Correlation Between Refractive Indices and Other Fuel-Related Physical/Chemical Properties of Pyrolysis Liquids Derived From Coal, Oil Shale, and Tar Sand

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ABSTRACT

In the literature, characterization techniques based upon the liquid's refractive index are used with petroleum distillates to predict fuel-related properties; however, essentially nothing has been reported on the application of this technique to pyrolysis liquids. Measurements of the refractive indices of the pyrolysis liquids derived from various feedstocks (coal, oil shale, and tar sand) were made and appear to correlate well with the liquids' physical and chemical properties. The refractive indices of the pyrolysis liquids show good correlations with liquid density (correlation coefficient of 0.98), carbon and proton aromaticities (correlation coefficients of 0.88 and 0.91, respectively), and liquid carbon residue (i.e., correlation coefficient of 0.88 with the Conradson carbon residue). The above and other correlations were developed using data from at least 7 to as many as 35 discrete samples. These correlations have been used to develop empirical models. These findings demonstrate the potential of using the liquid's refractive index as a rapid technique to characterize the fuel-related properties of fossil fuel liquids generated by pyrolysis (before they are hydrogenated).

INTRODUCTION AND OBJECTIVES

The Morgantown Energy Technology Center (METC) results demonstrated that relatively high-quality liquid fuels (low sulfur, high H/C) can be produced by low-temperature devolatilization of coal (1,2). Physical and chemical properties characterization of these liquids has been the focus of several studies during the last few years (1-5).

Correlations based on the data obtained from relatively simple characterization techniques for predicting fuel-related physical and chemical properties of pyrolysis liquids would facilitate the utilization of these liquids in various processing schemes. Properties such as molecular weight and aromaticity of liquids influence their utilization behavior/properties (e.g., viscosity, smoke point). Measurements of molecular weight or aromaticity can be difficult, time consuming, and expensive; can require skilled operators; and are often beyond the resources of most small laboratories.

The correlations between properties of petroleum liquids and their refractive indices are available in the literature (6-8). Sturm et al. (8a), fractionated the pyrolysis liquid generated in a rapid-rate reactor (Coal Oil Energy Development, COED) into various distillate cuts. It was not stated at what condition hydrogenation was effected. The COED liquids were hydrogenated (8b) to remove the heteroatom contents (e.g., sulfur, nitrogen) and to improve their fuel value.

White et al. (6) compared the refractive indices of coal liquefaction products with their chemical properties (e.g., molecular weight). These researchers also reported an excellent review of previous work in this area (6).

In previous studies, it was demonstrated by Khan (9) that the pyrolysis liquids generated from weathered fossil fuel samples (including coal and oil shale) had higher liquid refractive indices than those obtained from unweathered samples.

The objective of this paper is to illustrate the relationship between the refractive indices of pyrolysis liquids and their fuel-related physical (density, Conradson carbon residue) and chemical properties (aromaticity, molecular weight, hydrocarbon type, etc.).

EXPERIMENTAL SECTION

A fixed-bed reactor (slow heating-rate organic devolatilization reactor, SHRODR) was used to generate pyrolysis liquids at 500°C. More details on this reactor system as well as the experimental procedures used and the reproducibility of data are available (1,2,5). A range of feedstocks (primarily coal, but also oil shale, and tar sand) were devolatilized in this reactor. Coal samples were supplied by the Penn State/DOE coal data bank (10). The origin of shale samples (eastern and western) and the Pittsburgh No. 8 coal has been discussed elsewhere (9). Tar sand samples were procured from the Western Research Institute (WRI).

Sample preservation and avoidance of air oxidation of samples were key considerations to this investigation as reported in previous studies (9,11-14). Availability of fresh (well preserved, not weathered) samples was the criterion used for sample selection. Some coal samples utilized by Given et al. (15) for an investigation on direct liquefaction were selected in this study for comparison. Primarily bituminous coals were used in this study as these are known to yield the highest liquid product during pyrolysis (1,3). All sample preparation and handling were performed in an inert atmosphere.

