


RESEARCH ARTICLE

^1H NMR application in characterizing the refinery products of gasoline

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Abstract

We report on an application of ^1H NMR spectroscopy in characterizing the gasoline properties of its refinery products. In this work, a variety of gasoline samples obtained from different refinery stages are studied, and the aromatic, olefin, and paraffin contents as well as the octane number (ON) of the gasoline samples are characterized by ^1H NMR. The properties of two product gasoline samples are also studied by ^1H NMR spectroscopy; the NMR-determined values for the ONs are compared with the research octane number values measured in a standard test engine, and a good agreement is achieved. This work indicates that the characteristics of gasoline can be revealed by ^1H NMR, and the values derived from the NMR spectroscopy can be used to assess the gasoline quality during its refinery processes. Based on this work, we demonstrate that the ^1H NMR spectroscopy is a convenient tool in the continuous monitoring of the refinery processes of gasoline.

KEYWORDS

^1H NMR spectroscopy, aromatic content, gasoline, octane number

1 | INTRODUCTION

Nowadays, the quality control of product gasoline is essential in the petroleum refinery industry. Before the stage of gasoline blending, it is critical to continuously monitor the gasoline properties during the refinery processes of crude oils. Crude oils consist of hundreds of different hydrocarbon compounds, including the paraffins, naphthenes, aromatics as well as the organic compounds that contain sulfur, nitrogen, and oxygen atoms. Usually, the olefins are not found in the crude oils, and yet they are formed in many petroleum refinery processes.¹ The boiling points of the hydrocarbon compounds produced in the crude oil refinery processes span a wide temperature range, instead of a single temperature point.^{1,2} For instance, light naphtha, the fraction from the crude oils containing molecules with 5-6 carbon atoms, has a boiling temperature ranging from 30°C to 90°C; heavy naphtha that consists of molecules with 6-12 carbon atoms boils between 90°C and 200°C.

The hydrocarbon compounds can be further processed via hydrogenation to remove sulfur. Then the compounds can be reformed, through catalytic reactions, into more complex molecules with a higher octane number (ON), and finally become gasoline components.

Given the complexity of the crude oils, the gasoline refinery processes are a multistage procedure involving a series of distillations and several chemical reactions. The quality of the product gasoline depends not only on the qualities of the crude oils, but also on the delicate refinery processes which may be affected by various parameters such as the catalyst, temperature, pressure, etc. Therefore, it is necessary to characterize the gasoline properties during its refinery processes in order to achieve the high-quality product gasoline in the industry. Among the properties of gasoline, the ON is one of the most important parameter that characterizes the antiknocking performance of the engine. Generally, the gasoline with a higher ON value can withstand more compression before detonating, and are

used in the high-performance engines that require the higher compression ratios. In order for increasing the ON value, the high olefin content that has a high ON was pursued during the refinery of gasoline in early days, and yet the high olefin content was later found to be harmful to the environments. Instead, the hydrocarbon compounds containing oxygen were increased in order to achieve the high-ON gasoline, but it was later realized that the methoxyl group was poisonous to the underground water system. Then, the aromatic content that also has a high ON was increased to produce the high-ON gasoline; however, the aromatics had later been linked to the cancer, and recently the approaches for producing the high-ON gasoline with the lower aromatic content were proposed.³ Nowadays, the gasoline refinery procedure requires a sophisticated balance among various parameters to fulfill both a high ON and being environment friendly. Therefore, it is essential to closely monitor the refinery processes for achieving the high-quality gasoline with a desired ON.

The most common value for the ON is the research octane number (RON) that is measured by running the gasoline in a standard test engine.⁴ However, the measurement of the RON takes time and requires a relatively large amount of gasoline samples, and it normally is performed only for the purpose of quality inspections. In order to circumvent the drawbacks of the RON method, several other techniques have been proposed, such as the gas chromatography,⁵ fluorescent indicator adsorption,⁶ dielectric spectroscopy,⁷ phononic crystal sensing,⁸ flame spectroscopy emission,⁹ near infrared spectroscopy,¹⁰ ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy,^{11,12} etc. Among these techniques, ¹H NMR spectroscopy has been shown to successfully determine the ON for the product gasoline.^{13,14} With the advantages of requiring only a tiny amount of samples and taking a very short time, ¹H NMR spectroscopy has the potential to characterize the gasoline properties during its refinery processes and to facilitate the monitoring of the processes. In this article, ¹H NMR spectroscopy was performed on a variety of gasoline samples covering most stages of the refinery processes, and the gasoline properties including the aromatic, olefin, and paraffin contents, as well as the degree of branching, and the ON were determined by analyzing the ¹H NMR spectra.

