

RESEARCH ARTICLE

Open Access



A ^1H NMR method for the estimation of hydrogen content for all petroleum products

Sujit Mondal*, Ravindra Kumar, Veena Bansal and M. B. Patel

Abstract

Background: Hydrogen content is an important parameter for all petroleum products, because the performance of the products for specific application depends on the concentration of hydrogen in it. Further, hydrogen content can be used as a measure for quality control during the production process and assess the quality of the products, which is governed by the catalyst used. Therefore, to get the desired petroleum products like MS and HSD, pilot scale evaluation of different catalysts plays an important role in problem solving during troubleshooting in refineries. During evaluation studies the performance of catalyst depends upon the hydrogen consumption and mass balance in any catalytic process. In order to calculate total hydrogen consumption during production of different petroleum products an effort has been made to develop a universal method based on nuclear magnetic resonance (NMR) technique, that allows estimating hydrogen content in all petroleum fractions, ranging from IBP to 530+ °C.

Methods: The method uses hexamethyldisiloxane (HMDSO) for the first time as a quantitative reference standard respect to which the H content of unknown samples has been estimated. The newly developed method can also determine H/C and O/C ratio of ethanol blended fuel in a given sample without any additional experimentation.

Results: Hydrogen content for twenty five model compounds was determined along with nearly hundred petroleum fractions. There has been found to be good correlation between the existing ASTM D5291 and developed NMR spectroscopic based methods. For low boiling petroleum fractions, where ASTM D5291 is not suitable, there is no direct way to correlate the data. However, as the hydrogen content estimated for some model compounds shows a high degree of correlation $R^2 = 0.998$, between theoretical values and estimated values, indirectly validate the developed method.

Conclusions: A universal NMR based method for the estimation of hydrogen content in all sort of petroleum products irrespective of their origin, composition, boiling range has been developed.

Keywords: NMR; Crude oil; Petroleum fractions; Recycle delay; Hydrogen content

Background

Combustion of fossil fuel is what we think of as burning processes basically a reaction with oxygen. Fossil fuels are composed primarily of hydrocarbons. The amount of energy released during combustion is dependent on the oxidation state of the carbons in the hydrocarbon which is related to the hydrogen/carbon (H/C) ratio. The more hydrogen per carbon, the lower the oxidation state and the more energy that will be released during the oxidation reaction. The presence of oxygenates in fuels reduces the amount of carbon monoxide and unburned fuel in the exhaust gas. Oxygenate blending is basically the addition

of oxygen-bearing compounds such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and ethanol to gasoline/diesel. Throughout the USA, oxygenate blending is mandated by EPA regulations to reduce smog and other airborne pollutants. For example, in Southern California, a fuel must contain 2 % oxygen by weight, resulting in a mixture of 5.6 % ethanol in gasoline (Removal of reformulated gasoline oxygen content requirement (national) and revision of commingling prohibition to address non-oxygenated reformulated gasoline (national), 2006). The resulting fuel is often known as reformulated gasoline (RFG) or oxygenated gasoline. Ethanol-blended fuel has been a great success in Brazil where ethanol is being used as a primary fuel for several decades; E-85 to E-100 are the most common in them.

* Correspondence: mondals3@indianoil.in
Indian Oil Corporation Limited, R&D Center, Sector 13, Faridabad 121007, India

Several countries in the European Union also use ethanol-blended gasoline due to environmental consideration. In India, the government has mandated up to 5 % ethanol for metro cities, recently for all over the country, and has a plan to extend it up to 10 % in the future (Government to take a call on ethanol price soon, 2011). Thus, in the case of a blended fuel (oxy-diesel, reformulated gasoline), in addition to the H/C ratio, the O/C ratio would be a parameter of interest (Sarpal et al. 1997).

The pilot plants of refining technology division at the Research and Development Center of Indian Oil Corporation play an important role in troubleshooting problems in refineries. Pilot plant research is also essential in evaluating catalysts produced by IOC as well as from various vendors prior to the purchase. The quality of the research depends on accurate calculations of mass balance and hydrogen consumption during catalytic processes. Additionally, optimizing the feed severity for the existing process units, e.g., hydrocracker, FCC units is having great significance for the refineries. Identifying little changes in the catalyst performance can only be made possible with well-supported pilot plant studies. The quality of this support can be improved by enhancing the existing analytical methodologies. Even a small difference in the catalyst performance can substantially affect the bottom line of a refinery. The development of a universal nuclear magnetic resonance (NMR) technique which will allow us to calculate H/C (hydrogen content) ratio as well as O/C (oxygen content) ratio for all petroleum fractions, ranging from initial boiling point (IBP) to vacuum residue (VR), and in blended fuels is an effort in this direction.

