for gasoline blends with DCPD and ethanol (from Waqas *et al.* [27]) are presented in Figure 5. DRON for ethanol was calculated from DCN values obtained by Waqas *et al.* [27] The increase in resistance to auto-ignition is identical for both DCPD and ethanol. The synergistic blending quality of ethanol was well established by Foong *et al.* [11]. These results, along with the inferred reactivity of DCPD reported above, confirm the synergistic characteristic of DCPD, which appears greater than that of ethanol. The underlying mechanism contributing to this synergistic effect, however, are expected to be slightly different. The heat of vaporization of ethanol (905.2 kJ/kg) [29] is greater than DCPD (295 kJ/kg) [30]. The cooling of the chamber air due to ethanol vaporization would be greater, and will lead to lower chamber temperatures. However, the lower air requirement for ethanol to form

auto-ignitable mixtures, might allow for shorter mixing time scales to form ignitable mixtures. Also, the BRON and BMON of DCPD with PRF 60 were reported to be greater than ethanol [9][11]. This points indicates to a greater impact of base fuel RON on the blending nature of DCPD, compared to ethanol, possibly because a portion of ethanol's anti-knock quality derives from its charge cooling effect, whose action is independent of base fuel chemistry.

The error bars have been added. The IQT yields a fairly constant ignition delay with a maximum standard deviation of about 5%. This translates to an error within 1 octane number. Due to the scale adopted, the error bars appear insignificant. The error in volume % of the additive was estimated to be 1%. Blending was done at standard temperature and pressure (STP).

Table 8. Blending research octane number (BRON) of different fuel blends with varying DCPD and ethanol % vol. based on IQT measurement extrapolation to 100 vol. %

	Vol. %	BRON PRF 70	BRON FACE I	BRON FACE J	BRON PRF 84
DCPD	5	166	128	160	198
	10	185	175	176	206
	15	186	178	175	190
	20	181	175	170	180
Ethanol	5	182	196	196	221
	10	204	192	183	201
	15	193	187	171	189
	20	188	181	161	180

Generally, between 5% and 20%, the BRON values shows a linear response towards the addition of both DCPD and ethanol. Only few fuel blends can be considered outliers like, FACE I + DCPD, FACE J + ethanol, and PRF 84 + ethanol. Therefore, DCPD blends show more linear response.

HCCI Numbers

HCCI numbers calculated from compression ratios (CR), using transfer functions (3) and (4), are presented in Figure 6. The HCCI numbers measured near RON-like conditions (top) show a linearly increasing response to increasing DCPD content. The blending characteristics exhibited in IQT correlated well in the HCCI (RON) number. However, the HCCI numbers near MON-like conditions (bottom) for FACE A and PRF 84, exhibit a different trend. The extrapolated BRON and BMON are presented in Table 9.

Generally, at RON conditions, the BRON values are higher when the base fuel is blended with 5% of DCPD. Paraffinic fuels like FACE I and PRF 70 have similar RON of 70 and BRON values. Although FACE J has similar RON value to FACE I and PRF 70, it experience

slightly higher BRON at 5% blend. This could be attributed to the presence of higher aromatic content, 32%. For higher octane fuels like FACE A and PRF 84, the BRON values are higher at the 5% blend as well. It is much higher in case of PRF 84 which was also observed by Waqas et al.[27]. This observation is quite surprising considering there is small difference in their PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatic) composition. This cannot be explained with existing literature as the permutations of possible blending effect between different components within FACE A are too large. The use of complex surrogates and their chemical kinetic model along with that of the blending component could possibly provide an insight and an answer to this phenomenon. The BRON of the 15% DCPD blends for all FACE gasolines and PRFs converge to very similar values.
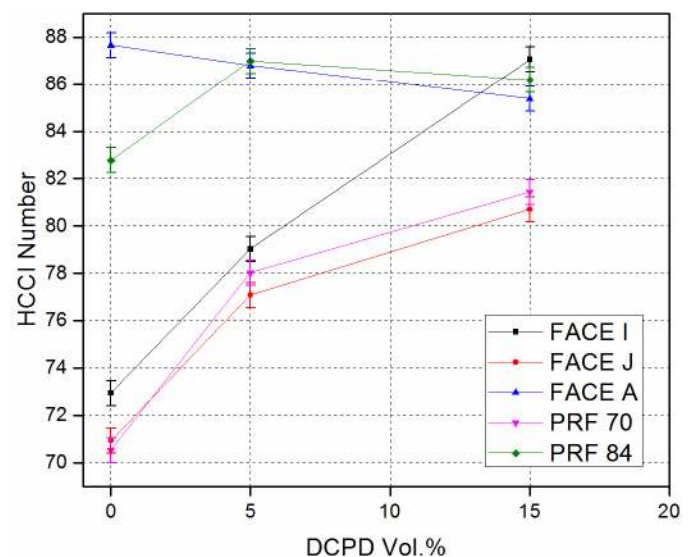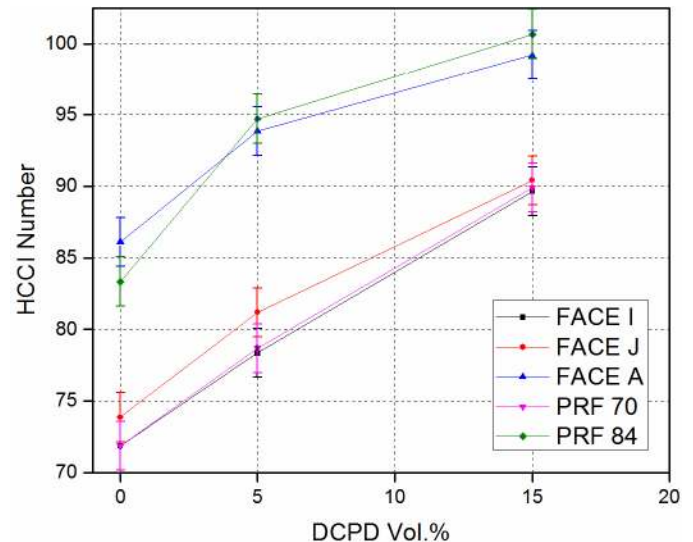

