Appendix D - Methane Number and Fuel Composition

Providing an optional methane number specification for the CNG motor vehicle fuel specifications satisfies both the need to control fuel variability according to the engine manufacturers requirements and to allow more flexibility in fuel composition. Several manufacturers of heavy-duty natural gas engines use either the methane number (MN) or motor octane number (MON) for specification of gas quality requirements.\textsuperscript{1, 2} Both the MON and the MN are measures of the knock resistance of the fuel with the difference being the reference fuels used.

A. Methane Number Correlation

The knock resistance of a fuel is determined by comparing the compression ratio at which the fuel knocks to a reference fuel blend that knocks at the same compression ratio. Different scales have been used to rate the knock resistance of CNG including the motor octane number (MON) and the methane number (MN). The differences in these ratings are the reference fuel blends used for comparison to the natural gas. The reference fuel blend used for comparison to the natural gas for the MON is composed of iso-octane, with an octane number of 100, and n-heptane with an octane number of 0. However, since natural gas has a higher knock resistance than iso-octane, tetraethyl lead (TEL) must be blended with the reference fuel to increase the reference MON.\textsuperscript{3, 4} The MON for CNG fuels range from approximately 115 to over 130. Methane number uses a reference fuel blend of methane, with a methane number of 100, and hydrogen, with a methane number of 0. The work documented in references 10 and 11 generated correlations between the reactive hydrogen/carbon ratio (H/C) and the MON and between MON and MN. The reactive hydrogen/carbon ratio, which excludes the carbon in the inerts, specifically the CO2, is the number of hydrogen atoms divided by the number of carbon atoms in the hydrocarbon components of the fuel. The correlations used by the engine manufacturers for MON as a function of H/C and MN as a function of MON are: \textsuperscript{1, 3, 4}

\[
\text{MON} = -406.14 + 508.04 \times (H/C) - 173.55 \times (H/C)^2 + 20.17 \times (H/C)^3
\]
\[
\text{MN} = 1.624 \times \text{MON} - 119.1
\]

The correlation of MON with H/C ratio is shown in Figure D-1 below. The MON correlation is not valid for H/C ratios below 2.5 or for inert concentrations greater than 5%.
Figure D–1 Motor Octane Number as a Function of Reactive Hydrogen / Carbon Ratio

Figure D–2 below shows the relationship between MON and MN. From this figure it can be seen that a MON of approximately 122.6 is equivalent to a MN of 80. From Figure D–1 above, it is apparent that a reactive hydrogen/carbon ratio of 3.758 results in a MON of 122.6. Consequently, a reactive hydrogen/carbon ratio of 3.758 is necessary to obtain a MN of 80. This is shown in Figure D–3 below.
The MN can be shown as a function of reactive hydrogen/carbon ratio as shown in Figure D-3 below.

Figure D-2 Methane Number as a Function of Motor Octane Number

Figure D-3 Calculated Methane Number as a Function of Reactive Hydrogen/Carbon Ratio
B. Fuel Composition Flexibility

The proposed optional MN fuel quality specification being considered would allow gas compositions that do not meet the current compositional specification requirement to be compliant if the calculated methane number was at 80 or above. Thus, a gas specie could be higher than allowed by the current compositional specification if the overall reactive H/C ratio for the entire gas composition was a value of 3.758 or greater. For example, a gas with high ethane content could be compliant if the C3+ content was sufficiently low to compensate for it in the overall reactive H/C ratio.

Table D-1 gives an array of hypothetical gas compositions and the calculated methane number for each composition. The first two compositions do not meet the compositional CNG motor vehicle fuel specifications; however they would meet the proposed optional methane number 80 specification. The first gas, labeled low ethane, high C3+, has a C3+ content of 4.65%, which is over 50% higher than the current allowable level of 3%. However, the ethane content of 2.2% is much lower than the 6% allowable. The overall reactive H/C ratio is greater than 3.758, which gives a methane number of 80.4 for the composition. The second gas in the table, labeled high ethane, low C3+, has an ethane content of 8.66%, nearly 50% over the allowable 6%. However, the C3+ content of 1.86% is well below the allowable 3%, resulting in a reactive H/C ratio of just over 3.758 and a methane number of 80.

