Effects of methyl substitution on the autoignition of C16 alkanes

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Abstract.

The autoignition quality of diesel fuels, quantified by their Cetane Number or Derived Cetane Number (DCN), is a critical design property to consider when producing and upgrading synthetic paraffinic fuels. It is well known that autoignition characteristics of paraffinic fuels depend on their degree of methyl substitution. However, there remains a need to study the governing chemical functionalities contributing to such ignition characteristics, especially in the case of partially branched ones, which have not been studied in detail. In this work, the autoignition of 2,6,10-trimethyltridecane has been compared with the reference hydrocarbons used for cetane number determination, i.e. n-hexadecane and heptamethylnonane, all of them being C16 isomers. Results from a constant-volume combustion chamber under different pressure and temperature initial conditions showed that the ignition delay time for both cool flame and main combustion events increased less from n-hexadecane to trimethyltridecane than from trimethyltridecane to heptamethylnonane. Additional experimental results from blends of these hydrocarbons, together with kinetic modelling, showed that autoignition times and combustion rates were correlated to the concentration of the functional groups indicative of methyl substitution, although not in a linear manner. When the concentration of these functional groups decreased, the first stage OH radical concentration increased and ignition delay times decreased, whereas when their concentration increased, H₂O₂ production was slower and ignition was retarded. Contrary to the ignition delay times, DCN was correlated linearly with functional groups, thus homogenizing the range of values and clarifying the differences between fuels.

Keywords: Autoignition, combustion, biofuels, diesel engine, branched alkanes

1. Introduction

The expected decline in oil production, together with the increasing concerns on greenhouse gas emissions have encouraged legislative and regulatory proposals to replace petroleum fuels with those obtained from renewable or residual domestic sources. In the case of diesel automotive engines, three options are nowadays considered realistic alternatives to petroleum-diesel fuels, based on their economic viability and on their capability to replace petroleum-diesel in significant proportions without substantial engine modifications or re-
design. These alternative fuels include: biodiesel fuels (fatty acid methyl esters), hydrotreated vegetable oils (HVO) and Fischer-Tropsch (FT) diesel fuels, either derived from natural gas, lignocellulosic biomass, coal or wastes. Contrary to oxygenated biodiesel fuel, both HVO and FT fuels are non-oxygenated and mainly paraffinic in their chemical structure, which provides closer properties to those of petroleum diesel fuel. As a consequence, paraffinic fuels (e.g. HVO and FT) are not expected to find the same regulatory barriers for increasing concentrations in blended diesel fuels as biodiesel fuels have suffered. Both the European Normalization Committee (CEN) and the American Society for Testing and Materials (ASTM) have recently developed a Technical Specification (TS 15940) [1] and a Work Item (WK 23320) [2], respectively, as an initial step for setting quality standards for paraffinic fuels.

In the case of HVO fuels, the hydrotreating reaction conditions (mainly temperature and pressure) can be adjusted to modify the ratio iso-alkanes/n-alkanes [3]. In FT processes, the final proportion of n-alkanes is very high [4], particularly if cobalt and/or iron based catalysts are used. The primary products obtained from both processes have notoriously poor cold flow properties due to the large fraction of high carbon number n-alkanes. Therefore, upgrading processes like hydrocracking and hydroisomerization are required before fractionating to separate the naphtha fraction from the diesel fraction. This upgrading is selectively designed to reach an optimal compromise between cold-flow properties and autoignition quality in the diesel fraction. Analyses of paraffinic fuels have revealed varying fractions of n-alkanes versus iso-alkanes [5-8]. The autoignition quality of such paraffinic fuels is not only dependent on the ratio of n-alkanes to iso-alkanes or on the average carbon number, but also on the autoignition behaviour of each specific iso-alkane structure in the mixture.

The autoignition quality is quantified by Cetane Number (CN, measured in a CFR engine) or Derived Cetane Number (DCN, measured in a constant-volume combustion chamber). In both cases, n-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane are used as reference hydrocarbons, and they are assigned CN=100 and CN=15, respectively. The CN is determined for any given fuel by matching its autoignition delay time with that of a n-hexadecane/heptamethylnonane blend. A linear interpolation of percentage volume between 15 (CN for heptamethylnonane) and 100 (CN for n-hexadecane) is then applied to determine the fuel’s CN. C16 hydrocarbons (with sixteen carbon atoms) are used as reference hydrocarbons because they are liquid at ambient conditions, have enough lubricity to avoid excessive wear in engine pistons and injection systems, have acceptable cold flow properties, and their molecular weight is not far from the average of both commercial FT or HVO fuels.

