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Relative Reactivities of the Isomeric Butanols and Ethanol in an Ignition Quality Tester

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ABSTRACT: Ignition quality tester (IQT) derived cetane numbers (DCNs) of binary blends of each individual alcohol (1-, 2-, *iso*-, and *t*-butanol and ethanol) with each second component (*n*-heptane and a real distillate fuel) have been measured to explore the autoignition behavior of these mixtures. This study pays particular attention to the effect of physical property variation within and among families of mixtures on their apparent reactivities. The relative reactivities of these blends are dominated by chemical kinetics, while blend-specific physical properties affect relative ignitability only slightly. The results firmly support DCN measurement as a means of characterizing mechanistic ignition chemistry behaviors among fuels and their blends. Surprisingly, *t*-butanol, which has been shown in other studies to be the least reactive pure C_4 alcohol, shows the least suppression of reactivity when blended with heptane or diesel fuel for most mixture fractions. This result is related to the lack of easily abstractable H atoms in *t*-butanol, relative to the other alcohols investigated, an explanation hitherto applied only to pure component butanol reactivity. Measured DCN values are shown to fit well a one-parameter cetane number blending model. Predictions from this model show that up to several percent of the considered alcohols can be blended into diesel-like fuels without significant deterioration of the cetane number.

1. INTRODUCTION

Interest in butanol isomers as fuel displacers/additives has garnered much recent attention in this journal.[1−6] Production of 1-, 2-, or *iso*-butanol from biomass is a topic of ongoing research,[7−9] while *t*-butanol has been used as gasoline additive for several decades.[10,11] A few studies have examined the relative reactivities of all four pure component isomers using different global experimental metrics: shock tube ignition delay,[12] laminar burning velocity,[13,14] and static reactor rates of reaction.[15] In each case, 1-butanol has been determined to be most reactive, *t*-butanol least reactive, and 2- and *iso*-butanol of intermediate and nearly equal reactivity. However, none of these studies was conducted at conditions stressing engine-like conditions, which involve a combination of lower temperatures, higher pressures, and undiluted fuel/air loadings. Moreover, these studies consider neat butanols only. As we show presently, relative reactivities of pure components may not indicate their relative reactivities when blended with other fuels, and butanol blended to supplement the conventional fuel pool is the most likely scenario under which these alternative fuels will be deployed.

Both fundamental and applied studies comparing combustion properties of blends of the isomeric C_4 alcohols in base fuels are scarce in the literature. However, it is clear that the reactivity of such butanol/fuel mixtures in applied systems will be governed by oxidation chemistry coupling of the butanol with the base hydrocarbon fuel, as well as by physical properties of the mixtures that may alter atomization- and distillation-related processes relative to their constituent pure components. In this work, we examine effects of both chemical structure and mixture fraction on ignition quality tester (IQT) ignition delay time, which we present below as the practically relevant derived cetane number (DCN).[16] The IQT is a direct injection, constant-volume ignition apparatus that measures DCN at preignition temperatures ranging from 788 to 848 K and a constant preignition pressure of 21.37 ± 0.07 bar (gage). A detailed description of the IQT

operating parameters during DCN determination can be found in the ASTM D 6890 standard.[16]

Ignition trends for two alcohol blend types are considered: mixtures with the well-studied, single component fuel *n*-heptane, and mixtures with a full-boiling range middle distillate fuel. This distillate is henceforth called CF13, and its properties are described in Table 1. In addition to butanol blends, ethanol blends are also studied for their current significance to the alternative fuel pool.

We chose heptane and CF13 as fuels to blend with the alcohols for several reasons. Both heptane and CF13 are relatively well-characterized reference fuels so far as IQT DCN studies are concerned. Moreover, heptane is a gasoline primary reference fuel, which enables heptane mixture trends from this study to be considered in the context of gasoline engine applications. These base fuels also have substantially higher autoignition reactivity in comparison to the pure alcohols, which better resolves alcohol/base fuel ignition coupling trends over the full mixture fraction range. Both base fuels have significantly different physical properties from each other and the alcohols, and we demonstrate below the relative insensitivity of IQT ignition to variation among the alcohol/base fuel blends. To our knowledge, this work is the first to consider, in depth, the decoupling of physical property and ignition chemistry influences on IQT reactivity trends among related fuel blends. Select physical and autoignition property values for the base fuels and alcohols are presented in Table 2.