NMR spectroscopic technique has long been used for both qualitative (Gillet et al. 1980; Kvalheim et al. 1985) and quantitative (Srivastava 1982; Allen 1985; Abu-Dagga and Ruegger 1988; Smirnov et al. 1992; Sarpal et al. 1998; Bansal et al. 1998; Bansal et al. 2007; Bansal et al. 2014; Mirotnik et al. 2001; Young and Galya 1984; Poveda and Molina 2012) studies of petroleum products. The main focus of these studies revolve around understanding the qualitative composition and to quantify average structural parameters such as aromatic and aliphatic content, average chain length for aliphatic moieties, and average number of substituents on the aromatic ring. A relatively few number of studies (ASTM D-4808 1992; ASTM D-3701 1992; ASTM D-7171 2011; Gautier and Quignard 1995; Kennedy et al. 1998) have appeared on the determination of carbon and hydrogen contents in crude oil and petroleum fractions using NMR technique. The traditional combustion method ASTM D5291 (ASTM D-5291 1996) has its own limitations for low boiling fractions and affords 0.4 % repeatability and 0.8 % reproducibility for a medium hydrogen content of 10 %. The ASTM methods D4808 (ASTM D-4808 1992) and D3701 (ASTM D-3701 1992) make use of a low-resolution continuous-wave NMR

spectrometer and also use dodecane (C₁₂) as an external standard for quantitative determination of hydrogen. The ASTM method D7171 (ASTM D-7171 2011) covers the determination of the hydrogen content of middle distillate petroleum products using a low-resolution pulsed NMR spectrometer. These methods are restricted to a low-resolution NMR equipment that involves large quantities of samples (~20 g), standard, and large volumes of organic solvents such as tetrachloroethylene (~½ l).

So far, only one report has come out in which Khadim et al. (2003) used high-resolution NMR spectroscopy to determine the hydrogen and carbon contents in crude oil and petroleum fractions. In their study, for the first time, a new reference standard, bis(trimethylsilyl)methane (BTMSM), has been used for both proton and carbon-13 NMR to quantify the hydrogen and carbon in petroleum products. BTMSM has two sets of proton coming at δ 0.02 ppm (CH₃) and δ -0.27 ppm (CH₂) with respect to tetramethylsilane (TMS) making the measurement less predictable.

Herein, we report the development of a simple and reliable spectroscopic method for determining hydrogen, carbon, and oxygen contents in a wide range of petroleum products including gasoline, naphtha, kerosene, diesel, vacuum gas oil (VGO), and residua as well as in composite mixture, reformulated gasoline, and oxy-diesel. The study is based on using hexamethyldisiloxane (HMDSO), as an internal reference standard for quantitative calculation of hydrogen content and oxygenates in petroleum brands. The method uses high-resolution NMR spectroscopy and small amount of sample along with 12 to 15 wt% of the aforesaid internal standard. HMDSO is used in liquid bandages to protect damaged skin from irritation from other bodily fluids. It is being studied for making low-*k* dielectric materials for the semi-conductor industries by plasma-enhanced chemical vapor deposition (PECVD) (Barni et al. 2012). HMDSO has recently been used in quantitative tissue oximetry (Kodibagkar et al. 2006; Kodibagkar et al. 2008). To our knowledge, HMDSO is highly inert and has not previously been employed as an internal standard or frequency reference for quantitative purposes in conventional NMR spectroscopy.

Methods

Twenty five model compounds and about 100 oil fractions were analyzed by the ¹H NMR method using HMDSO as the reference standard. In some cases, dioxane was also used as reference standard. Most of the samples were also analyzed by ASTM D5291 combustion method and the results were compared. Model compounds were purchased either from Sigma-Aldrich and Merck (New Delhi). Crude oil fractions, naphtha, gasoline, aviation turbine fuel (ATF), diesel, light cycle oil (LCO), clarified oil (CLO), light gas oil (LGO), vacuum gas oil (VGO), vacuum

residue (VR), and several composite samples were collected from different pilot plants (PP) and refineries of Indian oil.

Combustion method

The hydrogen content of all high boiling range (diesel and above) samples were analyzed by a CHNS analyzer Vario EL-III from M/s Elementar, Germany, as per ASTM D5291 method. The samples are weighed in tin or aluminum tray/capsule. The tray/capsule after folding properly is injected into a high-temperature furnace and combusted in pure oxygen under static conditions.