Figure 6. HCCI number of fuel with increasing DCPD % vol. (top) 600 rpm, 52°C inlet temperature; (bottom) 900 rpm, 149°C inlet temperature

BMON values of the 5% DCPD blends seems to rely on the octane rating of the base fuel. FACE I, J and PRF 70 show similar BMON results. However, PRF 70 have slightly higher BRON which might be a result of blending effect since PRF 70 has purely paraffinic composition. On the other hand, PRF 84 and FACE A exhibit a lower BMON values since they have a higher octane rating. In case of FACE A the effect is sever due to compositional blending effects within FACE A constituents. The BMON values for ethanol are similar to that of DCPD for FACE I, FACE J, and PRF 84. However, ethanol blend has higher BMON number than DCPD when blended with FACE A and PRF 84. The opposite is observed with the PRF 70 blend, in which, the ethanol blend has a lower BMON value compared to DCPD blend.

In general, the BMON values of the 15% DCPD blends seems to depend on the octane rating of the base fuel. Lower octane fuels like, FACE I, FACE J, and PRF 70 exhibit higher BMON values than higher octane base fuels like, FACE A and PRF 84. In comparison with Waqas et al. [27] results, all fuel blends with 15% ethanol have greater BMON values than the fuel blends with 15% DCPD expect for FACE I which has a similar BMON values for both ethanol and DCPD blend.

The BRON and BMON extrapolated from the HCCI numbers of the blends showed that the blending nature of DCPD was dependent upon the RON of the base fuel, as well as the amount of DCPD blended. The decline in the HCCI number, at MON-like conditions, realized with FACE A and PRF 84, is attributed to the high DCPD sensitivity which decreased the reactivity at high temperature. At these elevated temperatures the combustion occurs beyond the negative temperature coefficient (NTC) region. This phenomenon was observed when DCPD was blended with highly paraffinic fuel, which on their own, have an exaggerated NTC behavior [31]. Equation (1) can be rewritten in terms of HCCI, equation (5).

$$HCCI_{base} \times C_{base} + BON \times C_{booster} = HCCI_{blend}$$

(5)

Where,

$HCCI_{base}$ = the HCCI number for fuel without octane booster

C_{base} = concentration of fuel without octane booster

BON = blending octane number

$C_{booster}$ = concentration of octane booster

$HCCI_{blend}$ = the HCCI number of the final blend

Table 9. Blending octane number (BON) of different fuel blends with varying DCPD % vol.