2. EXPERIMENTAL SECTION

Binary fuel mixtures of *n*-heptane or CF13 with either ethanol or one of the isomeric butanols were prepared gravimetrically. Mixture volume

Table 1. Selected Properties of CF13 (Low Range Diesel Cetane Number Check Fuel)[17]

fuel property	average value	standard deviation	number of tests	ASTM test method
cetane number	41.99	0.97	17	D 613
derived cetane number[a]	42.1	0.46	6	D 6890
API gravity	35.05	0.06	14	D 287 or D 4052
viscosity, 40 °C, cSt	2.92	0.048	11	D 445
flash point, PMCC, °C	73.1	1.6	10	D 93
hydrocarbon type				D 1319
saturates	63.06%	2.32	9	
olefins	2.56%	1.01	9	
aromatics	34.38%	2.71	9	
distillation, °C, % recovered				D 86
IBP	182.2	3.8	14	
10%	224.0	2.3	14	
50%	271.4	1.1	14	
90%	321.0	2.2	14	
end	346.2	2.4	14	

[a] Determined in the present work from six sets of three measurements, spanning 6 months.

Table 2. Selected Physical and Chemical Property Values of Neat Fuels Used in This Work

fuel component	mass density at 298 K [g/mL]	molecular weight [g/mol]	molar density at 298 K [mmol/mL]	dynamic viscosity at 298 K [cP][a]	normal boiling point [K][b]	flash point [K][b]	heat of vaporization at 298 K [kJ/mol][c]	derived cetane number (DCN)[d]	DCN blending parameter, $\beta^{a,e}$
n-heptane	0.679	100.2	6.78	0.39	371	269	36.6	53.8	0.8420
CF13	0.850[b,f]			2.5[g]	455[h]	346		42.1	0.9756
ethanol	0.784	46.1	17.01	1.08	351	287	42.4	2.2[i]	1.5201
1-butanol	0.805	74.12	10.86	2.56	391	308	52.5	12.0	1.4589
2-butanol	0.802	74.12	10.82	3.09	371	300	49.7	8.5	1.1917
iso-butanol	0.798	74.12	10.77	3.31[j]	381	301	50.8	8.5	1.5356
t-butanol	0.787[k]	74.12	10.62	4.65	356	284	45.4	5.6[i]	0.4387

[a] From Perry's Chemical Engineers' Handbook.[18] [b] From MSDS or specification sheet provided with each fuel. [c] Most recent values from Chickos and Acree.[19] [d] Present work. [e] Discussed in section 3.4. [f] 289K. [g] Estimated. [h] Initial boiling point. [i] Extrapolated from fits to heptane and CF13 data, discussed in section 3.1. [j] Alternate reference.[20] [k] Subcooled liquid.[21]

fractions ranged from 0 to 100%, and the absolute error associated with preparing each mixture was less than 0.2 vol% for all CF13 mixtures and 0.1 mol % for all heptane mixtures. Room temperature correction for liquid fuel mass densities contributes negligible error in volume fraction computations for these blends.

The n-heptane used in these experiments was acquired from Chevron Phillips and met the ASTM D 6890-07a[16] calibration fuel quality standard in addition to ASTM gasoline primary reference fuel quality standard. Henceforth, we use "heptane" to refer unambiguously to this fuel component. The CF13 was also acquired from Chevron Philips and has been characterized at multiple facilities as part of the Diesel National Exchange Group program[17] (Table 1). Each of the alcohols used was acquired from Sigma-Aldrich, with stated purities of 99.5%, minimum.

All fuels were used without further purification, save filtration stipulated by ASTM D 6890 testing procedures. Purity of each of the filtered 5:1 (molar) alcohol/heptane mixtures was additionally verified by gas chromatography to ensure quality in the mixture preparation, filtration, and storage process.

Ignition delay times (ID) for fuel mixtures were measured in an IQT (Advanced Engine Technology, Ottawa), following the D 6890-07a protocol;[16] however, methylcyclohexane span checks were not performed due to unavailability of sufficiently pure fuel. Detailed description of the IQT apparatus, its operation, and correlation to the ASTM D 613 cetane number (CN) scale can be found in Standard D 6890-07a[16]

and the references therein. This standard also provides the correlation between ID and DCN; higher DCN corresponds to faster ignition/ higher autoignition reactivity. The DCN is defined as a function of the average ID of a set of 32 individual IQT ignition cycle results. Each fuel mixture was tested in a series of three or more sets resulting in at least 96 recorded IDs per mixture composition, and some blends were revisited to ensure test repeatability among IQT operators, sample batches, etc.