There have been limited studies on the ignition characteristics of paraffins in the diesel range (i.e., C_{10}-C_{22} with average carbon number of 14 or 15 [9]). In 2011, Pitz and Mueller [9] reviewed prior fundamental research conducted on the combustion of n-alkanes and iso-alkanes in the diesel range. Notable autoignition studies in shock tubes and rapid compression machines include those on n-decane [10,11,12,13], n-dodecane [10,14,15], n-tetradecane [10], and n-hexadecane [16,17]. The autoignition of iso-alkanes in the diesel range has not been studied in detail. Oehlschlaeger et al. [18] studied the ignition of heptamethylnonane in a shock tube and presented a detailed chemical kinetic model developed by Lawrence Livermore National Laboratory. Recently, 2,7-dimethyloctane autoignition was studied in a shock tube by Li et al. [19]. These shock tube studies and others on various C7 isomers [20,21] and C8 isomers [22,23,24] have shown that increasing the number of methyl substitutions increases autoignition delay times, while the position of the methyl substitutions also affects ignition reactivity. In particular, the work by Westbrook and coworkers [20,21] on the nine isomers of heptane have related fuel molecular structure with the rate of important chain propagating and chain terminating reactions that control ignition. Recently, Kang et al [25] utilized a CFR engine to study the ignition of cycloparaffins with various degrees of branching, specifically ethylcyclohexane, 1,3-dimethylcyclohexane, and 1,2-dimethylcyclohexane. Their results
showed that increasing branching decreases ignition reactivity of cycloparaffins. They [26] also performed a similar study on disobutylene addition to n-heptane/iso-octane mixtures, demonstrating the combined effects of branching and unsaturation on reducing ignition reactivity.

The aforementioned shock tube and CFR studies focus entirely on the chemical kinetic contributions to autoignition, and do not study physical contributions (droplet formation, vaporization, mixing, etc.) on the autoignition of diesel fuel sprays. Bogin et al. [27] conducted a study on the ignition of n-hexadecane and heptamethylnonane fuel sprays in an ignition quality tester (IQT), demonstrating that the former is considerably more reactive than the latter. A series of diesel spray ignition studies with n-dodecane as a surrogate fuel have been conducted in a constant volume combustion vessel (CVCC) and made available by the Engine Combustion Network (ECN) [28,29] for the validation of high fidelity models [30-34]. Rabl et al. [35] performed experiments on a range n-hexadecane/heptamethylnonane mixtures in a constant volume spray combustion vessel. They demonstrated the relationship between burn duration and ignition delay time, showing that higher cetane mixtures undergo mainly diffusion combustion while lower cetane mixture undergo mainly premixed combustion.

Recently, Won et al. [36] studied the ignition of 2,6,10-trimethyldodecane in a shock tube and an IQT. In an effort to identify the functional groups controlling the low temperature autoignition, they identified model mixtures of n-dodecane/iso-octane and n-hexadecane/heptamethylnonane with similar IQT derived cetane numbers as 2,6,10-trimethyldodecane. Shock tube ignition delay time measurements for the three sets of fuels indicated that hexadecane/heptamethylnonane and 2,6,10-trimethyldodecane display similar low temperature reactivity, while the mixture of n-dodecane/iso-octane was more reactive at low temperature. Won et al. [36] concluded that fuels matching CH₂ (methylene) to CH₃ (methyl) ratio display similar low temperature reactivity under shock tube conditions. Heck et al. [37] also showed a correlation between a fuel’s ignition delay/cetane number and the ratio of primary to secondary H atoms in the molecule.

Further, knowledge about the autoignition behaviour of partially branched paraffins can provide useful guidelines for the optimization of the temperature of distillation cuts, the fractions subjected to hydroisomerization or hydrocracking, and the fraction of straight-run components to be blended with the processed fractions. This knowledge is also necessary to identify the main compositional characteristics governing the chemical kinetics of autoignition in both positive and negative temperature coefficient regimes. In this paper, 2,6,10-trimethyltridecane was selected for investigation because it has an intermediate number of methyl branches with respect to n-hexadecane and heptamethylnonane and the same number of carbon atoms, thereby allowing us to study the effects of branching independently from those of the carbon number. First, the autoignition and combustion of these three fuels are compared at different initial temperatures and pressures. Next, blends with different proportions of these fuels are studied at specific conditions. Finally, numerical combustion simulations of n-hexadecane and heptamethylnonane are performed to provide chemical kinetic insights into the experimentally observed trends.

