



# Correlations among thermophysical properties, ignition quality, volatility, chemical composition, and kinematic viscosity of petroleum distillates



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## HIGHLIGHTS

- Thermophysical properties,  $dn/dT$  and  $D$ , are correlated with other distillate properties.
- PLS analysis of Raman spectra shows that molecular components affect  $-dn/dT$  values.
- $dn/dT$  and  $D$  exhibit considerable promise as fuel quality indicators.

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## ABSTRACT

Thermophysical measurements and Raman spectroscopy were utilized to investigate 17 hydrocarbon distillates derived from Canadian oil sands in this work. Thermal lens and optical interferometer techniques were used to determine the thermal diffusivity ( $D$ ) and temperature coefficient of the refractive index ( $dn/dT$ ), respectively. It was found that  $D$  and  $dn/dT$  are closely correlated with the cetane numbers, distillation temperatures, monocyclic aromatics contents, and kinematic viscosities of the fuels. Raman spectra yielded information on the chemical compositions of the distillates, with aromatic contents proving to be particularly relevant. Multivariate analysis elucidated the relationships among the samples, their properties according to ASTM analyses, and the influence of composition on  $D$  and  $dn/dT$ .

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## 1. Introduction

The reduction of greenhouse gas and criteria air contaminant emissions is an important goal of research into transportation fuel production and advanced combustion technology for internal combustion engines. While compression ignition (diesel) engines offer the advantage of lower CO<sub>2</sub> emission levels as compared with

spark-ignited engines, diesel engines emit higher levels of criteria air contaminants such as nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM) [1]. Low temperature combustion processes, e.g., Homogeneous Charge Compression Ignition (HCCI), Premixed Charge Compression Ignition (PCCI), and Partially Premixed Compression Ignition (PPCI), have been studied in the attempt to improve engine efficiency and attain ultra-low NO<sub>x</sub> and PM emissions [1,2].

Previous work has shown that physical and chemical properties of fuels play an important role in advanced combustion. For example, fuels with low cetane number (CN) and appropriate chemical composition (e.g., aromatic content) can improve HCCI engine performance [1–3]. The 90% distillation temperature (T90) also

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plays a significant role in HCCI combustion of diesel fuels with regard to fuel conversion efficiency and emissions [3].

Ignition quality (e.g., CN), volatility (e.g., T90), and aromatic content are key properties of diesel fuels for HCCI combustion [1]. However, characterization of these properties is not simple. For example, determination of CN for a diesel fuel entails the use of a Cooperative Fuel Research Engine under standard test conditions (ASTM D613). This analysis is time-consuming, requires large sample volumes (~1 L), and its reproducibility is low (~3–5 CN values) [4]. Cetane number and cetane index are conventionally reported only for middle distillate fuels, rather than the heavier streams analyzed in this work. Thus advanced combustion engines may benefit from novel methods to measure fuel quality.

Infrared spectroscopy and photothermal techniques were used to characterize gasoline obtained from various sources in earlier work. Specifically, infrared spectroscopy was employed to analyze the hydrocarbon constituents [5–8]. Shen et al. [9] studied the evaporation kinetics of three grades of gasoline using the thermal-wave resonant cavity (also known as thermal wave interferometer) technique to measure the thermal diffusivities of the saturated vapors in air. The results showed that thermal diffusivities can be used to distinguish among different gasoline grades. This capability probably arises from the clear correlation between the thermal diffusivity and motor octane number of these fuels that was identified by Vargas et al. [10,11].

Generalizing from the results obtained for gasoline, it seems likely that thermophysical properties are also related to distillate fuel quality. Seventeen oil sands-derived distillate streams were characterized in the current investigation. Two feeds to a distillate hydrocracker-based refinery were examined. In one case, the feed was a blended crude oil formed by coking technologies; in the other, the feed was a crude oil formed by residue hydrocracking. The refinery streams were selected such that coker-based and hydrocracker-based primary (or residue) upgrading could be compared. Thermal lens measurements yielded thermal diffusivity values for these hydrocarbon distillates. Temperature coefficients of the refractive index were determined using an optical interferometer system. Raman spectroscopy provided information on aromatics contents and chemical composition. Principal component analysis elucidated the relations among the 17 distillate streams, as well as those among the ten physicochemical properties measured for the samples. Several significant correlations involving the thermophysical properties, ignition quality, volatility, and chemical compositions of these fuels were identified. The temperature coefficient of the refractive index generally exhibits better correlations than those observed for the thermal diffusivity.

