

# OCTANE NUMBER AND ANILINE POINT OF PETROLEUM FUELS

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## Introduction

The quality of various petroleum fuels depends on their composition and types of hydrocarbons present in the mixture. Octane number is one of the characteristics of spark-ignition engine fuels such as gasoline and jet fuel. This number indicates anti-knock characteristic of a fuel and strongly depends on the hydrocarbon type. Octane number of fuels can be improved by addition of oxygenates such as TEL, MTBE or TAME. Octane number of fractions without additives is usually referred to as clear octane number. These additives are normally hazardous to the environment and for this reason methods to improve octane numbers through processes such as alkylation are used in refineries. Standards set in many countries and car manufacturers require a minimum octane number of 95. In Europe superstar gasoline should have minimum octane number of 98. Two commonly used octane numbers are research octane number (RON) and motor octane number (MON). RON is measured under low speed condition by ASTM D908 while the MON is measured under high speed condition by ASTM D 357 test method. The difference between RON and MON is called sensitivity and fuels with lower sensitivity are desirable. Conducting such experimental tests on every motor fuel is prohibitive in both time and cost. There are very few predictive methods for calculating octane number. Nelson methods are in the form of graphical correlations either in terms of boiling point and Watson characterization factor for naphtha fractions or in terms of boiling point and paraffin weight percent [1]. These methods have limited range of application and are not suitable for computer applications plus they produce high deviations in excess of 8 octane numbers. Other predictive methods that couple regression analysis with results from gas chromatography [2] or nuclear magnetic resonance [3] are also prohibitive in both time and cost which makes them unattractive for quick online analysis.

Aniline point (AP) is another characteristic of petroleum fractions that indicates the degree of aromaticity of hydrocarbon mixtures. Aniline point is defined as the lowest temperature at which equal volumes of aniline and the sample become completely soluble. As amount of aromatics in a petroleum fraction increase the aniline point decreases. Therefore, the aniline point is a parameter that is highly related to the hydrocarbon types in petroleum fractions. Aniline point is a useful parameter in calculation of heat of combustion, diesel index and hydrogen content of petroleum fuels. For non fuel products such as solvents aniline point is usually specified to quantify their effectiveness. Linden used the method of characterization of Watson and Nelson to develop a simple correlation for prediction of aniline point in terms of boiling point and API gravity [4]. However, the correlation was originally developed based on only 37 samples.

Most recently a set of data on crude assay and specification of petroleum products from around the world are collected and published by Oil and Gas Journal [5]. These data include boiling point, API gravity (or specific gravity), hydrocarbon type composition, kinematic viscosity, research and motor octane numbers, aniline point, flash, pour and cloud points for large number of various petroleum products. Although not all these specifications are given for a single fraction, but amount of information available

for each characteristic is sufficient to develop new predictive method or to re-evaluate the existing correlations. The main purpose of this paper is to use this data bank to develop new procedures for prediction of RON, MON and AP of various fuels with minimum information available.

## Technical Development

Clear octane number of some pure hydrocarbons generally found in naphtha and gasoline are given in the API-TDB [6]. For the same carbon number or boiling point, octane number of n-alkanes (n-paraffins), 2-methylalkanes (iso-paraffins), n-alkylcyclopentanes (naphthenes) and n-alkylbenzenes (aromatics) vary significantly. As shown in Figure 1, octane number of aromatics is generally higher than n-paraffins, iso-paraffins and naphthenes.

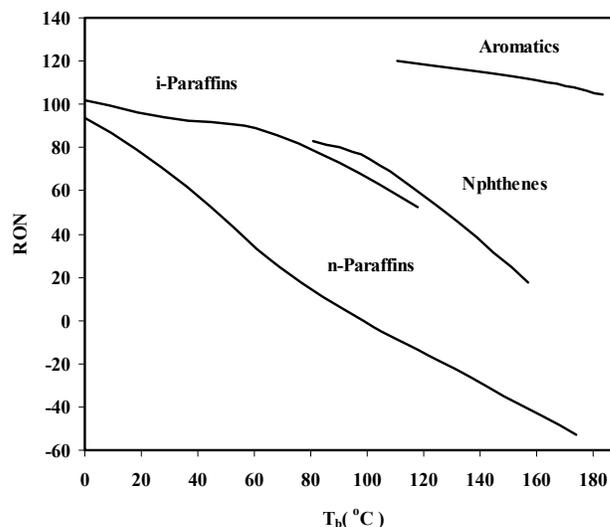


Figure 1. Research Octane Number of Pure Hydrocarbons from Different Families.