2. Test fuels, blends and experimental conditions

2.1. Experimental equipment and procedure

The present experiments were conducted in a constant volume combustion chamber system (Cetane ID 510™ [38]). Details of the experimental layout and operational procedure are described elsewhere [39,40]. A dynamic pressure sensor positioned at the end of a passage to facilitate its cooling was used to measure the pressure in the main chamber. DCN is calculated from the pressure versus time history. DCN correlates with Cetane Number (CN) of
diesel fuels and diesel-like fuels. For an accurate DCN measurement, experiments must be conducted with synthetic dry air and at specific coolant temperature, injection pressure, injection duration, initial chamber temperature and initial chamber pressure. The instrument utilizes a common rail injector (Bosch part no. 0445110181) with 6 nozzles, each having an orifice inner diameter of 0.17 mm. A fresh charge of high pressure synthetic air (21 mol% ± 0.05% oxygen and 79 mol% ± 0.05% nitrogen) enters the combustion chamber at the start of each test. The fuel mass injected is determined from the injection duration; the synthetic air charge mass is obtained from the pressure, temperature and chamber volume after intake closure; and the global equivalence ratio is then calculated. After the introduction of the charge and prior to fuel injection, several criteria must be satisfied. Thermal equilibrium with the combustion chamber walls is permitted by waiting for approximately one minute. During this time the pressure of the air is also recorded with a static pressure transducer (Honeywell MLH), and pressure loss is constrained to less than 0.0075 bar/s to minimize chamber leakage. The coolant temperature, chamber wall temperature and chamber pressure are verified to be within close tolerances of the set values (± 2 ºC, ± 0.2 ºC ± 0.02 MPa, respectively). Subjected to satisfying these criteria, fuel charges are injected. From twenty injections, the first five are discarded to guarantee stable conditions, and the instrument records pressure vs time for fifteen injection events, from which standard deviations are obtained.

2.2. Experimental conditions and definition of parameters

All tests were made with 1000 bar injection pressure and with an injection duration of 2.5 ms. Despite the small tolerance, slight variations in air composition may require different calibration temperatures for DCN measurement.

Different autoignition parameters were defined to characterize the autoignition behaviour:

- \( ID_{cf} \) = Ignition delay for cool flames. Defined as the time from the start of injection to the onset of the initial pressure rise (associated with cool flame). This onset is determined as the time for which the chamber pressure exceeds the initial pressure plus 0.2 bar.
- \( ID_{mc} \) = Ignition delay for main combustion. Defined as the time from the start of injection to the onset of the main combustion stage. This onset is determined as the time where the slope of the pressure rate (from linking pressure rates at a half and a quarter of the combustion pressure rise) crosses the initial pressure baseline.
- \( CD \) = Combustion delay. Defined as the time from the start of injection to the midpoint of the combustion pressure rise.

Derived cetane number is obtained from \( ID_{cf} \) and \( CD \) using the correlation described in [40].

2.3. Combustion diagnostic

A diagnostic model was developed [41] to analyze the results obtained from the dynamic pressure sensor located at the constant volume reactor. This model considers the change in the thermodynamic properties of the gaseous mixture due to combustion and includes a heat transfer submodel. The sampling frequency of the dynamic pressure data is 25 kHz, which is high enough to analyze the combustion characteristics of the fuels. The results delivered are the mean temperature at the combustion chamber, the heat release rate and the cumulative heat release.

2.4. Test fuels

Samples of n-hexadecane (abbreviated as n-H) and 2,2,4,4,6,8,8-heptamethylnonane (abbreviated as HMN) were purchased from Sigma Aldrich, and 2,6,10-trimethyltridecane (abbreviated as TMT) was purchased from ChemSampCo (Dallas, Texas, USA). Some of the prop-
erties of these samples, listed in Table 1, are useful to interpret the autoignition results. Theoretical and estimated properties of the pure hydrocarbons tested are shown in Table 2. Critical temperatures and critical pressures were calculated for each hydrocarbon from Joback’s group contribution method [42], while boiling temperatures were obtained from [43]. From the critical parameters, the acentric factor was also obtained from Lee and Kesler correlations for vapor pressure. Using the corresponding-state correlation proposed by Pitzer [42], the enthalpy of vaporization at standard conditions was then estimated. Enthalpies of formation at standard conditions were estimated with the Benson’s Group contribution method [44]. The lower heating value was obtained for each liquid fuel by substracting the enthalpy of vaporization from the enthalpy of formation and solving the enthalpy balance between products and reactants at standard gas phase conditions. Finally, the higher heating value was determined by adding the heat release derived from the condensation of the water in the burnt products, and a good agreement with the measured value was obtained. Densities and heating values were used as input data in the diagnostic model described above.

![Figure 1. Fuels tested in this study](image)

Table 1. Measured properties of the pure tested fuels

<table>
<thead>
<tr>
<th>Properties</th>
<th>Method</th>
<th>n-hexadecane</th>
<th>trimethyltridecane</th>
<th>heptamethylnonane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity (% v/v)</td>
<td></td>
<td>≥ 99</td>
<td>≥ 95</td>
<td>≥ 99</td>
</tr>
<tr>
<td>Density at 15°C (kg/m³)</td>
<td>EN ISO 12185</td>
<td>0.777</td>
<td>0.770</td>
<td>0.793</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C (cSt)</td>
<td>EN ISO 3104</td>
<td>2.848</td>
<td>3.087</td>
<td></td>
</tr>
<tr>
<td>Higher heating value (MJ/kg)</td>
<td>UNE 51123</td>
<td>47.45</td>
<td>47.23</td>
<td>46.89</td>
</tr>
<tr>
<td>Lubricity (µm corrected wear scar)</td>
<td>EN ISO 12156</td>
<td>572.91</td>
<td>569.63</td>
<td>567.15</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>ASTM D7668</td>
<td>100 a</td>
<td>60.85</td>
<td>15 a</td>
</tr>
<tr>
<td>Boiling temperature (ºC)</td>
<td></td>
<td>286.6</td>
<td>266.9</td>
<td>240.0</td>
</tr>
</tbody>
</table>

* a: calibration of the Cetane ID510 combustion chamber was made with blends of n-hexadecane and heptamethylnonane.

