Hydrocarbon composition of straight run middle distillate correlated with diesel index

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A Mathematical equation has been developed to predict the diesel index of middle distillate from %C_p, %C_N and %C_A data derived from n-d-m analysis. Regression coefficient of 0.96 with a standard deviation of residuals of 0.42 shows that the suggested equation is statistically satisfactory and is useful in assessing diesel index of distillate fuels from hydrocarbon composition.

Ignition quality of a distillate fuel is based on hydrocarbon composition. In diesel oil this quality is normally controlled by three parameters: cetane number; diesel index and cetane index. The diesel index and cetane index are assessed from analytical characteristics of the fuel\(^1\)\(^-\)\(^3\). However, the use of diesel index is more popular because its determination avoids the necessity of an engine for cetane number, which is time consuming and costly. Diesel index is found to be generally 1 to 3 units higher than the cetane number\(^6\) and correlations are available for predicting cetane index of synthetic fuels\(^7\)\(^-\)\(^9\).

In the present work, a mathematical equation has been developed to predict diesel index from hydrocarbon composition which is calculated from simple physico-chemical properties\(^10\)\(^-\)\(^11\) using n-d-m method. The n-d-m method was used as in most of the Indian refineries NMR facility is not available.

Experimental procedure—All the samples are prepared in a True Boiling Point (TBP) distillation apparatus as per ASTM D-2892 method\(^12\). An Oldershaw perforated sieve plate column with 16 theoretical plates (actual 30 plates), 2.54 cm internal diameter is used as a fractionating medium. Reflux ratio of 5:1 is maintained during the distillation operation. Densities of all the fractions are measured with PAAR automatic densitometer. Composition of straight run distillate is determined as per ASTM D 3238 method and aniline point of all the samples are determined by ASTM D 611 method\(^13\)\(^,\)\(^14\). All the samples were free from additives.

Results and discussion—The graph plotted between diesel index and %C_A (Fig. 1) indicates that the diesel index decreases with the increase of %C_A. The trend is not linear as most of the data points are scattered on both sides. Graph plotted between diesel index and %C_p (Fig. 2) shows an upward trend indicating an increase of diesel index with %C_p. The scattering of data points indicate the sensitivity of diesel index to %C_p. Effect of %C_N is not much pronounced on diesel index, as trend is a straight and data points are scattered on both sides of the line (Fig. 3). Therefore, a non-linear regression analysis is carried out to correlate the diesel index with %C_A, %C_p and %C_N.

Table 1 shows the equation developed on built multivariate regression analysis programme on IBM PC/AT 386 compatible computer system under LOTUS-123 environment. The equation derived on 38 data points has R Squared value 0.96, standard deviation of residuals 0.42 and 2.11 standard error of estimate.

Validity of equation is checked on six unknown straight run diesel samples and data are shown in Table 2. Diesel index obtained from the calculated values correlates well with values obtained from the existing equation as shown in Fig. 4. The variation of observed diesel index is shown in Fig. 5 and predicted values are in acceptable range.

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Table 1 – Equation developed for prediction of diesel index

\[
\text{DI} = 545.0179 - 5.6463 \times \%C_A - 6.3716 \times \%C_N - 1.8278 \times (\%C_p)^{-1.2}
\]

Regression Output

| R squared | 0.96 |
| No. of observations | 38.0 |
| Degree of freedom | 34.0 |
| Standard error of Y estimate | 2.11 |
| Standard deviation of residuals | 0.42 |
| Average absolute deviation | 1.61 |

**Limitations** – The present equation has been derived on straight run middle distillate fuels having heteroatoms (S, N & O) less than 2.5 wt%; diesel index ranging from 28 to 65. °API of the distillates are in the range from 21.3 to 47.4, aniline point in the range from 38.5 to 71.1°C and molecular weight from 131 to 292. The equation is valid for the fractions having %C_A from 9.2 to 70.

Table 2 – Experimental vs calculated diesel index for unknown samples

<table>
<thead>
<tr>
<th>°API</th>
<th>AP, °C</th>
<th>%C_A</th>
<th>%C_N</th>
<th>%C_p</th>
<th>Calc. DI</th>
<th>Exptl DI</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.62</td>
<td>73.55</td>
<td>21.0</td>
<td>15.8</td>
<td>63.2</td>
<td>57.28</td>
<td>56.91</td>
</tr>
<tr>
<td>40.92</td>
<td>43.59</td>
<td>18.3</td>
<td>37.2</td>
<td>44.5</td>
<td>44.61</td>
<td>45.20</td>
</tr>
<tr>
<td>44.21</td>
<td>55.17</td>
<td>16.9</td>
<td>24.6</td>
<td>58.5</td>
<td>57.16</td>
<td>58.05</td>
</tr>
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<td>38.90</td>
<td>39.06</td>
<td>22.5</td>
<td>35.3</td>
<td>42.2</td>
<td>39.30</td>
<td>39.80</td>
</tr>
<tr>
<td>29.53</td>
<td>47.32</td>
<td>32.8</td>
<td>20.7</td>
<td>46.5</td>
<td>35.97</td>
<td>34.60</td>
</tr>
<tr>
<td>45.38</td>
<td>41.23</td>
<td>19.0</td>
<td>33.2</td>
<td>47.8</td>
<td>47.16</td>
<td>48.20</td>
</tr>
</tbody>
</table>

46.2, %C_p from 38.5 to 71.1 and %C_N from 3.0 to 44.7.

**Conclusions** – The present equation calculates diesel index within ±2.1 units for 76% of the distillate fuels while the reproducibility limit of cetane number is between 2.5 to 3.3 units depending upon the cetane number measured.

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Nomenclature

AP = aniline point (°F)
DI = diesel index
\%C_A = % of carbon in aromatic structure
\%C_N = % of carbon in naphthenic structure
\%C_P = % of carbon in paraffinic structure

References