NMR method

All proton NMR spectra were recorded either on a Agilent DD2 NMR spectrometer operating at a proton frequency of 500 MHz, spectral width of 8012.8 Hz (-2.0 to 14.0 ppm), 90° pulse = 11.8 μ s, relaxation delay = 20 s, and digital resolution of 0.49 Hz/point or on a JEOL ECA-500 spectrometer operating at a proton frequency of 500 MHz and the same specified parameters as above (90° pulse = 10.7 μ s). Sixteen repetitions were averaged with 32K data points and 6.24- and 6.38-min experimental time, respectively, for DD2 and ECA machines. All the NMR spectra were integrated after baseline correction, and a mean of minimum three integration values has been taken for each calculation. It has been found that increasing the relaxation delay from 5 to 20 s does significantly influences the integral value and so most of the samples were recorded with 20-s relaxation delay.

Measurement of T1 by inversion recovery method

The spin-lattice relaxation times for proton, T1s (H), of HMDSO and T1s (H) for some model compounds and fractions have been measured following weighted linear inversion recovery method using 32 points. Best line fitting was ensured after phase and drift correction along with complete inversion during processing of T1 data in a JEOL ECA-500 spectrometer. The T1 (H) of HMDSO has thus been measured in CDCl₃ at different concentrations ~0.14, ~0.19, ~0.24, and ~0.25 M giving rise to corresponding T1s 4.15, 3.70, 3.26, and 3.17 s, respectively, at an ambient temperature (~25 °C) (see Additional file 1).

Results and discussion

Selection of a reference compound

Tetramethylsilane (TMS) has been widely used as an internal frequency reference for both proton and carbon-13 NMR spectroscopy. Dodecane (*n*-C12) is used as an external standard for quantitative determinations of hydrogen by the ASTM methods D4808, D3701, and D7171. Both TMS and dodecane have serious limitations. TMS is highly volatile and not suitable for quantitative purposes. Dodecane cannot be used as an internal reference as its signals would

be masked and overlapped by those arising from the hydrocarbon sample. Dioxane, a better reference standard in terms of boiling point, inertness, and single resonance signal, could be used for quantitative purpose, but overlapping its ¹H NMR signal at δ 3.66 with the OCH₂ of ethanol or other oxygenates makes it unsuitable for oxygenate-blended fuels, viz., reformulated gasoline and oxy-diesel. Bis(trimethylsilyl)methane (BTMSM), used by Khadim et al. for high-resolution NMR spectroscopy to determine the hydrogen and carbon contents in crude oil and petroleum fractions, has two different sets of protons and carbons making the use of BTMSM a little unpredictable for quantitative purpose. Hexamethyldisiloxane (HMDSO) meets all the desirable characteristics to be used as an internal reference for the following reasons:

- HMDSO is chemically inert, and it does not react with the usual NMR solvents or the solutes generally used in petroleum industry.
- The boiling point of HMDSO (101 °C) is suitable for quantitative measurement and handling purpose.
- HMDSO is highly hydrophobic and have strong nuclear magnetic resonance spin lattice relaxation rate, hence provides quantitative hydrogen in NMR (ASTM D-7171 2011). Molecular symmetry provides a single NMR signal.
- The hydrogen and carbon contents of HMDSO are 11.17 and 44.38 %, respectively. An H content of 11.17 % lies almost at the focal point of the H content of hydrocarbons ranging from 6 to 16 % making it suitable for quantification through comparing.

Purity of HMDSO

The formula weight of HMDSO, C₆H₁₈OSi₂, is 162.38, which corresponds to carbon (44.38 wt%), hydrogen (11.17 wt%), oxygen (9.85 wt%), and silicon (34.59 wt%). The purity of HMDSO was checked by proton, C13, and Si29 NMR spectroscopy. In its proton NMR spectrum in CDCl₃, HMDSO showed a peak at 0.065 ppm relative to TMS. ¹³C NMR spectrum of it also showed a resonance signal at 2.05 ppm. ²⁹Si NMR showed a signal at 7.03 ppm downfield from ²⁹Si signal of TMS. No additional signal was observable in the ¹H, ¹³C, or ²⁹Si NMR spectra. Moreover, the purity of HMDSO was also estimated with respect to ultrapure dioxane. While comparing with dioxane (99.99 %), the HMDSO was found to be pure enough as claimed by the Aldrich chemical company (>99.5 %). The results are summarized in Table 1. The percentage of hydrogen in HMDSO as calculated by NMR considering dioxane as pure component and is having 9.15 % hydrogen in it comes out to be 11.18, very close to its theoretical value of 11.17. In the same manner, the hydrogen in dioxane has been calculated as 9.13 %.