Table 2. Theoretical and estimated properties of the pure tested fuels

<table>
<thead>
<tr>
<th>Properties</th>
<th>n-hexadecane</th>
<th>trimethyltridecane</th>
<th>heptamethylnonane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₁₆H₃₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight (kg/kmol)</td>
<td>226.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stoichiometric air/fuel ratio</td>
<td>14.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of branches</td>
<td>0</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td>Standard enthalpy of vaporization (kJ/kg)</td>
<td>226.9</td>
<td>220.0</td>
<td>208.8</td>
</tr>
<tr>
<td>[CH₃] groups</td>
<td>2</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>[CH₂] groups</td>
<td>14</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>[CH] groups</td>
<td>0</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>
The experimental matrix is composed of two parts: In the first part, 24 tests were made for each pure hydrocarbon at three initial chamber pressures (21, 11 and 6 bar) and eight initial chamber temperatures (535, 550, 570, 590, calibration temperature, 610, 630 and 650 ºC). Calibration temperatures were 600.5ºC for n-hexadecane, 598.5ºC for trimethyltridecane and 595.5ºC for heptamethylnonane. The equivalence ratios corresponding to each test are listed in Table 3.

The second part of the test matrix is composed of eight tests, all of them carried out at the calibration conditions (21 bar and calibration temperature). Apart from the three tests for pure hydrocarbons (taken from the first part), five additional tests were made on selected blends. The composition of these blends, the test conditions and the equivalence ratios are shown in Table 4, together with the mean chemical characteristics of the blends tested, including the methylene to methyl ratios proposed by Won et al [37] and the number of methyl substituions.

The selection of the blends tested was made based on the following criteria:

- Tests 1, 5 and 6: pure compounds, at calibration conditions.
- Test 2: Blend of n-H/HMN with identical ([CH\_2]/[CH\_3]).([CH\_2]+[CH\_3]) as TMT. This ratio was proposed by Won et al. [37] as a key parameter controlling the autoignition kinetics of paraffins.
- Test 3: Blend of n-H/HMN with identical ([CH\_2]/[CH\_3]) as TMT. This ratio was also proposed by Won et al. [37] as another potential governing parameter.
- Test 4: Blend of n-H/HMN with identical average number of branches as TMT.
- Test 7: Blend of n-H/TMT with equivalent mole or mass fractions for both components. This blend was selected to extend the range between intermediate and high cetane numbers.
- Test 8: Blend of HMN/TMT with equivalent mole or mass fractions for both components. This blend was selected to extend the range between low and intermediate cetane numbers.

Table 3. Equivalence ratios for the first part of the experimental matrix.

<table>
<thead>
<tr>
<th>Test nº</th>
<th>Hydrocarbon</th>
<th>p (bar)</th>
<th>Chamber conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>p (bar)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>535</td>
</tr>
<tr>
<td>1-8</td>
<td>n-hexadecane</td>
<td>21</td>
<td>0.367</td>
</tr>
<tr>
<td>9-16</td>
<td></td>
<td>11</td>
<td>0.701</td>
</tr>
<tr>
<td>25-32</td>
<td>Trimethyltridecane</td>
<td>21</td>
<td>0.364</td>
</tr>
<tr>
<td>33-39</td>
<td></td>
<td>11</td>
<td>0.695</td>
</tr>
<tr>
<td>40-46</td>
<td></td>
<td>6</td>
<td>1.275</td>
</tr>
<tr>
<td>47-54</td>
<td>Heptamethylnonane</td>
<td>21</td>
<td>0.375</td>
</tr>
<tr>
<td>55-62</td>
<td></td>
<td>11</td>
<td>0.715</td>
</tr>
<tr>
<td>63-70</td>
<td></td>
<td>6</td>
<td>1.311</td>
</tr>
</tbody>
</table>
Table 4. Definition of the test matrix (second part) with description of the chemical characteristics of the blends.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Volume fraction</th>
<th>Mole and mass fraction</th>
<th>Chamber conditions</th>
<th>Equivalence ratio</th>
<th>Number of groups</th>
<th>Mass ratios proposed by Won et al. [37]</th>
<th>N° branches</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-H</td>
<td>TMT</td>
<td>HMN</td>
<td>n-H</td>
<td>TMT</td>
<td>HMN</td>
<td>p (bar)</td>
</tr>
<tr>
<td>B1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>B2</td>
<td>0.491</td>
<td>0</td>
<td>0.509</td>
<td>0.486</td>
<td>0</td>
<td>0.514</td>
<td>21</td>
</tr>
<tr>
<td>B3</td>
<td>0.519</td>
<td>0</td>
<td>0.481</td>
<td>0.514</td>
<td>0</td>
<td>0.486</td>
<td>21</td>
</tr>
<tr>
<td>B4</td>
<td>0.576</td>
<td>0</td>
<td>0.424</td>
<td>0.571</td>
<td>0</td>
<td>0.429</td>
<td>21</td>
</tr>
<tr>
<td>B5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>B6</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>B7</td>
<td>0.498</td>
<td>0.502</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>21</td>
</tr>
<tr>
<td>B8</td>
<td>0</td>
<td>0.507</td>
<td>0.493</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>21</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Results from pure hydrocarbons