The refractive index of liquid samples were measured at 20°C by Huffmann Laboratories, Inc., applying ASTM D-1218 methods. The refractive index of 1-bromonaphthalene was measured as a standard before the refractive index of each pyrolysis liquid. The refractive index measurement of 1-bromonaphthalene was within ± 0.0005 units of the reference value (reported by Hoffmann). Conradson carbon residue was determined at Saybolt Lab (Pasadena, Texas) using ASTM D-189. The density measurements were (reproducible within ± 0.0001), also performed at Saybolt at 15.5°C by ASTM D-70.

The aromaticity of the liquids was measured at the University of North Dakota Energy and Minerals Research Center (UNDEMRC) by proton NMR, using the Clutter et al. (16) procedure with a Varian XL200 NMR Spectrometer. ^{1}H NMR was used for determination of aromaticities. Molecular weights were calculated based on the NMR data applying the equation used by Clutter et al. (16).

Neutral fractions of pyrolysis liquids were generated chromatographically on activated alumina. A 20-inch x 3/8-inch column was loaded with 25 g of activated alumina (Biorad). A sample of 0.2 g was charged to the column and the neutral fraction was eluted with 50 mL of benzene. The benzene was removed from the sample by rotary evaporation. To ensure that the lower-boiling point components of the sample were not lost during benzene removal, the benzene was not completely removed from the sample. The concentration of the residual benzene was then determined by combined gas chromatography/mass spectrometry (GC/MS) and the final weights of the neutral fractions were adjusted to account for the residual benzene. The polar material was not eluted from the column, but was determined by difference.

The neutral fractions were analyzed using WRI's GC/MS hydrocarbon group type analysis. A Hewlett-Packard Model 5985B GC/MS system was used. The GC column was a 50-meter quartz capillary, coated with methylsilicone, and operated in programmed-temperature modes, which optimized the resolution of components. The method determines the composition of the hydrocarbon group by using selected ions that are

representative of each hydrocarbon group type and relies on the gas chromatographic separation to minimize interferences from fragment ions of other hydrocarbon groups. The results from the analyses are reported as weight percentages of the neutral fractions. The results are provided as weight percentages of the total sample that was charged to the column. The results for the neutral fractions reflect the adjusted weights of the neutral fractions after accounting for the residual benzene. Detailed analysis and distribution of the components identified in various fractions will be presented in a future communication. The distillate cut between 300° and 600°F is of interest because its properties is expected based on literature studies to match the target properties of the high-density fuels (17,18). Liquids were combusted in a thermogravimetric analysis system (TGA) at 100°C/min in air (flowrate of 120 cc/min). In addition TGA distillation of the liquids was performed (heating rate, 5°C/min, He flowrate 50 cc/min). Statistical Analyses System (SAS) Package developed by SAS Institute was used for data analyses. The linear regression analysis available in this package was applied to develop empirical models (19,20).

RESULTS

A detailed study on the influence of feedstock type on pyrolysis liquid product yield and composition will be presented separately. In addition, comprehensive characterization data for the liquids are the subject of a separate report. Table 1 presents a summary of equations used to predict the properties of pyrolysis liquids.

The hydrogen-to-carbon ratio (H/C) of the pyrolysis liquids is an important fundamental property of liquid fuels that influences various physical (e.g., viscosity, density) and chemical (e.g., molecular weight, aromaticity, etc.) properties. The relationship (negative) between the liquid H/C ratios and the refractive indices of the liquid is presented in Figure 1A (correlation coefficient of 0.90). The following regression model was used for predicting the liquid H/C ratios:

$$[H/C] = 6.876 - 3.50\ n. \qquad 1)$$

The refractive indices (n) of the liquids correlated with the corresponding weight percent (of tar) hydrogen (H) contents (correlation coefficient = -0.83; Figure 1B). A model defined by equation (2),

$$H = 57.264 - 30.5\ n, \qquad 2)$$

was used to predict the hydrogen contents.