Ignition in an IQT is not a purely homogeneous event, as in the case of the ideal shock tube or rapid compression machine ignition experiments that utilize prevaporized, uniformly premixed conditions. The ignition event in an IQT possibly involves simultaneous three-dimensional, transient spray mechanics, droplet evaporation, gas phase mixing, and ignition chemistry,[22,23] leading to the statistical basis for the DCN definition described above and in more detail in ASTM D 6890.

Total ID (and hence, DCN) in the IQT can be considered the sum of a characteristic time for physical injection/vaporization/mixing processes leading to onset of chemical reaction and a subsequent characteristic chemical ignition time.[22,24] Spray ignition events dominated by the so-called physical ignition delay time may confound chemical kinetic interpretation of IQT ignition trends. However, results of IQT experiments with well-controlled temperature/pressure/injection conditions have been used previously to study effects of additive blending and molecular structure on ignition chemistry,[24−30] as is the case in the present work. We show here that meaningful ignition kinetics behavior
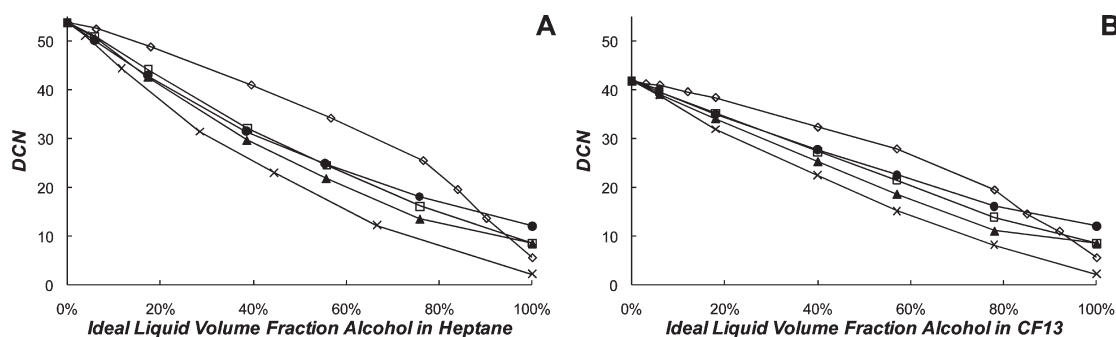
Figure 1. DCN results for volumetric blends of alcohols with (A) heptane and (B) CF13. Points are averages of experimental measurements, with shape indicating alcohol identity: (●) 1-butanol, (□) 2-butanol, (▲) *iso*-butanol, (◇) *t*-butanol, and (×) ethanol. Lines have been added for clarity.

can be extracted from DCN measurements with thoughtful consideration of fuel blending effects.

3. RESULTS AND DISCUSSION

3.1. General DCN Trends in Pure Component and Blended Fuels. Derived cetane number values for alcohol−heptane and alcohol−CF13 blends as a function of linear (ideal) liquid volume fraction are reported in Figure 1. With the exception of pure heptane, ethanol, and *t*-butanol, each data point represents the average of three or more DCN determinations (a total of 96 ignition events). Since heptane is a required calibration fuel for the ASTM D 6890 test with an exactly defined and bounded DCN target, we report this point as heptane's nominal on-calibration DCN. The DCN values for both ethanol and *t*-butanol extend beyond the present measurement capability of the IQT. We plot these points, although their measured DCN values are indeterminately less than or equal to the device-limited DCN of 7.2. Their pure component DCN values have been computed by fitting cubic polynomials ($R^2 > 0.999$) to the respective heptane and CF13 mixture data and taking the average of the values predicted from these two data sets. Pure alcohol extrapolated values from both heptane and CF13 blend trends are within 0.3 DCN units of the averages reported in Table 2.

Error bars of ±1 DCN apply to all measurements in Figure 1. This exceeds, often generously, the maximum measured deviation from the average for any of the 63 blends considered in this work. Standard ASTM D 6890[16] addresses the precision and accuracy of the test method in more detail, although that analysis is restricted to 34 < DCN < 61.

Relative reactivity results for the pure butanols agree with prior experiments:[12−15] 1-butanol is the most reactive of the butanol isomers, followed by essentially equal ignitability of the 2- and *iso*-isomers, and with *t*-butanol as least reactive. However, *t*-butanol mixtures in both heptane and CF13 are distinctly the most reactive mixtures over most of the blending range, while *iso*-butanol mixtures ignite slightly slower than 2-butanol mixtures. In comparison, ethanol blends tend to be the least reactive as a function of linear volume fraction.