2 | MATERIALS AND METHODS

First, six different gasoline samples were studied in this work, covering the refinery processes as follows: (1) the continuous distillation at the normal pressure with an initial boiling point of 24.7°C and a final boiling point of 171.6°C, (2) the continuous distillation at the normal

pressure with an initial boiling point of 46.8°C and a final boiling point of 174.9°C, (3) the fluid catalytic cracking (FCC) stabilization with an initial boiling point of 32.7°C and a final boiling point of 184.9°C, (4) light cracked naphtha (LCN) with an initial boiling point of 29.1°C and a final boiling point of 84.1°C, (5) the heavy cracked naphtha (HCN) with an initial boiling point of 99.2°C and a final boiling point of 191.1°C, and (6) the etherification with the additives being methyl *tert*-butyl ether and/or *tert*-Amyl methyl ether. Then, two product gasoline samples with the ONs of roughly 92 and 95 were also studied (labeled No. 92 and No. 95 below, respectively).

The ¹H NMR experiments were performed on all the samples at the room temperature using a Bruker Ascend 500 MHz spectrometer. The samples were dissolved in CDCl₃, and the chemical shifts were measured relative to tetramethylsilane. The 90° pulse width was 9.5 μs and the spectral width was 10 kHz. The recycle delay time was as long as 1 second so that the spectra were fully relaxed and the number of scans was 16. The resulting ¹H NMR spectrum of Sample III is shown in Figure 1 as an example.

The properties of the gasoline samples including the aromatic, olefin, and paraffin contents (labeled C_a, C_o, and C_p, respectively), and the degree of branching (labeled *D*) are quantified by the empirical equations given in literature¹⁵ as follows:

$$C_a = 0.7216H_a + 1.3323H_x - 0.1400H_d + 10.692 \quad (1)$$

$$C_o = -0.4980H_a + 3.5374H_o + 0.5267H_{c1} + 6.9846 \quad (2)$$

$$C_p = -4.2327H_o - 1.2499H_x + 0.4106H_d + 62.576 \quad (3)$$

$$D = H_d/H_{c2} \quad (4)$$

where H_a, H_o, H_x, H_{c1}, H_{c2}, and H_d are the normalized intensities (ie, normalized to the total intensity) for the different regions of hydrogen types on the ¹H NMR spectrum, and the details are shown in Table 1.¹³

For the gasoline without the methoxyl groups, the octane number (labeled ON(Base)) is determined by the following equation:¹⁵

$$\text{ON(Base)} = 0.2009H_a + 0.4063H_o - 0.0855H_x - 0.3280H_{c1} - 1.1329H_{c2} + 120.5 \quad (5)$$

and for the gasoline with the methoxyl groups, the ON is modified by considering the contribution of the methoxyl groups as follows:¹⁶

$$\text{ON} = \text{ON(Base)} \times \left[1 - \frac{1.25H_m}{H_d} \right] + 115.34 \times \frac{1.25H_m}{H_d} \quad (6)$$

where H_m is the normalized intensity for the methoxy proton region of the ¹H NMR spectrum, and the corresponding chemical shift is also tabulated in Table 1.

FIGURE 1 ^1H NMR spectrum for the gasoline sample obtained in the process of the fluid catalytic cracking stabilization. H_a , H_o , H_α , H_{c1} , H_{c2} , and H_d represent different hydrogen types, and the corresponding chemical shift regions (indicated in double arrows) are detailed in Table 1. Note that the y-axis is the intensity that is normalized to the total intensity of the spectrum

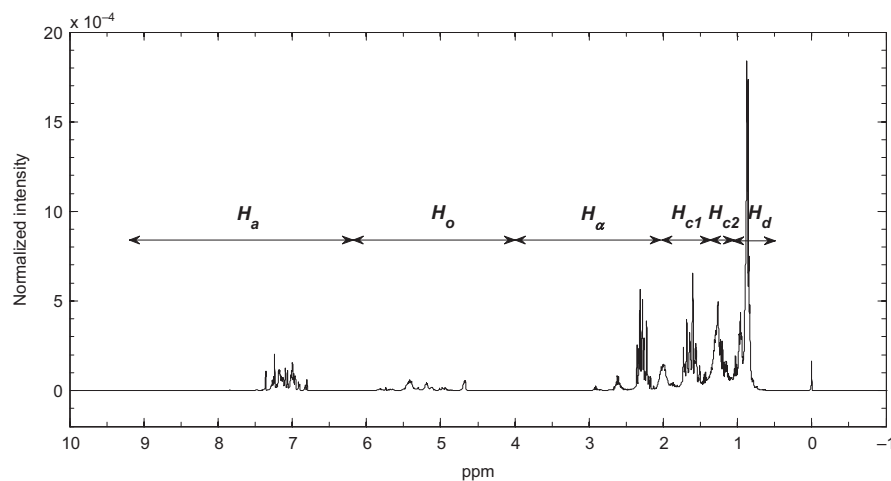


TABLE 1 Hydrogen types and the corresponding chemical shift regions on the ^1H NMR spectrum