Figure 2 shows the correlation between the carbon aromaticities (C_{aro}) and the refractive indices (n) for the pyrolysis liquids derived from various fossil fuels. The correlation coefficient between the variables was 0.91. The carbon aromaticity (C_{aro}) could be predicted by equation (3) using a linear regression fit:

$$C_{aro} = 3.657\ n - 5.228. \qquad 3)$$

The carbon aromaticity of the same data set could be predicted somewhat better with a two-variable model that includes the liquid H/C atomic ratio:

$$C_{aro} = 2.887\ n - 0.227\ (H/C) - 3.71. \qquad 4)$$

Figure 3 compares the proton aromaticity with the refractive indices of the liquids (correlation coefficient of 0.88). The actual aromaticity data can be predicted based on a single-variable model, defined by

$$H_{aro} = 2.102\ n - 3.103. \qquad 5)$$

TABLE 1

Summary of Predictive Equations for Pyrolysis Liquids

	Model	R^2*	F	P
1.	$(H) = 57.264 - 30.50\ n$	0.70	65.3	0.0001
	$(H/C) = 6.876 - 3.50\ n$	0.55	35.4	0.0001
	n = refractive index H/C = hydrogen-to-carbon ratio of liquids (atomic)			
2.	$C_{aro} = 3.657\ n - 5.228$	0.82	131.9	0.0001
	$C_{aro} = 2.887\ n - 0.222\ (H/C) - 3.71$	0.86	82.5	0.0001
	C_{aro} = carbon aromaticity			
3.	$H_{aro} = 2.102\ n - 3.103$	0.77	96.8	0.0001
	$H_{aro} = 1.739\ n - 0.105\ (H/C) - 2.39$	0.79	50.5	0.0001
	$H_{aro} = n^{-0.56168} \times (H/C)^{-4.484}$	0.97**	531.5	0.0001
	H_{aro} = proton aromaticity			
4.	$MW = 4383.2 - 2655\ n$	0.70	65.3	0.0001
	$MW = 1.332\ T_{50} - 1573.28d + 1589.1$	0.82	9.03	0.033
	$MW = 1.348\ T_m - 1249.24d + 1234.6$	0.94	23.0	0.015
	MW = molecular weight T_{50} = temperature of mid-distillation point (TGA) T_m = temperature of mid-distillation point (ASTM D-86)			
5.	$d = 1.977\ n - 2.08$	0.97	155.2	0.0001
	d = density, gm/cc			
6.	$C_{con} = 37.75\ n - 55.29$	0.77	16.5	0.0097
	C_{con} = Conradson carbon residue			

* R^2 measures how much variation in the dependent variable can be accounted for by the model (i.e., independent variable).

** R^2 is redefined for the no-intercept case by SAS (20). Note that this is a non-linear equation.

The F-ratio is the ratio produced by dividing the mean square for the model by the mean square of error. It tests how well the model as a whole (after adjusting for the mean) accounts for the behavior of the dependent variable (20).

P defines the "observed level of significance." In statistical terms, the level of significance, α, of a test is defined as the probability of rejecting the null hypothesis (i.e., no linear relationship between the dependent and independent variables) given the null hypothesis is true. P gives us the largest value of α that would lead to the acceptance of the null hypothesis.

The predicted model, based on a two-variable model, can be defined by the equation

$$H_{aro} = 1.739\ n - 0.105\ (H/C) - 2.39. \qquad 6)$$

Proton aromaticity could also be predicted based on the following nonlinear model (see also Table 2).

$$H_{aro} = n^{-.56168} \times (H/C)^{-4.484}.$$

The molecular weights (MW) of the pyrolysis liquids (determined using NMR data) could be predicted from the refractive indices. For example, a single-variable model based on the refractive indices of the liquid could be used for this prediction. This model is given by the equation

$$MW = 4383.2 - 2655\ n \qquad 7)$$

A two-variable model based on the liquid density (d) and the mid-distillation point (T_m) could also be used for predicting the MW of the pyrolysis liquids (Figure 4):

$$MW = 1.348\ T_m - 1249.24d + 1234.6. \qquad 8)$$

The distillation data were obtained using the ASTM D-86 procedure. A new model, based on the same two-variable model (similar to Equation 8) but the distillation data are obtained from TGA evaporation, can be defined by the equation

$$MW = 1.332\ T_{50} - 1573.28d + 1589.1. \qquad 9)$$

In the above equation, T_{50} stands for the mid-distillation temperature as determined by a TGA. The correlation coefficient between the refractive index and the density (Figure 5) of the liquids was 0.98. A linear regression fit provided the following model:

$$d = 1.977\ n - 2.08. \qquad 10)$$

The correlation coefficient between the refractive indices of various distillation cuts and the corresponding density for the COED syncrudes (reported by Strum et al.[10]) was 0.99, calculated in this study.