3.2. DCN Sensitivity to Mixture Physical Properties. To elucidate sensitivity of DCN behavior to mixture physical properties (liquid phase thermophysical properties and vapor−liquid equilibrium (VLE) properties), we compare trends in DCN vs blend fraction for the ten blend families represented in Figure 1. This comparison among blend families supports the conclusion
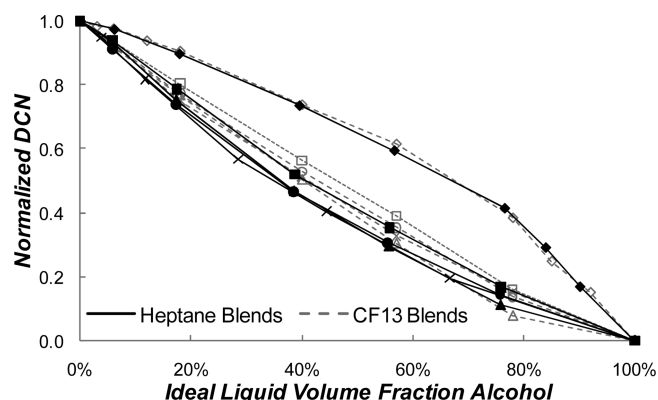

Figure 2. Normalized DCN vs liquid volumetric blend fraction for blends of alcohol in heptane (solid symbols) or CF13 (open symbols). Alcohol identity by shape indicated as in Figure 1; lines have been added for clarity.

that ignition chemistry effects, not physical property effects, primarily explain both the relatively distinct ignition behavior of *t*-butanol/base fuel blend families and the otherwise similar ignition behavior among the other blend families.

3.2.1. Reactivity Trend Similarities between Heptane and CF13 Blends. We first consider the DCN vs volume fraction data of Figure 1 suitably normalized in Figure 2 to account for the differences in pure component DCN values. The normalized DCN is defined on a linear scale, with base fuel DCN assigned a value of one and pure alcohol DCN assigned a value of zero. Such a scaling for correlative autoignition parameters presupposes similarity in autoignition chemistry and is empirically supported for both octane and cetane number scales (see, e.g., Ghosh and Jaffe[30]); a point we return to in section 3.4. We concentrate in this subsection, however, on the physical property aspects of the heptane and CF13 data sets.

Figure 2 shows similarity, within experimental uncertainties, in normalized DCN trends between heptane and CF13 mixtures for each alcohol's blend family, particularly for the *t*-butanol blend families. This simple linear DCN scaling returns these remarkably similar trends while spanning wide time scales (factor of ∼30) and physical property variations (e.g., factor of ∼10 in viscosity, ∼20% in mass density). For this data set, the contribution of the chemical ignition delay time appears sufficiently resolved from the contribution of the physical ignition delay time such that the results support the presupposed similarity in
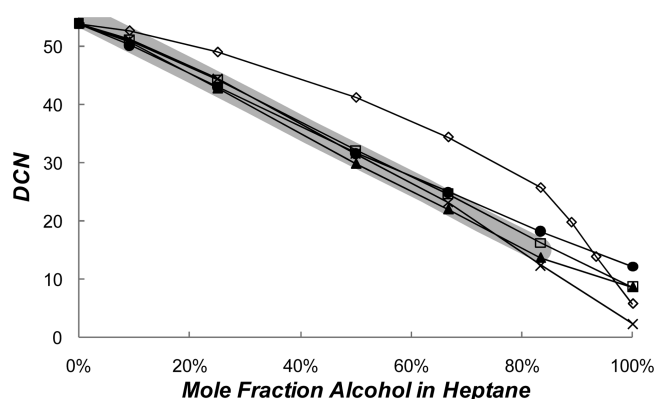
Figure 3. DCN results for molar blends of alcohols with heptane. A gray band of ±2 DCN units is indicated over much of the primary and secondary alcohol blend range. Points are averages of experimental measurements with alcohol identity indicated as in Figure 1; lines have been added for clarity.

autoignition chemistry. In other words, the substantial differences in physical property values between heptane and CF13 base fuels (Tables 1 and 2), which also applies to their blends with the alcohols, especially at low alcohol blend fraction, do not appear to significantly influence relative reactivity trends when comparing normalized DCN results to absolute DCN scale results of Figure 1.

3.2.2. Molar Blend Ratio Trends among Heptane Blends. Figure 3 displays ignition trends for alcohol/heptane mixtures as a function of mole fraction, rather than linear volume fraction. This scaling primarily accounts for disparate liquid phase molar densities among the alcohols (Table 2), particularly for ethanol. Note that relative to liquid volume blending coordinates (Figure 1), the molar blending coordinates (Figure 3) show DCN behavior of the ethanol blend family which are markedly more similar to behavior of the 1-, 2-, and *iso*-butanol blend families. Molar scaling also provides straightforward ratios of the types and abundances of chemical bonds in each alcohol/heptane fuel blend, which facilitates later discussion of chemical coupling effects.