Hydrogen type	Chemical shift (ppm)
H_a Proton in aromatic ring	9.2-6.2
H_o Olefin proton	6.2-4.0
H_α Proton in α position of aromatics	4.0-2.1
H_{c1} CH proton of paraffins; proton in β position of aromatics	2.1-1.4
H_{c2} CH_2 proton of paraffins; CH_2 proton in γ and farther positions of aromatics; CH_3 proton in β position of aromatics	1.4-1.05
H_d CH_3 proton of paraffins; CH_3 proton in γ and farther positions of aromatics	1.05-0.5
H_m Methoxy proton	3.26-3.15

3 | RESULTS AND DISCUSSIONS

In this work, the ^1H NMR experiments were first performed on Samples I-VI. Referring to the regions for different types of proton, which are shown in Table 1, the intensities regarding different regions were measured from the resulting ^1H NMR spectra for each sample. The values of H_a , H_o , H_α , H_{c1} , H_{c2} , H_d , and H_m were then determined by normalizing the corresponding intensities to the total intensity of each spectrum. Based on Equations (1)-(6), the properties of the gasoline studied were obtained, including the aromatic, olefin, and paraffin contents, as well as the degree of branching, and the ON, which are shown in Table 2.

It is known to the petroleum refinery community that the continuous distillation processes are the early stages in the refinery of gasoline; the distillation process at the lower temperatures, from which Sample I was obtained, is followed by the distillation process for Sample II at the higher

temperatures. Referring to the results for Sample I in Table 2, it is obvious that the aromatic and olefin contents are low while the paraffin content is high, and the degree of branching is as low as approximately 1. This observation is reflective of the primary constituents of the crude oils, from which Sample I is distilled, since the mixture of the crude oils is dominated by the paraffins and it has a low degree of branching. By comparing the results for Samples I and II, it is found that the aromatic and olefin contents of Sample II are further reduced, while the paraffin content and the degree of branching of Sample II are increased. This trend illustrates the scenario where more paraffins are distilled in this further distillation process for Sample II, and meanwhile the chemical reactions that involve producing more branched-chain hydrocarbons may occur at higher temperatures. It is also observed that the ONs for Samples I (ie, 77.7) and II (ie, 74.6) are both low, which is accounted for by the low aromatic and olefin contents of the gasoline that is obtained from the continuous distillation of the crude oils. The reason why the ON for Sample II is slightly smaller than that for Sample I is that the aromatic and olefin contents, which possess greater ON values, are less in Sample II.

Regarding the results for Samples III and IV in Table 2, it is clear that the aromatic and olefin contents for both samples are substantially enhanced, when compared with Sample II, while the paraffin contents for Samples III and IV are reduced to a v/v ratio below 50%. Besides, the degrees of branching for both samples are dramatically increased up to a value >1.7 . This observation is due to the fact that more aromatics and olefins are produced during the FCC stabilization process for Sample III, and meanwhile a great amount of branched-chain hydrocarbons is also formed. In the hydrogenation process at the low temperatures for Sample IV, a large number of olefins are produced, and the quantity of the branched-chain hydrocarbon molecules are further increased (ie, $D=2.63$), when

TABLE 2 Aromatic, olefin, and paraffin contents, as well as the degree of branching, and the octane number for Samples I-VI, determined from the ^1H NMR spectra and Equations (1)-(6)

Sample	Aromatics (v/v %)	Olefins (v/v %)	Paraffins (v/v %)	Degree of branching	Octane number
I	18.3	21.0	60.4	1.06	77.7
II	6.3	12.4	81.1	1.30	74.6
III	27.5	30.4	42.0	1.79	94.0
IV	11.2	43.3	45.3	2.63	95.8
V	37.0	11.6	50.9	1.24	87.9
VI	18.2	25.0	56.2	1.26	94.9

TABLE 3 Aromatic and olefin contents, as well as the octane number for two product gasoline samples (No. 92 and No. 95), determined from the ^1H NMR spectra and Equations (1)-(6)

Sample	Aromatics (v/v %)	Olefins (v/v %)	Aromatics+Olefins (v/v %)	Octane number
No. 92	33.5	11.6	45.1	91.4
No. 95	35.8	14.8	50.6	95.3

Sample	Aromatics* (v/v %)	Olefins* (v/v %)	Aromatics**+Olefins* (v/v %)	RON
No. 92	28.8	15.7	44.5	92.2
No. 95	35.0	18.2	53.2	96.1

Aromatics* and Olefins* were obtained by chromatography, and RON is the research octane number which was determined by running the gasoline in a standard test engine. The values of Aromatics*, Olefins*, and RON were directly provided by the petroleum company.

compared with the FCC process (ie, $D=1.79$) in which Sample III was obtained. Note that the small aromatic content of 11.2% for Sample IV is indicative of the fact that the light naphtha products of Sample IV contain most of the hydrocarbon molecules with six or fewer carbon atoms. For both Samples III and IV, the greater v/v ratios of the aromatic and olefin contents, together with the large values of the degrees of branching, result in the higher ONs which are above 94, as shown in Table 2. Specially, the LCN (Sample IV) with an ON of as great as 95.8 can directly be employed in the final blending of the product gasoline, which would then be ready for commercial use.