The correlation coefficient between the Conradson carbon (C_{con}) residue of the mild pyrolysis liquids derived in this study and the refractive indices of the liquids was 0.88 (Figure 6). A single-variable model was defined by the equation

$$C_{con} = 37.75\ n - 55.29 \qquad 11)$$

A liquid combustion parameter (second maximum peak of combustion) measured in a thermogravimetric analyses system (TGA) could be positively correlated somewhat with the refractive indices of the liquids (data not shown).

The significance of this TGA peak is not known. It may be worthwhile to attempt correlations of liquid combustion properties with their refractive indices, keeping previous relationships observed in this study in mind.

Additional correlations between the refractive indices and the pyrolysis liquid characterization data are presented in Figures 7 and 8. Figure 7 shows a relationship between the refractive indices of the whole liquid and the tricyclic saturated compound (so-called "high density fuels") in the 300° to 600°F cut of the neutral fraction of the pyrolysis liquids as determined by a GC/MS technique (the correlation coefficient of the data set was 0.8). The liquid distilled between 300° to 600°F was

of particular interest because this boiling range approximates the range of JP-8, a high-density aviation fuel (17,18,21). The total naphthalenes content in Cut 2 (boiling between 300° and 600°F) of the pyrolysis liquids present in the neutral fraction could be directly correlated with the refractive indices of the whole liquids (Figure 8, correlation coefficient 0.98).

Conradson carbon residue (C_{con}) could be correlated with the hydrogen content (correlation coefficient of - 0.92). C_{con} also showed correlations with the carbon and proton aromaticities (correlation coefficients of 0.91 and 0.84, respectively). Thus, the observed correlation between the refractive index and C_{con} is not surprising. The observed relation may reflect the well known fact that aromatic compounds are more susceptible to coke formation during severe heat treatment. Figure 9 compares the cetane index of the hydrogenated (8b) COED liquids distilled at various temperature ranges [data from Strum et al. (8a)] with the corresponding refractive index. A summary of correlations developed in this study are presented in Table 1.

DISCUSSION

The results of this study demonstrate that the refractive index, used in petroleum literature to correlate fuel properties, is a relevant property to evaluate pyrolysis liquids derived from coal, oil shale, and tar sand. It is demonstrated that the liquids' H/C, density, hydrogen content, molecular weight, and aromaticity correlate with refractive indices of the pyrolysis liquids.

The relationship between the refractive index (n) and density (d) and other properties (e.g., Conradson carbon residue) of the liquids is consistent with our physical understanding of the structural properties of hydrocarbons. Paraffins have the highest hydrogen content and tend to have "fluffy" chain structures with low densities. For pure compounds, the lower the density, the lower the refractive indices. On the other hand, relatively compact cyclic (dense) aromatics are deficient in hydrogen. Cycloparaffins, which are both cyclic and hydrogen saturated, represent the best compromise between density and hydrogen content (21).

The refractive indices of pyrolysis liquids correlate with the liquid H/C ratio (correlation coefficient 0.90) or the hydrogen contents of the liquid (correlation coefficient 0.86). In this study, models have been developed to predict the H/C ratio or hydrogen contents of the liquids based on their refractive indices.

It is not surprising that refractive index correlates well with the liquid aromaticity. An increase in hydrogen content of fuels often lead to a decrease in aromaticity. For example, benzene with H/C = 1 has fa = 1, while C_6H_{12} (cyclohexane) with H/C = 2 has fa = 0. Here, fa is the proton or carbon aromaticity. The correlation coefficients between refractive index and proton, or refractive index and carbon aromaticity were 0.88 and 0.91, respectively. One- and two-variable models were applied to predict the carbon and proton aromaticities of the pyrolysis liquids, based on their refractive indices.

Molecular weights are fundamental properties of liquids. For various classes of pure compounds, refractive indices tend to change rapidly at low molecular weight but less rapidly at higher molecular weight. It appeared that refractive indices of the pure liquids correlated with the negative one-half power of molecular weight (data not shown). In this study, molecular weight could be predicted based on a single (e.g., refractive index, n) or a two-variable model [including density (d) and temperatures of 50 percent evaporation as determined in a TGA (T_{50}) or by an ASTM technique (ASTM D-86, T_m)].