Over most of the mole fraction range, ignition behavior of the primary and secondary alcohol blend families collapses within a linear band of ±2 DCN units, while the *t*-butanol blend family reactivity remains distinct. These reactivity trends appear to be predominantly due to chemical kinetics since, at comparable blend fractions, significant effects due to variation in mixture physical properties can be excluded, especially for heptane-rich blends.

While the *absolute* values for physical properties such as mass density, viscosity, or surface tension change as a function of blend fraction for all five blend families, the *relative* values at *fixed blending fraction* in heptane-rich blends are dominated by the physical properties of the heptane base fuel and are very similar among the blend families. Since, at fixed blending fraction, the physical ignition delay time is essentially fixed by heptane physical properties, the observed differences/similarities in ignition behavior arise predominantly from the chemical ignition delay time.

3.2.3. Suitability of IQT for Studying Relative Combustion Kinetic Behavior. The preceding arguments provide compelling evidence that the relative reactivities of these blend families do not strongly depend on mixture physical property values, except

possibly in cases corresponding to high alcohol blend fractions (exceeding 80% molar or volumetric) where physical properties are the most divergent. However, at these alcohol-rich blend fractions, the chemical ignition delay is significantly longer than the physical ignition delay,[22] suggesting that ignition chemistry effects remain dominant in a relative sense. Whether in blends with heptane or CF13, the consistent, similar, significant departure in behavior of the *t*-butanol blend families from the behavior of the other alcohol blend families and the consistent similarity in behavior of the ethanol blend families to the behavior of the primary and secondary butanol families indicate that IQT testing can identify combustion chemistry-dependent effects when fuels are compared in a relative sense. Having now considered the (in)sensitivity of the reactivity trends in Figures 1 and 3 to mixture physical properties, we address the relative chemical kinetic behavior of the various blends.

3.3. Chemistry-Dependent DCN Trends among the Alcohols. Detailed chemical kinetic models for the butanols remain under development (e.g., see discussion in Harper et al.[31]) and generally lack validation at lower temperature, higher pressure conditions similar to DCN testing conditions of near 820 K and 21 bar (gage). This fact, coupled with the complex physical model of the IQT ignition process, focuses our analysis on mechanistic interpretation of the data rather than detailed numerical analyses. Here, we interpret the preceding ignition results with a simple kinetic model intended to phenomenologically explain both the similar DCN trends among primary and secondary alcohol blends and the distinctly different DCN behavior for *t*-butanol blends. This qualitative interpretation considers homogeneous chemistry early in the ignition event, which effectively establishes the radical pool growth leading to ignition.

The common feature among the primary and secondary alcohols is the presence of one or more relatively weak C—H bonds in the molecular structure, a feature *t*-butanol lacks. Facile H-abstraction reactions at these bond locations have been used to explain the reactivities of the pure butanols over a wide range of experiments and conditions.[12−15] To our knowledge, this explanation has not been applied to describe the relative reactivities of the isomeric butanols when in blends with other fuels. We now extend this explanation to blends of these alcohols with heptane and CF13. In particular, we find this H-abstraction interpretation to be consistent with the observed inversion in relative reactivity of pure *t*-butanol with respect to its blends with heptane or CF13.