Different from Sample IV where the light naphtha products are obtained at the low temperatures below 90°C, in the hydrogenation process at the high temperatures (ie, above 90°C) for Sample V, the heavy naphtha products that consist of most of the hydrocarbons with more than six carbon atoms are produced. At the high temperatures, more aromatics are likely to form while fewer olefins remain; this gives rise to the reverse features for the aromatic and olefin contents upon comparing Samples IV and V, as revealed in Table 2, that is, 11.2% aromatics and 43.3% olefins for Sample IV vs 37.0% aromatics and 11.6% olefins for Sample V. It is also observed that the degree of branching for Sample V is low, and this may be attributed to the high v/v ratio of the aromatics. Although the net ratios of the aromatics and the olefins are similar

(ie, Aromatics+Olefins=48.6% for Sample V and 54.5% for Sample IV), the degree of branching for Sample V is much lower than that for Sample IV. Therefore, the resulting ON for Sample V (ie, 87.9) is measured to be lower than that for Sample IV (ie, 95.8). Unlike the LCN, given the relatively low ON of the heavy cracked naphtha, it may need to be fed into further etherification processes in order to increase the ON of the gasoline. For Sample VI, it is observed from Table 2 that although the net v/v ratio of the aromatics and the olefins (ie, Aromatics+Olefins=43.2%) and the degree of branching (ie, $D=1.26$) are similar to that for Sample V (ie, Aromatics+Olefins=48.6%, and $D=1.24$), the ON for Sample VI is significantly increased to a value of 94.9. This greater value of the ON for Sample VI is attributed to the introduction of the methoxyl additives in the etherification process, which can greatly raise the ON of the gasoline, and the v/v ratio of the methoxyl molecules in Sample VI was measured to be roughly 12% (not shown in Table 2 for clarity). Based on the results for Sample VI, it is clear that the gasoline obtained from the etherification process has a higher ON, and the etherified gasoline is thus ready for the final blending for the product gasoline.

So far, with measuring the parameters including the aromatic, olefin, and paraffin contents, the degree of branching, as well as the ON, we have demonstrated that the ^1H NMR spectroscopy can be implemented in the

characterization and the monitoring of the refinery processes of the gasoline. In order to verify the aforementioned discussions, further experiments were also carried out on two product gasoline samples. The ^1H NMR determined results are presented in Table 3, together with the values for the related parameters that were directly provided by the petroleum company where the product gasoline samples were obtained.

Referring to Table 3, it is evident for each product gasoline sample that although the individual aromatic or olefin content, determined from the ^1H NMR spectroscopy, is slightly different from that provided by the petroleum company, the net v/v ratios of the aromatics and the olefins are similar. Take No. 92 for example, the ^1H NMR derived value of “Aromatics+Olefins” is 45.1% and the company provided value of “Aromatics*+Olefins*” is 44.5%. This similarity in the aromatic and olefin contents result in the similar ONs between the values measured by ^1H NMR (ie, 91.4 for No. 92 and 95.3 for No. 95) and the RON values that were determined by running the gasoline in a standard test engine (ie, 92.2 for No. 92 and 96.1 for No. 95). The good agreements for both product gasoline samples indicated in Table 3 clearly illustrate that the ^1H NMR spectroscopy can be used as a useful tool to assess the properties of gasoline.

4 | CONCLUSION

In this work, ^1H NMR spectroscopy has been performed on a variety of gasoline samples, which have covered most stages of the refinery processes of gasoline. The gasoline properties, including the aromatic, olefin, and paraffin contents, as well as the degree of branching, and the ON, have been determined by analyzing the ^1H NMR spectra. The results have shown that the gasoline samples obtained from different refinery processes can be characterized by employing the ^1H NMR spectroscopy, and the refinery processes of gasoline can thus be monitored accordingly. The ^1H NMR experiments have also been applied on two product gasoline samples. The results have shown that the NMR-determined ONs are similar to the RON values measured by running the gasoline in a standard test engine; this agreement has clearly verified that the ^1H NMR spectroscopy can be used as a convenient and fast tool to assess the gasoline properties. Based on the results, we have successfully applied the ^1H NMR spectroscopy in the characterization of the refinery products of gasoline.

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