## 2. Experimental

### 2.1. Samples

Seventeen hydrocarbon distillates, previously characterized in an HCCI combustion study [2], were analyzed in this work. These samples, derived from Canadian oil sand, represent a variety of processing options and blending strategies. In this investigation, a number of refinery streams were sampled with two different feeds to the refinery. One feed was an upgraded crude oil derived from coking/hydrotreating operations, while the second originated from an ebullated-bed hydrocracker. The hydrocarbon stream types, as well as their boiling point ranges, are summarized in Table 1. An upgrading/refining block diagram is included in Supplementary Material. Two samples – one from coker feed and another from hydrocracker feed – were associated with each of eight different refinery streams. An additional diesel fuel, stream 9, was derived only from coker feed.

**Table 1**

Hydrocarbon streams analyzed in this work. Boiling point ranges (initial–final) measured by ASTM test method D86 are given in °C.

Hydrocarbon stream	Label	Hydrocracker feed	Coker feed
Straight-run heavy gas oil	1	189.4–377.6	180.6–376.6
Straight-run light gas oil	2	171.0–295.7	173.6–296.8
Hydrocracker heavy gas oil	3	212.8–410.1	230.0–351.9
Hydrocracker light gas oil	4	206.9–305.1	214.7–305.4
Hydrotreater feed	5	170.1–368.8	172.6–333.4
Hydrotreater product	6	178.0–367.7	170.8–334.2
Jet fuel	7	155.9–247.8	164.1–252.4
Diesel fuel A	8	170.8–365.2	165.2–361.1
Diesel fuel B	9		176.2–354.3

### 2.2. Chemical and physical properties

Selected chemical and physical properties of the 17 refinery streams were determined using the American Society for Testing and Materials (ASTM) methods shown in Table 2. Results of both standard and advanced characterization analyses will be discussed in a separate publication.

### 2.3. Thermophysical measurements

Thermal diffusivities of the samples were determined at room temperature using the thermal lens experimental apparatus described in Ref. [12]. Each sample was contained in a 5-mm quartz cuvette. The time-resolved thermal lens signal was fitted to the equation

$$I(t) = I(0) \left[ 1 - \frac{\theta}{2} \tan^{-1} \left( \frac{2mV}{[(1+2m)^2 + V^2](t_c/2t) + 1 + 2m + V^2} \right) \right]^2, \quad (1)$$

yielding results for  $\theta$  and the thermal diffusivity ( $D$ ) of the fuel sample [12,13]. In Eq. (1),  $I(t)$  is the time-dependent intensity of the probe laser beam at the detector;  $I(0)$  is the initial value of this intensity.  $\theta$  is related to the thermally induced phase shift of the probe beam after it passes through the sample.  $V = Z_1/Z_c$  when  $Z_2 \gg Z_c$ , where  $Z_c$  is the confocal distance of the probe beam and  $Z_1$  is the distance from the probe beam waist to the sample.  $Z_2$  is the distance between the sample and photodetector.  $t_c = \omega_e^2/(4D)$  is the characteristic thermal time constant of the sample, where  $\omega_e$  is the spot size of the excitation laser in the sample.  $m = (\omega_{1p}/\omega_e)^2$  quantifies the degree of mode-mismatch of the probe and excitation laser beams, while  $\omega_{1p}$  is the probe-beam radius at the sample position. The quantities  $V$  and  $m$  were measured experimentally.

Unusual time-resolved thermal lens signals were observed for most of the hydrocarbon distillates. These signals, which resemble those for edible oil samples [14], were probably due to unwanted photochemical reactions induced by the excitation laser [12]. To minimize the effect of these reactions on the measured thermal diffusivity values, a short-time least-squares curve fitting algorithm was employed using software Mathematica; the curve-fitted period for the time-resolved thermal lens signal was much smaller than the photochemical reaction time [12].

Temperature coefficients of the refractive index ( $dn/dT$ ) for the hydrocarbons were measured using an optical interferometer system. In this method the sample is uniformly irradiated by a weak 632.8-nm He–Ne laser. Reflections from both inner surfaces of the cuvette interfere to create fringes. A slow uniform variation of the sample temperature was induced by use of a heating device, causing the fringes to move. Temperature-dependent interferograms were then used to calculate  $dn/dT$ . Experiments were performed at temperatures from 15 to 45 °C, with the average  $dn/dT$

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