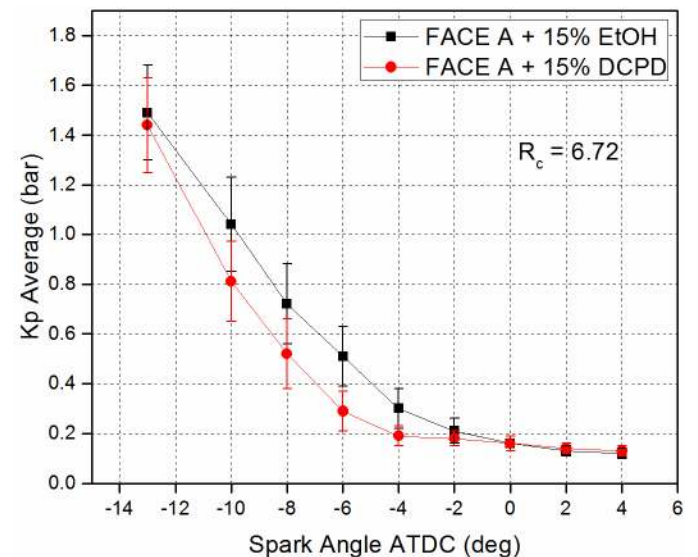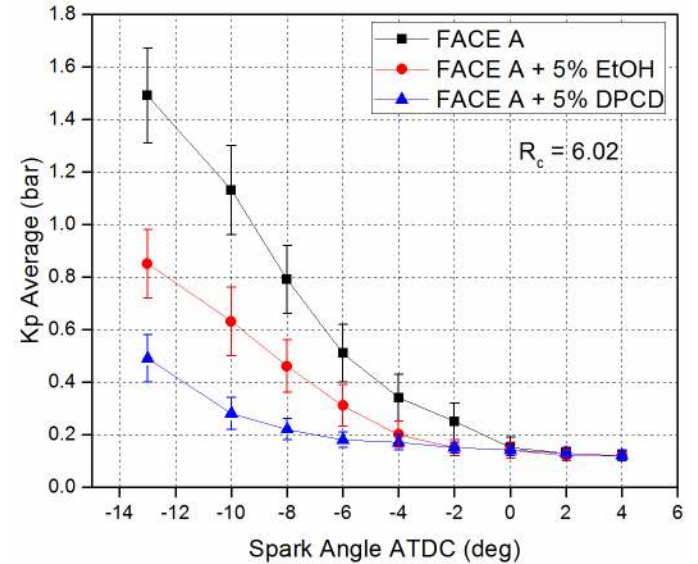| Fuel	BRON	BMON	Fuel	BRON	BMON
FACE I + 5% DCPD	201	195	FACE A + 15% DCPD	173	72
FACE I + 15% DCPD	190	167	PRF 70 + 5% DCPD	208	220
FACE J + 5% DCPD	220	194	PRF 70 + 15% DCPD	192	143
FACE J + 15% DCPD	184	136	PRF 84 + 5% DCPD	311	167
FACE A + 5% DCPD	241	70	PRF 84 + 15% DCPD	199	82

Knock Limited Spark Advance (KLSA)

Figure 7. KLSA of (top) FACE A, and FACE A with 5 % vol. of DCPD and EtOH (CR = 6.02), (bottom) FACE A with 15 % vol. DCPD and EtOH (CR = 6.72).
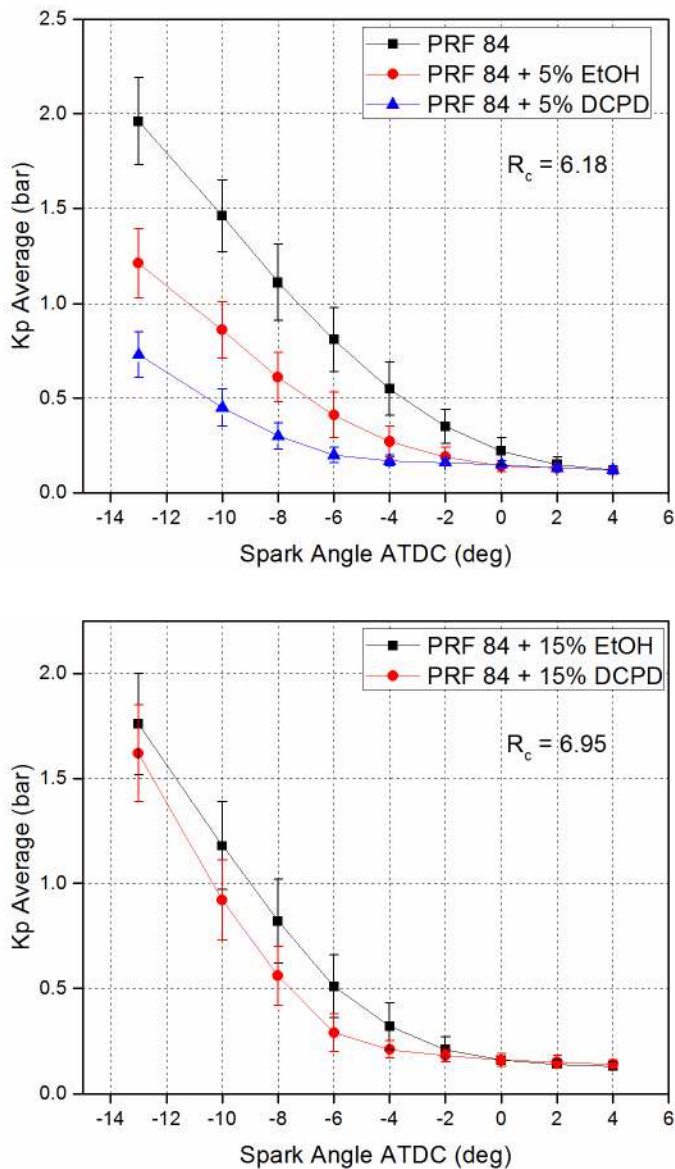
Figure 8. KLSA of (top) PRF 84, and PRF 84 with 5% vol. of DCPD and EtOH (CR = 6.18), (bottom) PRF 84 with 15% vol. DCPD and EtOH (CR = 6.95)