SUMMARY AND CONCLUSIONS

It is demonstrated that the refractive indices of pyrolysis liquids derived from coal, oil shale, and tar sand serve as a useful property to evaluate the fuel-related physical/chemical properties of these fuels. The refractive indices of the liquids correlate well with the liquid hydrogen content (weight percent) and the H/C ratio, aromaticity (carbon and proton), molecular weight, density, and Conradson carbon residue. A number of empirical equations have been developed based on these correlations.

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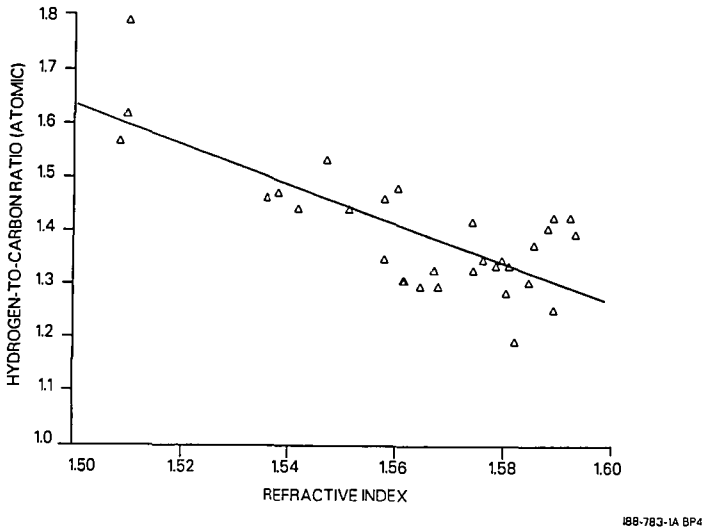

FIGURE 1A. Correlation between the liquid hydrogen-to-carbon ratio and the refractive indices of the liquid.

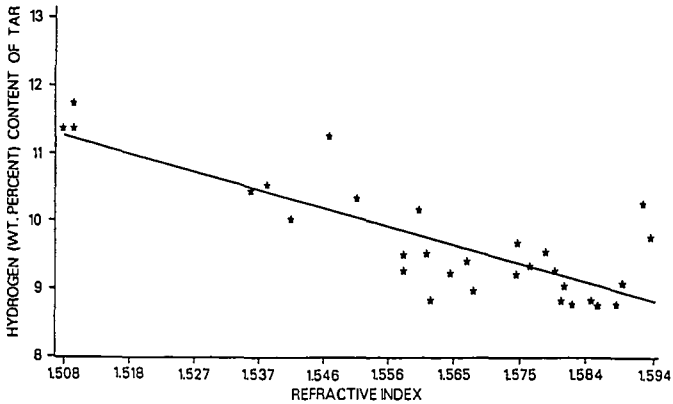

FIGURE 1B. Correlation between the liquid hydrogen content (dry basis) and the refractive indices of the liquid.

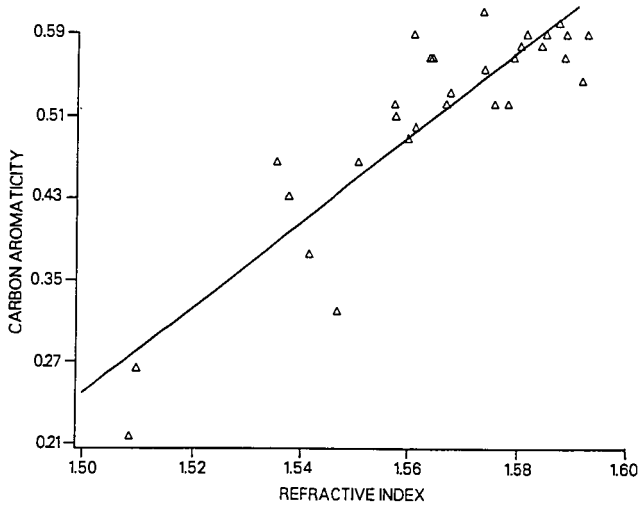

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FIGURE 2. Correlation between the carbon aromaticity and the refractive indices (correlation coefficient 0.91).