3.3.1. Blends with Primary and Secondary Alcohols. Under IQT ignition conditions, both heptane and CF13 essentially serve as sources of active OH radicals produced from generally posited low temperature chemistry pathways. As the primary and secondary alcohols are blended into these base fuels in increasing amounts, they consume active radicals as readily as the base fuel but do not regenerate additional radicals as easily as the base fuel. Extending reasoning presented by Haas et al.[32] for ethanol/heptane blends and Zhang and Boehman[33] for 1-butanol/heptane blends, this high pressure, low-to-intermediate temperature process is simply described as a redirection of OH from H abstraction of the base fuel hydrocarbons to H abstraction at the internal C—H bonds of these alcohols. Recent bond dissociation energy computations for the butanols[14] and ethanol[34] give bond strengths of ∼94−95 kcal/mol for the weakest C—H bonds (alpha to the OH group) in ethanol and 1-, 2-, and *iso*-butanol, comparable to the ∼95 kcal/mol secondary C—H bonds in heptane.[35] The similarity in bond energies results in nearly equal
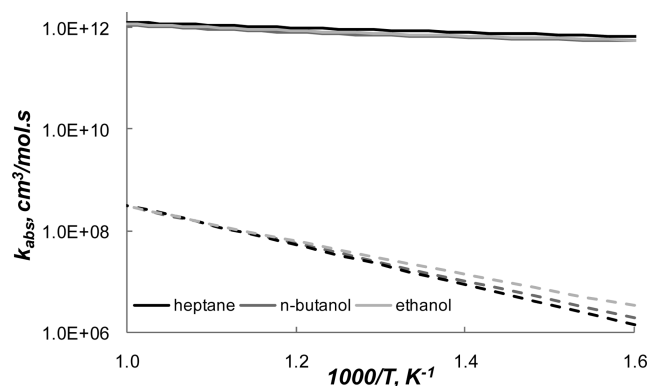
Figure 4. Abstraction rate coefficients, per fuel H atom, for H atom abstractions of heptane, 1-butanol, and ethanol by OH (solid lines) and HO$_2$ (dashed lines) over the temperature range of 625–1000 K. The HO$_2$ rate coefficients were extracted from recent kinetic models[38–41] due to the lack of recent experimental or theoretical rate coefficient determinations. Rate coefficient behavior specific to the weaker secondary or alpha C–H bonds in heptane or alcohol, respectively, is quantitatively similar.

H-abstraction rate coefficients at IQT ignition conditions (Figure 4), suggesting competition for OH between alcohol and heptane that is roughly proportional to the mole fraction of blended primary or secondary alcohol.

After α-H abstraction from a primary or secondary butanol by OH

$$OH + C_4H_9OH \rightarrow \alpha\text{-}C_4H_8OH + H_2O \qquad (R1)$$

two further reaction pathways are likely, either (1) molecular oxygen removes the weakly bound H atom on the OH moiety to form a stable carbonyl molecule and HO$_2$

$$O_2 + \alpha\text{-}C_4H_8OH \rightarrow \alpha\text{-}C_4H_8O + HO_2 \qquad (R2)$$

or (2) the remaining α-H atom is removed by O$_2$ to form a stable enol molecule and HO$_2$

$$O_2 + \alpha\text{-}C_4H_8OH \rightarrow C_4H_7OH + HO_2 \qquad (R3)$$

Either sequence R1 + R2 or R1 + R3 effectively removes a very reactive OH radical, producing the much less reactive HO$_2$ radical, which itself leads to formation of the stable molecule H$_2$O$_2$. These low-reactivity pathways compete with the re-entry of OH in the low temperature hydrocarbon oxidation cycle, which would lead to regeneration of OH and radical chain branching through oxygen addition reactions.

To illustrate the ability of the primary and secondary alcohols to compete for OH, we plot overall H atom abstraction rate coefficients for heptane, 1-butanol, and ethanol by OH, compiled from the recent literature[34,36,37] in Figure 4. Nearly identical rate coefficients imply competition between alcohol and heptane is weighted purely by mole fraction of either component present in the fuel blend. In this figure, we additionally plot rate coefficients for abstractions by HO$_2$. This demonstrates that HO$_2$ is several orders of magnitude less active than OH and also that, like OH, alcohol–heptane competition for HO$_2$ is essentially mole fraction weighted.

This active radical competition model manifests in observed DCN trends as a direct result of the alcohol fraction reducing the rate at which active radicals are regenerated: (1) DCN decreases (ignition delay increases) monotonically within a blend family

with increasing alcohol fraction, and (2) DCN trends are comparable among primary and secondary alcohol blend families, consistent with nearly equal weak C–H bond strengths in this group and suggesting that H abstractions from these alcohols occur at nearly the same rates for both of these alcohol moieties.

3.3.2. Blends with t-Butanol. Unlike the primary and secondary alcohols, *t*-butanol has a relatively higher C–H bond dissociation energy, ~101 kcal/mol,[14] compared to the secondary hydrocarbon C–H bonds in species found in the base fuels. As a result, little OH flux from low temperature hydrocarbon chemistry couples into abstraction reactions with *t*-butanol through reactions similar to R1. Instead, OH remains available to abstract from the base fuel, regenerating and branching additional active radicals through low temperature hydrocarbon oxidation reactions.

The active radical competition observed with the primary and secondary alcohol blends is unavailable in *t*-butanol blends with the base fuels. The inability for *t*-butanol to inhibit further low temperature hydrocarbon chemistry manifests in the present DCN observations as an apparently higher blend reactivity relative to that of primary or secondary alcohols. However, this is more properly viewed as *reduced suppression* of reactivity relative to that achieved with primary or secondary alcohol blending.