Pressure signals directly obtained from the combustion chamber for the three tested hydrocarbons are shown in Figure 2 for the three tested initial pressures and for an initial temperature of 590°C, as an example. As expected, n-H has the shortest ignition delay time followed by TMT and then HMN. However, the delay times are far from being inversely proportional to the cetane numbers (see Table 1): the ignition delay of TMT is much closer to that of n-H than to that of HMN. As shown in Table 1, the physical properties for the three fuels are similar (e.g., density, viscosity, etc.) due to their identical molecular formula. The trends in observed differences in ignition delay time cannot be attributed solely to differences in physical properties. Most notably, HMN has the lowest boiling point so it would vaporize and enter the gas-phase faster than the other C16 isomers, thereby having the shortest physical delay time. Thus, the differences that chemical structure and functionality impart on chemical kinetic reactivity are primarily responsible for controlling their overall ignitability.

It can be observed that pressure peaks are significantly lower for n-hexadecane than for the other two isomers, because slower autoignition delay time results in a merging of combustion with spray development, thereby hindering the mixing process and reducing the combustion rate in the final ignition stage. The differences in peak pressure decrease when the initial pressure decreases, because increased autoignition delay time results in more premixed combustion. This trend can be better observed from heat release rates obtained from the diagnostic model, as shown in Figure 3. Integrated values of heat release along time (not shown here) confirm that slower combustion did not lead to reduced heat release (indicative of incomplete combustion). Another interesting observation from both Figures 2 and 3 is that heptamethylene nonane has the slowest combustion rate despite being completely premixed. Two reasons can explain this trend: one is related to the reduced chemical reactivity of heptamethylene nonane, as will be discussed later in section 3.4. The other is related to the longer ignition delay time for heptamethylene nonane, which, in the case of high chamber pressures, leads to a leaner mixture and thus to slower kinetics, as pointed out by Rabl et al. [35].
Figure 2. Measured chamber pressure for all tested hydrocarbons and three initial pressures and 590°C as initial temperature.

Figure 3. Heat release rates for all tested hydrocarbons at three initial pressures and 590°C as initial temperature.

The autoignition parameters defined in Section 2.2 are shown in Figures 4, 5, and 6. From these results, it can be concluded that autoignition time of trimethyltridecane is much closer to that of n-hexadecane than that of heptamethylnonane at all chamber pressure and temperature conditions.

As shown in Table 3, the high chamber pressure experiments are at globally lean conditions (equivalence ratios around 0.4), while those at intermediate pressure are at equivalence ratios around 0.8, and those at low pressure are at rich conditions (around 1.4). The chamber temperature also affects the equivalence ratio albeit to a lower extent. This implies that at high pressure conditions, combustion products are diluted in excess air if ignition delay times are sufficiently long, whereas at low pressure, combustion was incomplete regardless of the ignition delay times. Note, the error bars in Figures 4, 5, and 6 indicate that results are more stable and repeatable for n-hexadecane and trimethyltridecane than for heptamethylnonane.

As indicated in Figure 4, cool-flame heat release was visible in all cases except for n-hexadecane at 21 bar and the highest temperatures (630°C and 650°C) and for heptamethylnonane at 6 bar and high temperature. For n-H at high pressure and high temperature, the main combustion event is very fast, so the cool-flame heat release period is very short and not prominent, while for HMN at low pressure and high temperature, cool-flame chemistry is not prominent compared to the high temperature chemistry. Although inferred from all the parameters displayed (Figures 4, 5, and 6), the ignition delay of the main combustion (Figure 5) shows that, at high pressure conditions (21 bar, left panel), only heptamethylnonane presents a negative temperature coefficient (NTC) region. At medium pressure (11 bar, central panel), an NTC region can be observed for heptamethylnonane and (slightly) for trimethyltridecane. At
low pressure (6 bar, right panel), the NTC region can be observed for all fuels, especially at lower temperature and increased methyl branching.