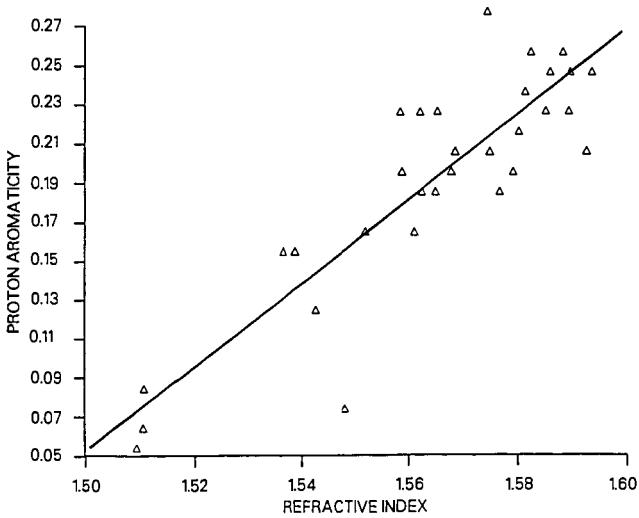

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FIGURE 3. Correlation between proton aromaticity and refractive indices (correlation coefficient 0.88).

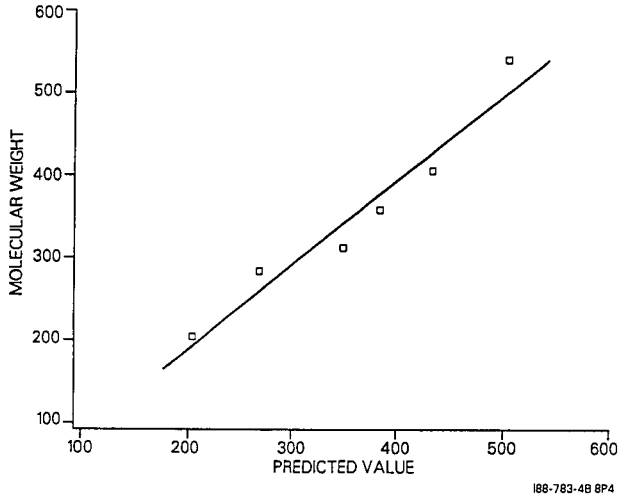

FIGURE 4. Predicted and measured molecular weight based on a two-variable model (including density and mid-distillation point (T_{50}). (R^2 = 0.93); distillation data obtained by a TGA unit.

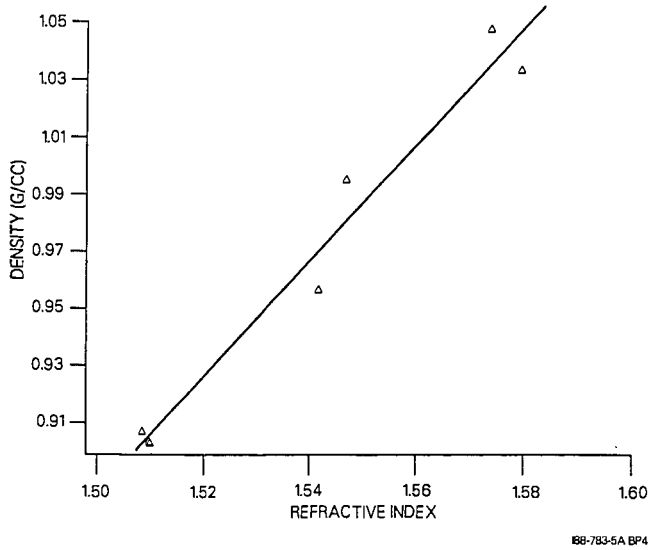

FIGURE 5. The relationship between the density and the refractive indices of the pyrolysis liquids (correlation coefficient 0.98).