The relatively high C–H bond strength in *t*-butanol reconciles the observed, seemingly contradictory, inversion in relative reactivity for pure *t*-butanol and its blends compared to the other alcohols and their blends. The apparently high reactivity of *t*-butanol/base fuel blends follows from these C–H bonds rendering *t*-butanol effectively unable to compete with the base fuel for active radicals. With no active radical scavenging, no subsequent radical pool suppression due to *t*-butanol can occur, and the system ignites primarily as a function of the radical pool governed by alkane kinetics.[42] The relatively high C–H bond strength in *t*-butanol also underlies its lower pure component reactivity when compared to the other pure butanols. In the pure component case, the higher C–H bond strength of *t*-butanol reduces the rates of H abstraction by any radical, leading to generally lower reactivity for this fuel as a pure component.

3.4. Relevance to Applications. Table 2 presents regressed DCN blending parameters, β_i, fit from the DCN measurements in Figure 1, following the cetane number model of Ghosh and Jaffe.[30] In this model, the parameter β_i can be thought of as a measure of a component's ability to enhance/suppress ignition relative to linear volumetric blending ignition results. Hence, at cetane number-relevant conditions, components with $\beta > 1$ apparently suppress ignition while those with $\beta < 1$ apparently enhance ignition, relative to linear blending. Their model does not discriminate between cetane number and derived cetane number; though these quantities are not exactly the same, here, we specifically limit discussion to DCN.

The β_i values of Table 2 capture the apparent ignition synergism of *t*-butanol and ignition suppression of the other alcohols seen in the present work. Whether measurements of DCN are sufficiently resolved to differentiate behavior from among the primary and secondary alcohol blend families remains a topic of ongoing research; however, we call attention to the comparable β values (Table 2) for primary alcohols ethanol, 1-butanol, and *iso*-butanol and the distinctly lower value for secondary alcohol 2-butanol.

Comparison of the cetane number model to experimental DCN measurements in Figure 5 indicates this one-parameter
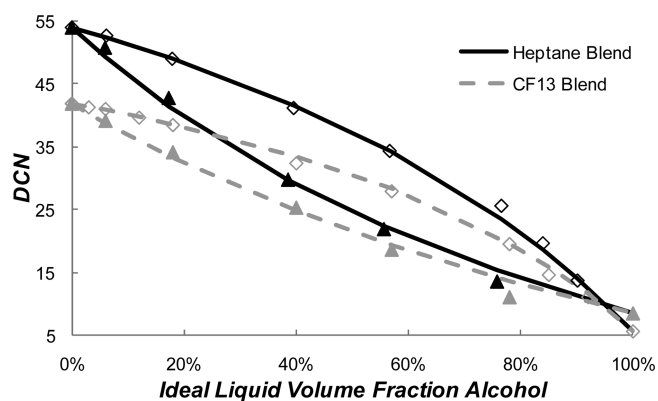
Figure 5. Comparison of one-parameter cetane model[30] to present experimental DCN measurements. Not all blend family comparisons are shown; those presented are the most deviant (in SSE sense) of all 10 blend families. Points are experimental measurements for *iso-* and *t*-butanol blends, and lines are model fits.
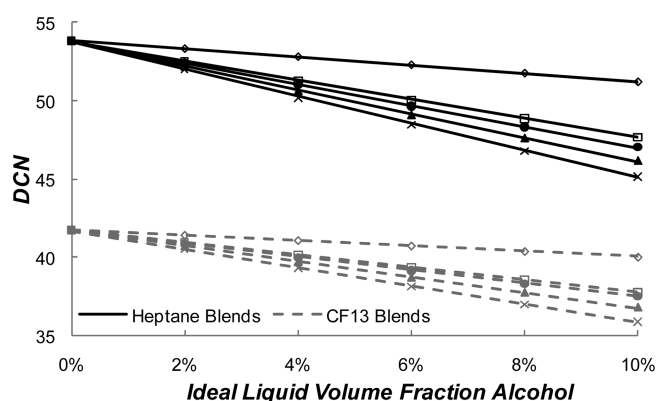
Figure 6. Modeled DCN dependence on volumetric blend fraction suggests little, quite linear, deterioration in ignition quality when small amounts of alcohol are blended into base fuels with diesel fuel-like reactivity. Lines are model results, with alcohol identity indicated as in Figure 1.

model fits the present data well. The rms error is <0.75 DCN over the present 63 ignition measurements, which is essentially within experimental precision. To our knowledge, this is the first validation of a simple cetane number model, and this model, in particular, for relatively low molecular weight alcohols. Its present predictive success suggests the model can be used for other molecules or molecular classes which fall generally outside of cetane number applications.