The KLSA results presented in Fig. 7, 8, 9, 10, 11 show that the DCPD-gasoline blends have greater resistance to knock compared to ethanol-gasoline mixtures. The differences in FACE A and PRF 84 blends comprising DCPD and ethanol are significant at lower blending fraction of 5%, but the difference is smaller at 15% blending. This is consistent with derived RON values from IQT testing. PRF 70, FACE I, and FACE J at 5% blending of DCPD, show a small difference in Kp values compared to ethanol. The difference widens significantly in Kp at 15% blending.

Figure 7 shows the considerable difference in Kp between pure FACE A and FACE A blended with 5% ethanol and DCPD. However, the difference is larger in DCPD, which means that DCPD exhibits better anti-knock behavior. When 15% of ethanol

and DCPD is blended with FACE A, the observed difference in Kp is not as great. The same trend can be observed with PRF 84 (Figure 8); this can be attributed to the fact that both FACE A and PRF 84 have about the same octane rating, and both are predominantly paraffinic fuels.
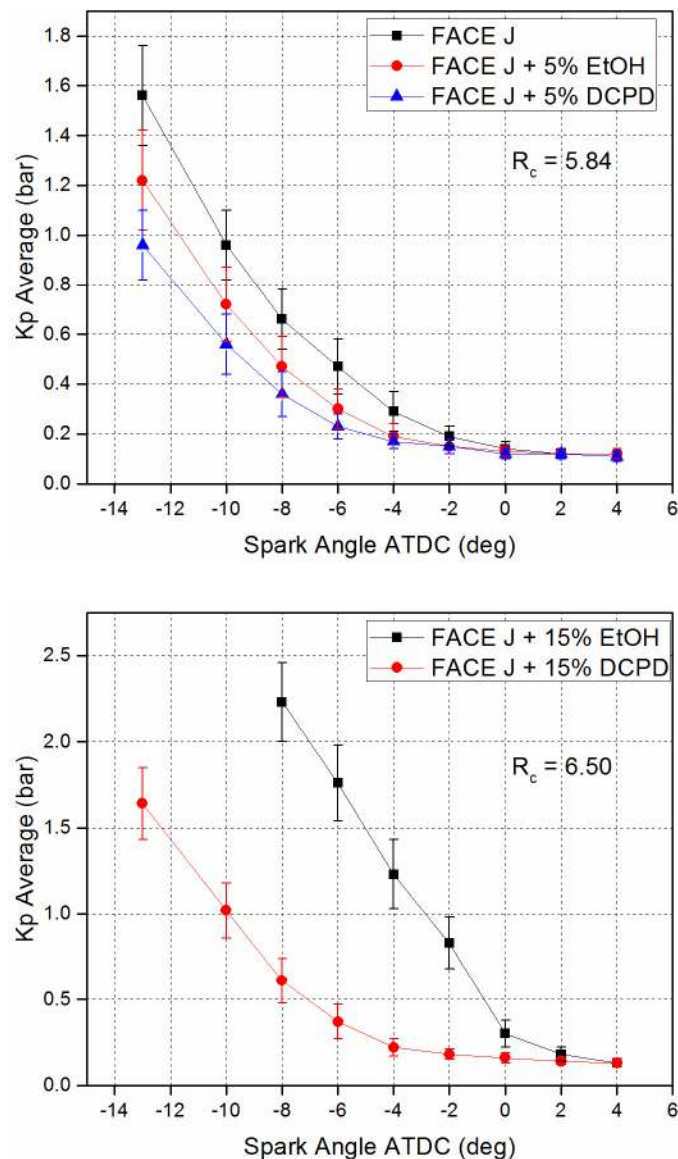
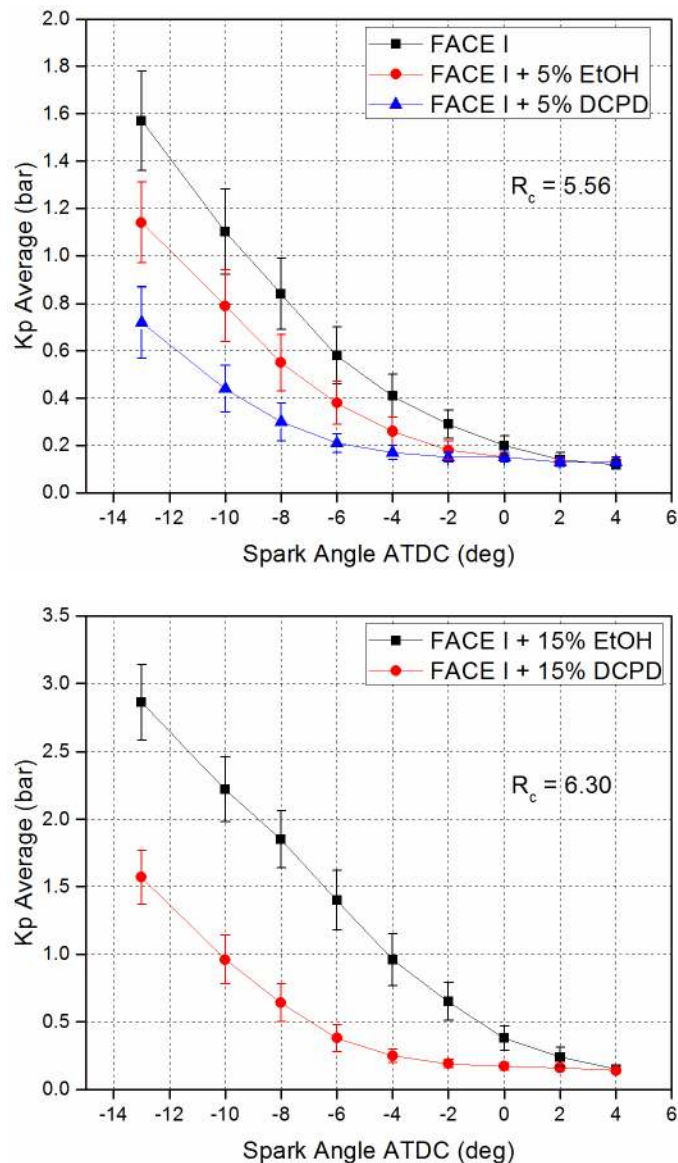Figure 9. KLSA of (top) FACE J, and FACE J with 5 % vol. of DCPD and EtOH (CR = 5.84), (bottom) FACE J with 15 % vol. DCPD and EtOH (CR = 6.50)