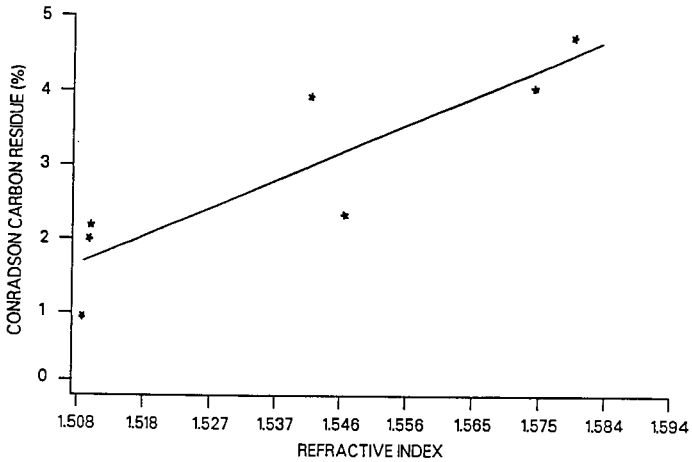

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FIGURE 6. The relationship between the refractive indices and the Conradson carbon residue (correlation coefficient 0.88).

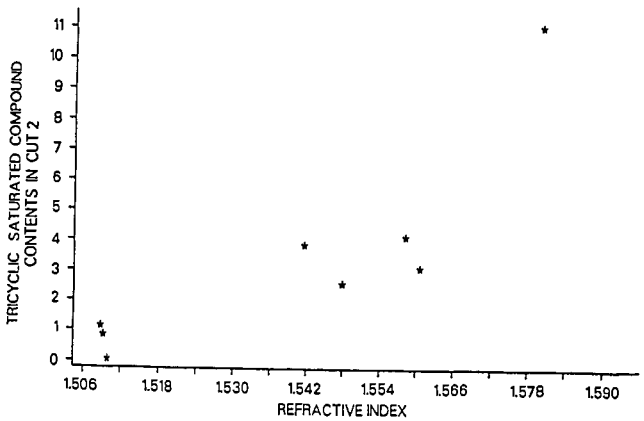

FIGURE 7. Correlation between refractive indices and triaromatic content of the liquids (in Cut 2; i.e., 300° to 600°F fraction of the neutral position of pyrolysis liquids) (correlation coefficient of 0.8).

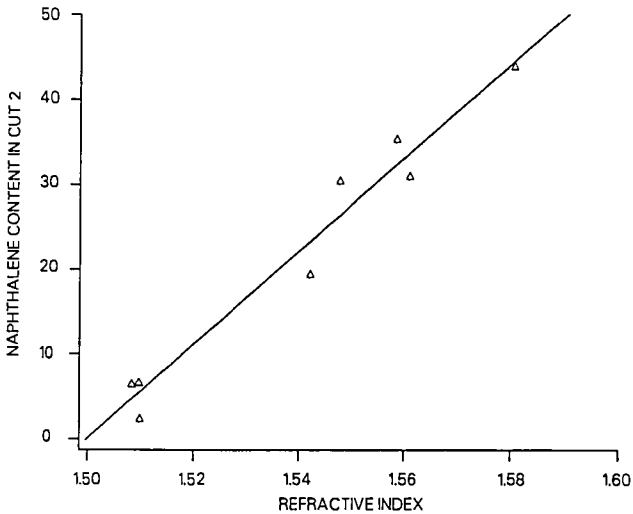

FIGURE 8. Relationship between the total naphthalene contents of the pyrolysis liquids with the refractive indices of the liquids.

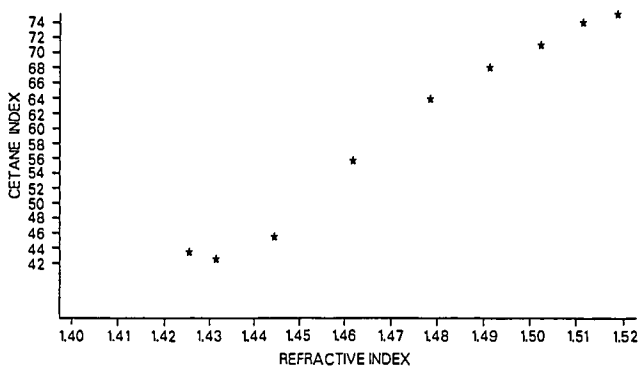

FIGURE 9. Relationship between the Cetane index with the refractive indices for the COED (hydrogenated) syncrude.