We employ our fit to the cetane number model to additionally examine behavior of alcohol-dilute alcohol/hydrocarbon blends. Figure 6 shows a slight and quite linear diminution of mixture DCN with increasing alcohol blend fraction (≤ 10 vol%) in both heptane and CF13 base fuels. Over this restricted blending range, *t*-butanol suppresses DCN by 0.17/0.28 units per volume percent when blended into CF13/heptane, ethanol suppresses DCN by 0.56/0.87 units per volume percent blended, and the other butanols suppress at an intermediate rate.

These results suggest that up to several volume percent of these alcohols, particularly *t*-butanol, could be blended into autoignitive fuels without significantly reducing the mixture reactivity. However, application-specific fuel specifications such as flashpoint, solubility, water extractability, and distillation characteristics would still need to be satisfied in these cases. Presently, such alcohol mixtures do not meet constraints of standard fuel oil applications, but as in the case of dimethyl ether[43] or biodiesel,[44] alternative applications may exist for these fuel blends in propulsion or stationary power generation.

Much of the recent interest in the butanols actually stems from their potential application in gasoline engine applications, where the relevant ignition quality metrics are the research and motor octane numbers (ONs). While ON and (derived) cetane number may be considered essentially inverse in nature, we caution against extrapolating the present DCN data for quantitative ON applications. At present, there are few if any studies on research or motor ON correlation to the DCN scale. Alcohol/heptane blends studied in the present work suggest future work with blends containing isooctane to better map ignition behavior in gasoline-like fuels.

4. CONCLUDING REMARKS

Derived cetane numbers (DCNs) of 63 binary mixtures of one of the four butanol isomers or ethanol with either *n*-heptane or CF13, a full-boiling range diesel fuel, have been measured using an ignition quality tester (IQT). These mixtures represent ten blend families of one of these five alcohols with one of two hydrocarbon base fuels. Both within and among blend families, the liquid phase properties and vapor—liquid equilibrium properties vary widely. However, careful consideration of comparative blend family reactivity and physical property trends showed that relative reactivity trends at similar mixture fraction are largely insensitive to physical property effects for the fuels considered in this study. In other words, DCN measurement is a suitable technique to study chemical influences on ignition when physical property effects are properly taken into account.

The present results showed very similar ignition behavior for all primary and secondary alcohol blend families, as well as similar behavior between the two *t*-butanol blend families. While as a pure component, *t*-butanol was found to be the least reactive of the butanol isomers in this study, as well as others, the *t*-butanol/base fuel blends were more reactive than the other alcohol/base fuel blends over most of the blending range. A simple ignition kinetic model, related to C—H bond strengths of the alcohols and base fuels, satisfactorily explains these features of the collected DCN measurements: (1) Radicals generated by low temperature chemistry (of heptane or CF13) abstract the relatively weak internal H atoms of the primary or secondary alcohols, effectively forming HO_2 from a more active radical. Not only does this reduce the rate of subsequent H atom abstractions but also it effectively diverts radicals from low temperature chemistry branching pathways into radical propagation. (2) Since *t*-butanol lacks relatively weak internal H atoms, it couples less with the low temperature chemistry of the hydrocarbon base fuel. Active radicals from this process, not scavenged by *t*-butanol, re-enter low temperature chemistry branching pathways, permitting faster growth of the radical pool. (3) In the absence of an active radical source (hydrocarbon low temperature chemistry), the weak internal C—H bonds of the primary and secondary alcohols enable faster development of the radical pool (hence, faster ignition) than the stronger C—H bonds in *t*-butanol.

The ability of DCN measurement to reveal a chemical mechanism of ignition in the present work suggests the utility

of this method in future studies. Moreover, the results and present interpretation indicate more fundamental investigation of alcohol combustion chemistry is warranted, especially studies of kinetic coupling of alcohols with a base fuel.

In addition to studying mechanistic ignition behavior, the present measurements have applied relevance. The one parameter cetane number model of Ghosh and Jaffe[30] quantitatively describes the present small alcohol data set well, which suggests it may have validity for other molecular classes or smaller molecules generally not considered in cetane number applications. Moreover, detailed DCN results are in accord with the physical interpretation of the global β parameters found in this work. Our fit to the model was used to determine mixture DCN sensitivity to small amounts of alcohol blending. Only a modest diminution in DCN resulted from blending up to 10 volume percent alcohol into the base hydrocarbon. This result may have implications for alternative fuel utilization, subject to additional application constraints.

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