In Figure 9 the difference in Kp intensity between pure FACE J and the 5% blends is shown to be moderate; but the difference is much larger when comparing FACE J with 15% ethanol to the blend with 15% DCPD, implying the much improved anti-knock characteristic of DCPD.

Figure 10 shows that when FACE I is blended with 5% ethanol and DCPD, the effect is even greater than that of FACE J, although they have similar RON and MON values. This is due to

the compositional differences between the two FACE gasolines. FACE I has minor aromatic content (3.87 vol. %), while the aromatic content of FACE J is 31 vol. %. However, both experience a larger Kp intensity when blended with 15% ethanol compared to the 15% DCPD.

PRF 70 (Figure 11) behaves like FACE I with 5% blends. However, it shows an extreme knock intensity in the blend with 15% ethanol compared to the 15% blend with DCPD. Further investigation into the kinetics of DCPD oxidation is needed to explain the reason for this difference in behavior, as the available data is insufficient.

Figure 10. KLSA of (top) FACE I, and FACE I with 5% vol. of DCPD and EtOH (CR = 5.56), (bottom) FACE I with 15 % vol. DCPD and EtOH (CR = 6.30)
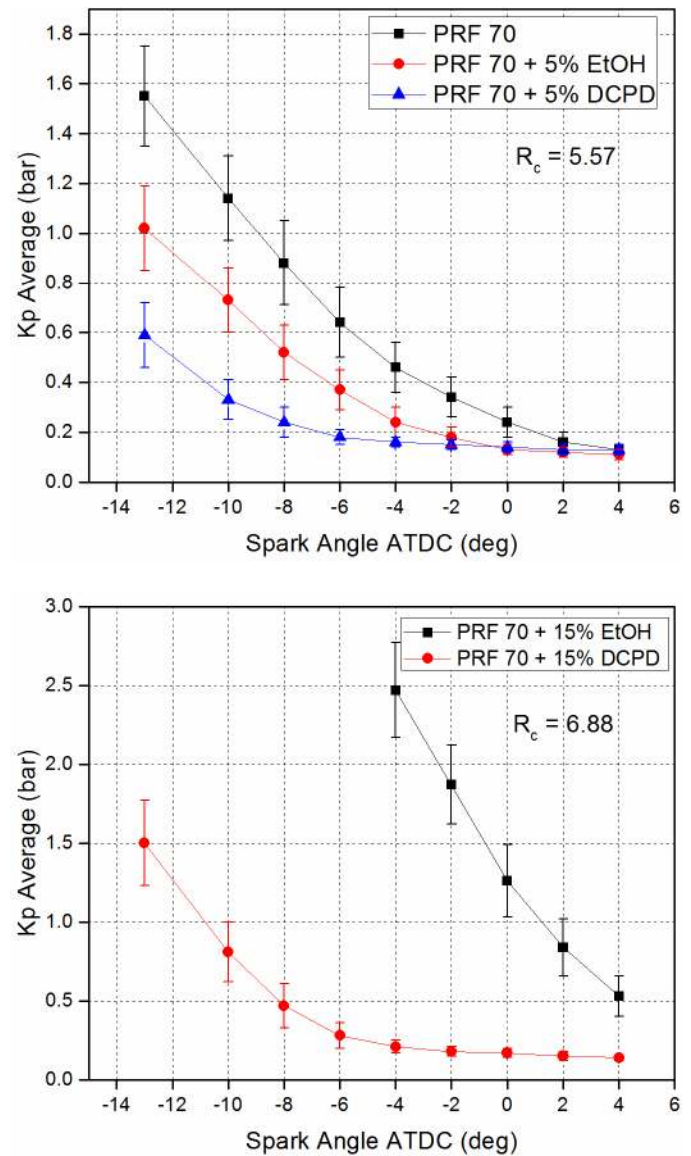
Figure 11. KLSA of (top) PRF 70, and PRF 70 with 5% vol. of DCPD and EtOH (CR = 5.57), (bottom) PRF 70 with 15% vol. DCPD and EtOH (CR = 6.88)

HCCI and IQT Correlation