Even different types of iso-paraffins have different octane numbers. However, most petroleum fractions are olefin free and the main hydrocarbon families present in a fuel are n-paraffins (NP), iso-paraffins (IP), naphthenes (N) and aromatics (A). Clear research octane number of these homologous hydrocarbon families have been correlated to normal boiling point through the following relation:

$$\text{RON} = a + b(T) + c(T)^2 + d(T)^3 + e(T)^4$$

where  $T = T_b/100$  in which  $T_b$  is the normal boiling point in °C and coefficients a-e are given in Table 1. To calculate RON of a fuel it is assumed that the mixture contain four model compounds from n-paraffins, iso-paraffins, naphthenes and aromatics families. Then the RON of the mixture is calculated as:

$$\text{RON} = x_{\text{NP}}(\text{RON})_{\text{NP}} + x_{\text{IP}}(\text{RON})_{\text{IP}} + x_{\text{N}}(\text{RON})_{\text{N}} + x_{\text{A}}(\text{RON})_{\text{A}}$$

where  $x_{\text{NP}}$ ,  $x_{\text{IP}}$ ,  $x_{\text{N}}$  and  $x_{\text{A}}$  are volume fractions of n-paraffins, iso-paraffins, naphthenes and aromatics groups, respectively.  $(\text{RON})_{\text{NP}}$  is the clear RON of a hydrocarbon from n-paraffin family whose boiling point is the same as the mid-boiling point or ASTM D86 temperature at 50% point of the fraction and can be calculated from Equation (1). Similarly values of  $(\text{RON})_{\text{N}}$  and  $(\text{RON})_{\text{A}}$  are calculated from Equation (1) using boiling point of the mixture.

**Table 1. Coefficients for Equation (1) for Estimation of RON**

Hydrocarbon Family	a	b	c	d	e
<b>n-Paraffins</b>	92.809	-70.97	-53	20	10
<b>iso-Paraffins</b>					
2-Methylpentanes	95.927	-157.53	561	-600	200
3 - Methyl-pentanes	92.069	57.63	-65	0	0
2,2 - Dimethyl-pentanes	109.38	-38.83	-26	0	0
2,3 - Dimethyl-pentanes	97.652	-20.8	58	-200	100
<b>Naphthenes</b>	77.536	471.59	-418	100	0
<b>Aromatics</b>	119	144.8	-12	0	0

However, to calculate  $(RON)_{IP}$ , Equation (1) should be used for four different iso-paraffin families given in Table 1 and an average value (also shown in figure 1) is used for  $(RON)_{IP}$ . This is to account for the large differences in octane number for the various iso-paraffins in the gasoline fraction. When the amount of iso-paraffins is not reported,  $x_{NP}$  and  $x_{IP}$  are taken equal to half of volume fraction of paraffins. When experimental data on the composition are not available it can be estimated through methods proposed by Riazi et. al [7-10]. These correlations require refractive index, density and molecular weight all of which can be estimated from mid-boiling point and specific gravity of a petroleum fractions using methods proposed by Riazi and Daubert [6,11,12].

Once clear RON is known, clear MON can be estimated from the following correlation derived from the correlation proposed by Jenkins [13] for olefin free fuels.

$$MON = 22.5 + 0.83 RON - 20.0 SG$$

where SG is the specific gravity of the fuel at 15.5 °C. Summary of results for calculation of RON and MON using both experimental and predicted composition are given in Table 2 where AAD and MAD are average absolute and maximum absolute deviations, respectively. To develop a predictive method for the aniline point of petroleum fractions, we use parameters that quantify the amount of aromatics in a hydrocarbon mixture. It has been shown that parameters  $R_i$  and SG are suitable for prediction of aromatic content of petroleum fractions

where  $R_i$  is defined as:

$$R_i = n - d / 2$$

in which n is the refractive index and d is the liquid density in  $g/cm^3$  both at 20 °C. These two parameters can be estimated from boiling point and specific gravity through available relations [11]. Based on a data bank consisting of 300 data points on aniline point of petroleum fractions from crude oils from around the world [5], the following relation is proposed to predict the aniline point.

$$AP = -9805.269 + 711.85761(R_i) + 9778.7069(SG)$$

where AP is in °C. This equation is compared with the following relation in terms of  $T_b$  and API gravity developed by Linden [4]:

$$AP = 0.4(API)T_b^{1/3} + 0.317T_b - 298$$

**Table 2. Summary of Results for Prediction of RON and MON**

	No. of Data Points	Method	API Gravity Range	RON Range	RON		MON	
					A A D	M A D	A A D	M A D
1	19	NP-IP-N-A	51 - 87	26 - 74	4	11	5	12
2	97	P-N-A	44 - 88	30 - 80	6	19	1	7
3	100	Pred. P-N-A	44-88	30-80	7	22	--	--
4	18	Nelson 1	58 - 78	45 - 73	5	19	--	--
5	39	Nelson 2	47 - 74	18 - 72	6	14	--	--

where AP is in °F and  $T_b$  is in °R. For 300 petroleum fractions with AP range of 45 to 106 °C and API gravity range of 14 to 56, the proposed method gives an AAD of 2.5 °C (AMD of 7 °C) while the Linden method gives AAD of 6.5 °C (AMD of 28 °C) for the same fractions. Results presented in this paper show that the proposed methods are capable of estimating octane number and aniline point of petroleum fuels with a wide range of data points from oils from around the world with accuracy greater than similar existing methods. The proposed methods require minimum information on boiling point and specific gravity, however, when additional data are available from experimental measurements the proposed methods predict RON and aniline point with higher degrees of accuracy.

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