The effect of pressure on low temperature chemical kinetics can explain the decreasing NTC behaviour with increasing pressure. Studies by Villano et al. [45,46] have shown that RO₂ radicals are more stable and produced in higher concentrations as pressure increases. RO₂ radicals are the first intermediate in low temperature chain branching leading to ignition, so an increase in their concentration decreases ignition delay times. The dissociation of RO₂ back to R+O₂ decreases overall reactivity and is the primary reason for NTC phenomenon, and thus, decreasing pressure increases NTC.

Figure 4. Ignition delay for cool flame, for n-hexadecane, trimethyltridecane and heptamethylnonane at different chamber pressures and temperatures.

Figure 5. Ignition delay for main combustion stage, for n-hexadecane, trimethyltridecane and heptamethylnonane at different chamber pressures and temperatures.

Figure 6. Combustion delay, for n-hexadecane, trimethyltridecane and heptamethylnonane at different chamber pressures and temperatures.
3.2. Results from blends

Figure 7 shows the average pressure and heat release rate (HRR) signals for each blend tested, including pure hydrocarbons. The horizontal axis is broken to include heptamethylnonane because its ignition delay time is much longer. It can be observed that, among the HMN/n-H blends (B2, B3 and B4), increasing n-H content advances combustion and shortens HRR peak. Pure trimethyltridecane shows the largest HRR peak while pure HMN shows the smallest. Combustion for the blend n-H/TMT (B7) falls between those of its pure components with intermediate heat release rate peak. Finally, the blend HMN/TMT (B8) is considerably delayed and reduces the heat release peak to the same intensity as n-hexadecane.

Figure 7. Chamber pressure files and heat release rate for all tested blends, at calibration initial conditions. Mole fractions are displayed in legends.

Numerical results are listed in Table 5. Apart from ignition and combustion delays, DCN results are also included, since these tests were all made under calibration conditions. From these results it is easy to conclude that none of the parameters proposed by Won et al [37] correlates linearly with any of the ignition delays or with DCN. As noted above, the autoignition kinetics is only slightly slower for trimethyltridecane compared to n-hexadecane but it is in both cases much faster than heptamethylnonane. This is unexpected given the DCN values, which are evenly spaced (100, 61 and 15). However, all autoignition parameters are approximately similar when the ratios defined from functional groups are similar (compare, for example, results from tests 2, 3 with those from test 6), and roughly similar when the number of branches is similar (compare tests 4 and 6). This confirms that the chemical structure has a direct effect on the autoignition kinetics.

Table 5. Experimental results for $ID_{cf}$, $ID_{m}$, CD, including standard deviations (ms), and DCN.

<table>
<thead>
<tr>
<th>Blend</th>
<th>$ID_{cf}$</th>
<th>SD ($ID_{cf}$)</th>
<th>$ID_{m}$</th>
<th>SD ($ID_{m}$)</th>
<th>CD</th>
<th>SD (CD)</th>
<th>DCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>7.1136</td>
<td>0.1552</td>
<td>85.3695</td>
<td>3.8537</td>
<td>91.5056</td>
<td>3.3482</td>
<td>15.00</td>
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<tr>
<td>B2</td>
<td>2.0505</td>
<td>0.0361</td>
<td>3.1193</td>
<td>0.0571</td>
<td>3.4497</td>
<td>0.0433</td>
<td>59.68</td>
</tr>
<tr>
<td>B3</td>
<td>2.0006</td>
<td>0.0199</td>
<td>3.0414</td>
<td>0.0418</td>
<td>3.3414</td>
<td>0.0355</td>
<td>61.71</td>
</tr>
<tr>
<td>B4</td>
<td>1.8639</td>
<td>0.0356</td>
<td>2.8445</td>
<td>0.0522</td>
<td>3.0522</td>
<td>0.0462</td>
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<tr>
<td>B5</td>
<td>1.613</td>
<td>0.0429</td>
<td>1.9882</td>
<td>0.0687</td>
<td>2.3934</td>
<td>0.0279</td>
<td>100.00</td>
</tr>
<tr>
<td>B6</td>
<td>1.9824</td>
<td>0.0319</td>
<td>3.0846</td>
<td>0.0315</td>
<td>3.3764</td>
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<tr>
<td>B7</td>
<td>1.718</td>
<td>0.0291</td>
<td>2.3811</td>
<td>0.0499</td>
<td>2.6836</td>
<td>0.0431</td>
<td>81.75</td>
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</table>
3.3. Chemical kinetics discussion