HCCI numbers and DRON values are similar from a qualitative perspective; however, DRON values are lower than the HCCI values (Figure 12). There are several reasons for this discrepancy. First, both methods use fittings and correlations that lead to deviation in the predicted values [21,23]. Second, HCCI combustion is conducted under lean conditions, while in an IQT there is a spectrum of the fuel/air mixture regimes. The ignition is rapid in the rich zones ($\varphi > 2$) [32], wherein heat release triggers reactivity in the leaner regions, causing ignition. This is proven in Ref. [33,34].

IQT testing is a standardized test while the HCCI test - being quite new and not an established procedure - is prone to several sources of measurement errors [35]. The important sources of error in the present experimental setup could be day-to-day variations; the compression ratio determination; determination of the air/fuel ratio (λ); and the cycle-to-cycle variation of combustion phasing [35]. Furthermore, the most important source of error is the extrapolation process.
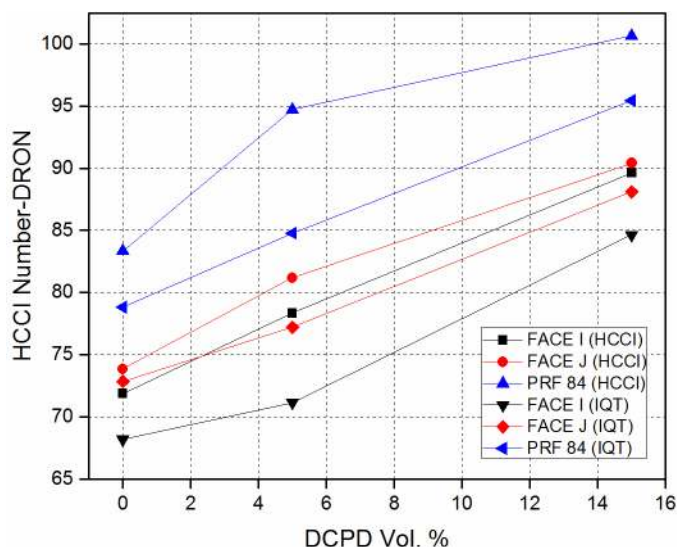
Figure 12. HCCI number and IQT derived octane numbers (DRON) of FACE I, J, and PRF 84

Chemical Nature of Synergistic Blending

Toluene is a well-known high octane booster: It has a high BRON of 124 when blended with PRF60 at 20 vol% [9]. It is also used in toluene PRFs (TPRFs) as a surrogate fuel for aromatics. Toluene is a good example of a non-synergistic octane booster that shows a linear blending effect. The non-synergistic blending behavior of toluene makes it inferior to other synergistically blending fuels like DCPD, which is lower in octane than toluene. The chemistry of toluene auto-ignition is well understood. This is why toluene was selected to be compared to DCPD here.