The last three hypothetical gases in Table D-1 meet the current compositional specification but have different C3+ compositions to illustrate the effect of heavier hydrocarbon components on methane number. All three gas compositions have 3% C3+. However the first of the three gases has C3+ that contains only propane whereas the other two gases have increasingly more of the heavy hydrocarbons in the C3+. The C3+ of the second of the three gases averages to a carbon atom number of 3.5 (C3.5) and that of the last gas averages to a carbon atom number of 4 (C4). The heavier hydrocarbons in the gas, which are those components with lower H/C ratios, lower the overall reactive H/C ratio of the gas and reduce the methane number, as shown in Figure D - 3 above. Consequently, the methane number for the three gases range from MN 82, for the gas with C3+ that is all propane (C3), down to MN 77, for the gas with the C3+ that averages to a C4.

The proposed methane number optional specification gives gas producers with non-compliant CNG motor vehicle fuel gas more flexibility in cleaning up their gas. Since heavier hydrocarbons condense at higher temperatures than the lighter hydrocarbons, they are easier to remove from the gas. This is evident from typical natural gas liquids (NGL) recovery efficiencies for different processes. Actual recovery efficiencies will vary with plant design and feed gas quality, however, a lean oil absorption plant can typically recover 99 percent of the butane and heavier hydrocarbons, 65 to 75 percent of the propane and 15 to 25 percent of the ethane from a natural gas. A typical refrigeration process can recover 100 percent of the butane and heavier hydrocarbons, 98 percent of the propane and 50 percent of the ethane. A typical cryogenic process can recover all of the propane and heavier hydrocarbons and 50 percent to over 90 percent of the ethane.\(^5\)
Consequently, a gas producer with a high ethane content gas could chose to remove a portion of the heavier hydrocarbons to meet the proposed methane number 80 specification rather than reducing the ethane, which is more difficult to remove. Additionally, these heavier hydrocarbons are more marketable in California than ethane. One possible option is re-injection of these heavier components into the crude oil.
Table D-1  Example Gas Compositions Meeting Either the Proposed Methane Number 80 Specification or the Current Specifications

<table>
<thead>
<tr>
<th>Mole Fraction:</th>
<th>inerts</th>
<th>methane</th>
<th>ethane</th>
<th>C3+ total</th>
<th>propane</th>
<th>iso-butane</th>
<th>n-butane</th>
<th>iso-pentane</th>
<th>n-pentane</th>
<th>C6+</th>
<th>Reactive H/C</th>
<th>MON</th>
<th>MN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CNG meeting MN80:</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Low ethane, high C3+</td>
<td>0.0179</td>
<td>0.9137</td>
<td>0.02</td>
<td>0.0465</td>
<td>0.032</td>
<td>0.0031</td>
<td>0.0092</td>
<td>0.0008</td>
<td>0.0009</td>
<td>0.0005</td>
<td>3.763</td>
<td>122.9</td>
<td>80.4</td>
</tr>
<tr>
<td>High ethane, low C3+</td>
<td>0.046</td>
<td>0.8488</td>
<td>0.0866</td>
<td>0.0186</td>
<td>0.0142</td>
<td>0.0006</td>
<td>0.0014</td>
<td>0.0008</td>
<td>0.0012</td>
<td>0.0004</td>
<td>3.759</td>
<td>122.6</td>
<td>80.0</td>
</tr>
<tr>
<td><strong>CNG meeting current specifications:</strong></td>
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<td></td>
</tr>
<tr>
<td>Spec gas, C3+ all propane</td>
<td>0.03</td>
<td>0.88</td>
<td>0.06</td>
<td>0.03</td>
<td>0.03</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.780</td>
<td>123.9</td>
<td>82.1</td>
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<tr>
<td>Spec gas, C3+ averages to C 3.5</td>
<td>0.03</td>
<td>0.88</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
<td>0.001</td>
<td>0.001</td>
<td>3.756</td>
<td>122.4</td>
<td>79.7</td>
</tr>
<tr>
<td>Spec gas, C3+ averages to C 4</td>
<td>0.03</td>
<td>0.88</td>
<td>0.06</td>
<td>0.03</td>
<td>0.01</td>
<td>0.0055</td>
<td>0.0055</td>
<td>0.0035</td>
<td>0.0035</td>
<td>0.002</td>
<td>3.731</td>
<td>121.0</td>
<td>77.4</td>
</tr>
</tbody>
</table>

2 Paul Delong of John Deere, Telephone conversation with ARB Staff, 3/6/01.