The experimental results presented in this work are controlled by both physical and chemical kinetic fuel properties. As mentioned previously, all the fuels studied herein have similar physical properties, so differences in chemical kinetics can help to understand the effects of molecular structure on ignition and burn rate. To this end, 0-D homogeneous constant-volume simulations of fuel/air ignition delay were conducted to understand the mechanisms leading to the differences observed not only autoignition time but also in combustion rate between HMN and n-H. The simulations were performed at 21 bar, 590°C and equivalence ratio (phi) of 0.4 using CANTERA software [47,48], implemented on CLOUDFLAME [49,50] with the established chemical kinetic models from LLNL [18,51]. n-H, HMN, and their binary blends (Blends 1-5) were simulated with their actual mole fractions. Blends 6-8 comprise TMT for which a chemical kinetic model is not available. However, the experimental work shows that the \( \text{CH}_2/\text{CH}_3 \) functional group parameter proposed by Won et al [37] accurately matches the reactivity of TMT (compare Blend 3 and Blend 6 in Table 5). Thus, mixtures of n-H and HMN were formulated to match the \( \text{CH}_2/\text{CH}_3 \) mass ratio of the HMN/TMT blends 7 (i.e., 0.765 n-H / 0.235 HMN) and 8 (i.e., 0.247 n-H / 0.753 HMN) for their simulation.

As mentioned above, heptamethylnonane has the slowest combustion rate despite being completely premixed. The simulation results presented in Figure 8 indicate that n-H displays prominent two-stage combustion with the pressure rising rapidly soon after the first-stage heat release. n-H is highly reactive in the low temperature regime because the large number of secondary C-H sites (14 in total) have easily abstractable H-atoms, permitting rapid low temperature isomerization reactions that accelerate radical chain branching and ignition [22,51]. Simulations of blend 3, which is used to represent TMT (blend 6), also show minor first heat release followed by the main ignition event. On the other hand, HMN has much longer ignition delay time without a prominent two-stage characteristic. A slower rise in pressure is observed prior to the main ignition due to the slower rate of radical build up and heat release. HMN has 9 primary C-H sites that have H-atoms that are harder to abstract, slowing down the rate of fuel oxidation at both low and high temperatures. Therefore, even when a critical pool of radical (e.g. OH, HO\(_2\), etc.) have been formed, the main ignition is slowed in HMN because of slower fuel oxidation rates at the hot ignition temperature.

| B8 | 2.5179 | 0.0363 | 4.8472 | 0.1078 | 5.432 | 0.1070 | 41.77 |

Figure 8. Homogeneous batch reactor simulations of heat release rates and pressure for n-H, HMN, and Blend 3 (0.514 n-H / 0.486 HMN) at 21 bar, 599 °C, and phi=0.4
The effects of molecular structure on chemical kinetic reactivity is further clarified in Figure 9, which shows OH concentration at the 1st stage ignition regime and overall H$_2$O$_2$ concentration and temperature for each of the blends. Won et al. [37] have shown that the maximum OH mole fraction in the 1st stage regime correlates with ignition delay time and DCN of various n-alkane/iso-alkane mixtures. The present simulations confirm this trend, showing that n-H has the largest 1st stage OH concentration, followed by decreasing 1st stage OH concentration as the blends CH$_2$/CH$_3$ mass ratio decreases. HMN does not produce any OH in the 1st stage due to the inability to undergo RO$_2$=QOOH isomerization reactions. Blend 8 with 0.753 HMN shows a small 1st stage OH peak, which is attributed to the small amount of n-H in the mixture.

The overall H$_2$O$_2$ concentration profiles and temperature profiles in Figure 9 can be used to understand the effects of molecular structure on combustion rate. As presented by Westbrook, the second stage ignition event occurs due to the buildup of and subsequent H$_2$O$_2$ decomposition to 2 OH radicals at around 950-1000 K [52]. n-H has the shortest combustion rate because it rapidly populates the H$_2$O$_2$ pool and reaches the decomposition temperature. As the ignition delay time increases with decreasing CH$_2$/CH$_3$ mass ratio, the H$_2$O$_2$ buildup is slowed and the combustion rate at the main ignition event is retarded. H$_2$O$_2$ is primarily produced via fuel H-atom abstraction by HO$_2$ radicals; increasing the number of CH$_3$ groups slows down this abstraction rate, the rate of H$_2$O$_2$ production, and the combustion rate.
3.4. Functional group relationship

To check which of the functional groups provide the best correlations with $ID_{cf}$, $ID_m$, $CD$ and $DCN$, a general equation was formulated to see the dependence of each “parameter” on the mole fraction of each functional, as follows:

$$\text{Parameter} = A + B \cdot [\text{CH}_2] + C \cdot [\text{CH}_3] + D \cdot [\text{CH}] + E \cdot [\text{C}]$$  (1)

A regression analysis was performed to determine the values of the exponents that offer best estimation of the dependent parameter. When a functional group’s exponent was close to zero, the corresponding term was eliminated to simplify the correlation as much as possible. When the exponents were close to unity, the exponent was removed. The following optimal correlations for the calculation of the parameters (shown in Figure 10 in front of measured parameters) were found by maximizing the coefficients of determination $R^2$ (also displayed in the figure):