Although pure DCPD is lower in octane rating than pure toluene, it behaves as a better octane booster when blended with gasoline fuels. The synergistic blending nature of DCPD is very interesting: The octane rating of pure DCPD is lower than pure toluene and ethanol. This is caused by high temperature combustion which induces the ring opening of CPD. However, as a pure compound, toluene can withstand high temperature combustion due to the very stable aromatic ring in its structure. When combusted, toluene does not decompose until the temperature is above 1000°C. However, benzene is still detected at 1100°C [36]. Consequently, low temperature chemistry was investigated to further understand why DCPD is a better octane booster than toluene.

Because of its higher blending octane number, DCPD has a greater effect on boosting fuel octane than toluene, Fig. 1 and Table 9. This is because of the oxidation behavior of DCPD, which decomposes to yield two CPD molecules upon oxidation. CPD contains a bis-allylic site which has allylic hydrogens that are easily abstracted. The formed cyclopentadienyl radical is extremely stable due to resonance stabilization of the radical at the bis-allylic position. CPD acts as a radical sync, leading to the formation of the stable ketone, cyclopentadienone [17]. The suggested pathway for low temperature oxidation of DCPD is shown in Figure 13.
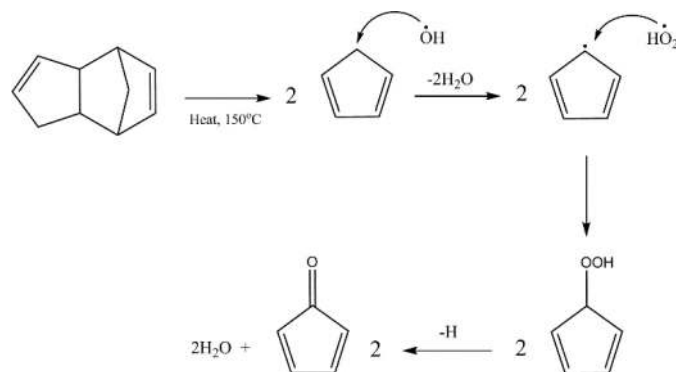

Figure 13. Low-temperature oxidation mechanism of DCPD.

The toluene aromatic ring is an electron withdrawing group which does not stabilize the formed radical that resulted from the H abstraction from the methyl group, as effectively as the bis-allylic radical in CPD. Instead it reacts further, to produce more radicals [37]. The low-temperature oxidation reaction mechanism of toluene is shown in Figure 14. It is clear that addition of hydroperoxy (HO_2) radicals to the benzylic radical leads to the eventual formation of OH radicals, which increases reactivity.
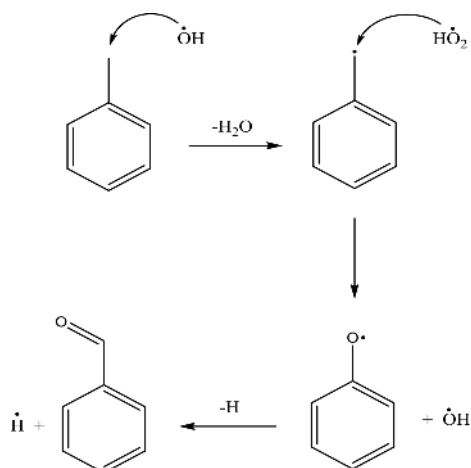

Figure 14. Low-temperature oxidation of toluene.

Summary and Conclusions

This study explored the auto-ignition property of a high-potential octane booster, dicyclopentadiene (DCPD). The blending octane quality of DCPD with various gasoline fuels and PRFs was tested using different experimental procedures and covering a wide range of operating conditions. The results revealed the synergistic nature of DCPD blending with base gasoline fuels. The increase in octane quality per unit volume of DCPD diminished with increased DCPD volume and the RON of the base gasoline fuel. The composition of the base gasoline also appeared to have an effect on blending octane number (BON), which will be explored further in future work. Summary and conclusions are listed below:

1. Using DCPD as an octane booster might be a smarter utilization of byproducts from petrochemical refinery processes than conventional high octane gasoline streams.
2. IQT data showed a higher synergistic blending of DCPD compared to ethanol.