- $ID_{cf} = 1.548 + 0.075 \cdot [\text{CH}]^{0.758} + 0.462 \cdot [\text{C}]^{0.524}$  (2)
- $ID_m = 1.849 + 0.273 \cdot [\text{CH}]^{0.592} + 1.266 \cdot [\text{C}]^{0.019}$  (3)
- $CD = 2.132 + 0.257 \cdot [\text{CH}]^{0.704} + 1.366 \cdot [\text{C}]^{0.029}$  (4)
- $DCN = 7.39 \cdot [\text{CH}_2] - 2.27 \cdot [\text{C}]$  (5)

It must be pointed out that these correlations are useful to explain the effect of methyl substitution on autoignition only when the carbon number remains unchanged. In case of extending these correlations to different carbon numbers, the correlations would require including the effect of [CH$_2$] group.

From these correlations it can be concluded that correlations for autoignition/combustion delays are not linear and require exponents. The correlations can better fit when groups specifically associated with methyl substitutions are used (such as [CH] and [C]) rather than when non-specific groups (present in any paraffin) are used (such as [CH$_3$] and [CH$_2$]). This suggests that different blends of n-H and HMN with matching ratios of [CH] and [C] groups would simulate the autoignition of intermediately branched isomers as accurately or even more accurately than blends with matching ratios of [CH$_2$] and [CH$_3$] groups.
Also, it can be observed from equations (3) and (4) that correlations for $ID_{m}$ and $CD$ are very similar, which is explained because the contribution of the combustion rate to $CD$ is minor compared to that of autoignition time. Correlations for $ID_{m}$ and $ID_{cf}$ reveal that fully substituted carbon atoms ([C] groups) have a greater effect on increasing the main autoignition time than the cool-flame autoignition time, as indicated by larger exponent in the former.

The $DCN$ could be correlated with [CH] and [C] groups (since it is derived from $ID_{cf}$ and $CD$). However, the best correlation was found with [CH$_2$] and [C] groups, and it was linear. Consequently, the $DCN$ definition (and thus cetane number in general) is useful to linearize the relation with functional groups and homogenize the range of values, contributing to clarify the differences between fuels.

Figure 10. Optimal correlations found to simulate ignition and combustion delays and derived cetane numbers from functional groups.

4. Conclusion

This work investigated the ignition of three C$_{16}$H$_{34}$ isomers (n-hexadecane, 2,6,10-trimethyltridecane, and 2,2,4,4,6,8,8-heptamethylnonane) in a spray chamber at varying chamber pressures and temperatures. Both cool flame and main ignition characteristics were observed at most conditions, and these features were utilized to obtain derived cetane numbers. The experimental results show that ignition delay times increased with decreasing pressure and temperature and with increasing number of methyl branches. Combustion rate was maximum for trimethyltridecane and minimum for heptamethylnonane, as a consequence of the compromise between the kinetic effect, which enhances the combustion rate with increasing branching, and the mixing effect, which slows down combustion when fuel is not sufficiently premixed. To further assess the effect of functional groups on ignition and combustion rate, 8 mixtures with varying C$_{16}$H$_{34}$ compositions were studied at a fixed temperature and pressure condition. It was observed that mixtures with matching CH$_2$/CH$_3$ mass ratios dis-
played nearly identical ignition delay time, suggesting that this can be considered as a governing parameter for autoignition of large alkanes.

The experimental observation of a CH$_2$/CH$_3$ governing parameter justified chemical kinetics simulations of all mixtures using “CH$_2$/CH$_3$-equivalent” mixtures of n-hexadecane and 2,2,4,4,6,8,8,-heptamethylnonane. The simulations qualitatively reproduced the observed trends in ignition delay times and combustion, and thus were used for kinetic insight. It was shown that ignition delay decreases and 1st stage OH concentration increases as the blends CH$_2$/CH$_3$ mass ratio increases. Furthermore, as ignition delay time increases with decreasing CH$_2$/CH$_3$ mass ratio, the combustion rate at the main ignition event is retarded due to slower buildup of H$_2$O$_2$.

Finally, a regression analysis was performed to identify which functional groups are best descriptors for ignition delay time and $DCN$. It was shown that CH and C functionalities are the best predictor of ignition delay times, albeit the fitting relationship was non-linear. For prediction of $DCN$, CH$_2$ and C functionalities provided a linear correlation across the entire range of values.

The results and analysis presented in this work are of relevance to the fuel industry and to the combustion chemists. To the former, the experimental results and correlations presented herein provide needed guidance on the molecular design of paraffinic fuels for diesel spray combustors. For the latter, fundamental insights on the effects of molecular structure on ignition and the underlying governing functionalities create opportunities for simplifying kinetic models. Nevertheless, it must be noted that our conclusions are specific to the experimental conditions and fuels studies herein. Further work is required to determine if such simplifications can be applied to other fuel isomers and experimental conditions.

5. Acknowledgements

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6. References