3. HCCI tests were performed to assess the auto-ignition behavior of DCPD-gasoline blends at RON-like and MON-like conditions. The HCCI mode blending research octane number (BRON-like) and blending motor octane number (BMON-like) for DCPD blended with various based fuels was determined.

4. The various BRON-like and BMON-like values computed from test results showed decreasing synergy with increasing research octane number (RON) and motor octane number (MON) of the base gasoline fuel.

5. Running the engine in the knock limited spark advance (KLSA) mode revealed that fuels for advanced combustion engines (FACE) A experiences a substantial difference in knock (Kp) intensity compared to the 5% blends with both ethanol and DCPD. The same trend is observed with PRF 84, however, in the 15% blends with ethanol and DCPD, the latter shows better anti-knock quality in the form of lower Kp.

6. For FACE J, there is little difference in Kp between the pure fuel and the 5% blend with ethanol and DCPD. However, the difference in Kp is much greater with FACE J + 15% ethanol and FACE J + 15% DCPD, with the latter having much smaller Kp.

7. FACE I showed a greater difference in Kp between pure FACE I and the 5% blend with ethanol and DCPD. The same phenomenon with FACE J recurred with FACE I when blended with 15% ethanol and DCPD. The latter showed much smaller Kp than the ethanol blend.

8. Primary reference fuel (PRF) 70 showed similar results in 5% blends with ethanol and DCPD; once again however, Kp was lower when blended with 15% DCPD.

9. A correlation between homogenous charge compression ignition (HCCI) numbers and derived RON from ignition quality tester (IQT) showed deviation because both methods involved fitting procedures and calculation in addition to the fact that HCCI is run under lean conditions where IQT is run under rich conditions. This is where auto-ignition behavior differs. However, HCCI seems to better predict the RON.

10. DCPD was found to be a better anti-knock agent than toluene; this was attributed to structural aspects and chemical reactions of each compound.

11. Overall, DCPD has a greater synergistic effect than ethanol and toluene, especially in low octane base fuels.

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Acknowledgments

Abbreviations

DCPD - Dicyclopentadiene

IQT - Ignition quality tester

CFR - Cooperative fuel research

HCCI - Homogeneous charge compression ignition

KLSA - Knock limited spark advance

RON - Research octane number

S - Sensitivity

K - Engine empirical constant

OI - Octane index

BRON - Blending research octane number

BMON - Blending motor octane number

BOI - Blending octane number

MON - Motor octane number

PRF - Primary reference fuel

CPD - Cyclopentadiene

BHT - Butylated hydroxytoluene

FACE - Fuels for advance combustion engines

ID - Ignition delay

DCN - Derived cetane number

DRON - Derived research octane number

CR - Compression ratio

CA - Crank angle

ATDC - After top dead center

BTDC - Before top dead center

STP - Standard temperature and pressure

NTC - Negative temperature coefficient

Kp - Knock pressure

PIONA - Paraffins, Isoparaffins, olefins, naphthene, and aromatics

APPENDIX

Table 1. Repeated HCCI test for PRF 84 + 15% DCPD fuel blend (900 rpm, 149°C)

Trail	Compression ratio	HCCI number
1	13.28	86.32
2	13.25	86.12
3	13.26	86.18

Standard deviation is 0.1
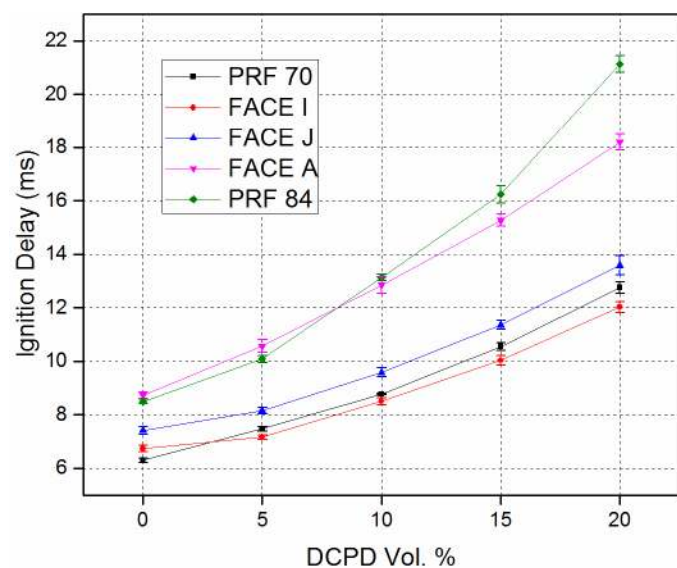
Figure 1. Ignition delay time measurements for DCPD fuel blends at standard conditions

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