Table 1 Mutual purity check of HMDSO and dioxane by proton NMR (d1 = 20 s, scan = 32) in CDCl₃

No. of entry	Dioxane (Fluka, 99.99 %)			HMDSO (Aldrich, >99.5 %)		
	C, 54.53; H, 9.15; O, 36.32 (wt%)			C, 44.38; H, 11.17; O, 9.85; Si, 34.59 (wt%)		
	Weight taken (mg)	Weight (mg) by NMR ^a	H, by NMR ^a (wt%)	Weight taken (mg)	Weight (mg) by NMR ^b	H, by NMR ^b (wt%)
Solution 1	12.06	11.99	9.10	14.85	14.92	11.19
Solution 2	10.18	10.20	9.15	11.39	11.4	11.21
Solution 3	9.08	9.14	9.14	15.57	15.65	11.14

^aHMDSO as reference standard^bDioxane as reference standard**Effect of recycle delay (d1) on hydrogen content**

It has been noticed that the variation of the number of scan (16 to 64) does not have any significant effect on the integral values in the different region of a ¹H NMR spectrum for a fairly concentrated solution and hence on the estimated H content thereof. A rather variation of the relaxation/recycle delay (d1) has dramatic effect on the outcome of H content. Quantitative representation of a NMR active nuclei to the corresponding integral value depends primarily on the spin-lattice (or longitudinal) relaxation time (T1) for that nuclei and the d1 given during data acquisition. Though the T1 (H) of HMDSO diverge a little in a mixture of various samples (model compounds, gasoline, diesel, VGO, naphtha, etc.) depending on the concentration of the sample and HMDSO in the solution, it has always been found varying from 3.0 to 4.4 s at various samples examined (see Additional file 1). So to get a representative H content using HMDSO as internal standard, the experiment was run at d1 = 20 s (minimum) and scan = 16.

Survey of model compounds

Hydrogen contents of 25 selected model compounds as determined by proton NMR have been shown in Table 2. Almost all of the compounds listed in the table show that proton NMR determination gave the hydrogen contents within ±2 % of the theoretically calculated value except few compounds which have the T1s (H) much higher than that of HMDSO. These compounds gave excellent result while recorded at a higher d1 (40 or 60 s). The NMR method successfully and accurately determined hydrogen content in molecules containing as low as 1.67 wt% hydrogen and as high as 15.88 wt%. For example, the proton NMR method yielded hydrogen contents of 1.51 wt% for 1,2,4-trichlorobenzene, 2.55 wt% for 1,2-dichlorobenzene, and 3.90 wt% for furfuraldehyde compared to the theoretical values of 1.67, 2.74, and 4.20 wt%, respectively, giving high relative errors. While the spectra were recorded at d1 = 40 or 60 s, these compounds provided excellent result, devoid from any error (entry 1-3, 9, 11). The compounds having lower T1s (H) also require an optimum relaxation delay (20 s) to avoid erroneous H content (entry 17, 22, and 25) pertaining to

the T1 (H) of HMDSO. For example, while recorded with d1 = 20 s, dodecane and 2,2,4-trimethylpentane (isooctane) gave H contents of 15.44 and 16.01 wt% compared to their theoretical values 15.39 and 15.88 wt%, respectively, but gave highly erroneous H content with d1 = 5 s (16.64 and 16.30 wt%) or 10 s (15.77 and 16.08 wt%) (entry 22 and 25) due to incomplete relaxation of the reference compound. Comparable results were also obtained for tetralin [8.94 wt% by NMR vs. theoretical 9.15 wt%], pentacosane [15.0 wt% by NMR vs. theoretical 14.86 wt%], 2,5-dimethyl-2,4-hexadiene [13.15 wt% by NMR vs. theoretical 12.81 wt%], and decane [15.73 wt% by NMR vs. theoretical 15.59 wt%].

Crude oil fractions

Around 50 different crude oil samples covering lower middle to high boiling fractions have been subjected to both 1H NMR as well as ASTM-5291 combustion methods to determine the hydrogen content. The results are summarized in Table 3. As expected, the lower boiling fractions showed substantial difference in their H content by these two methods. It is noted that for low boiling fractions combustion method provides less hydrogen than the NMR method. As the boiling range increases, the differences in H content by these two methods decrease. A total of 32 crude oil fractions covering light (IBP-95) to higher (250-369) hydrocarbons (entry 1-32) and 18 other fractions (entry 33-50) covering ATE, diesel, to VGO were analyzed for their hydrogen content by the NMR method. All samples were analyzed by the NMR method using both HMDSO and dioxane as internal reference separately. Table 3 shows that the comparison for estimated percentage of hydrogen content is fairly good between HMDSO and dioxane. Equation 1 has been used for the estimation in all the cases. In the case of dioxane, HMDSO has been replaced by dioxane in Eq. 1:

$$\begin{aligned}
 \text{H (wt\%)} &= \frac{I (\text{Sample})}{I (\text{HMDSO})} \times \frac{W (\text{HMDSO})}{W (\text{Sample})} \times \text{H (HMDSO)} \\
 &= \frac{89.02}{10.98} \times \frac{14.65 \text{ mg}}{100.60 \text{ mg}} \times 11.17 \text{ wt\%} \\
 &= 13.19
 \end{aligned} \tag{1}$$

Table 2 H content in model compounds by proton NMR

No.	Name of the compound	%H, by NMR ^a	%H, theoretical	%Rel Err	H at d1 = 5 s/10 s/40 s/60 s/Scan = 16
1	1,2,4-Trichlorobenzene, Spectrochem, 99.5 %	1.51	1.67	-9.58	1.32/1.4/1.66/1.67 ^b
2	1,2-Dichlorobenzene, Spectrochem, 99.5 %	2.55	2.74	-10.58	2.24/2.34/2.68/2.77 ^b
3	Furfuraldehyde, freshly distilled	3.90	4.20	-7.14	3.42/3.54/4.00/4.20 ^b
4	2-Methylnaphthalene, Aldrich, 98 %	6.94	7.09	-2.11	
5	Toluene, Merck, 99.8 %	8.70	8.70	0.00	
6	4-(Decyloxy)benzoic acid, Aldrich, 98 %	8.91	9.08	-1.98	
7	Tetralin, Merck, 98 %	8.94	9.15	-2.30	9.10/8.97/8.95/8.95 ^c
8	Dioxane, Fluka, 99.99 %	9.13	9.15	-0.22	
9	Ethylbenzene, Aldrich, 99 %	8.84	9.49	-6.85	8.37/8.52/9.16/9.47 ^b
10	Mesitylene, Aldrich, >99 %	10.18	10.06	1.19	
11	Propylbenzene, Merck, >98 %	10.09	10.06	0.30	9.73/9.97/10.12/10.12 ^b
12	2-(2-Ethoxyethoxy)ethanol, 98 %	10.25	10.52	-2.57	
13	Octylphenol, Aldrich, 98 %	10.51	10.75	-2.23	
14	Tricyclo[5.2.1.0]decane, Aldrich, 98 %	10.90	11.84	-7.94	
15	2,4-Dimethyl-1,3-pentadiene, Aldrich, 98 %	12.46	12.58	-0.95	
16	2,5-Dimethyl-2,4-hexadiene, Aldrich, >96 %	13.15	12.81	2.65	
17	2-Ethylhexanol, Aldrich, 99 %	13.85	13.93	-0.57	14.60/13.86/13.87/13.88 ^d
18	Pentylcyclohexane, Koch-Light Lab Ltd., >99 %	14.55	14.29	1.82	
19	2,4,4-Trimethyl-1-pentene, Aldrich, 99 %	14.00	14.37	-2.59	14.30/14.20/14.05/14.07 ^c
20	Pentacosane, Aldrich, 99 %	15.00	14.86	0.95	
21	Octadecane, Aldrich, 99 %	15.25	15.05	1.33	
22	Dodecane, Aldrich, >99 %	15.44	15.39	0.32	16.64/15.77/15.41/15.41 ^d
23	Decane, Aldrich, >99 %	15.73	15.59	0.90	
24	Nonane, Aldrich, >99 %	15.89	15.72	1.02	
25	2,2,4-Trimethylpentane, SDH, >99 %	16.01	15.88	0.82	16.30/16.08/16.03/16.03 ^d

All the samples were recorded in CDCl₃ using HMDSO as internal reference, the peak of which is fixed at 0.07 ppm

^ad1 = 20 s, scan = 16

Measured T1 for the compound protons are ^btoo high, ^ccomparable with HMDSO, and ^dless than that of HMDSO

Standard diesel

As a representative example, NMR spectrum of #2 diesel oil standard (AR330, Lot No. 330903) from Alpha Resources, Inc., a certified reference material having hydrogen content of 13.08 % (by ASTM D5291) is shown in Fig. 1. The hydrogen content of #2 diesel thus calculated by the NMR method following Eq. 1 is 13.19 (entry 36, Table 3) and by combustion method in our laboratory is 13.11 wt%. It is interesting to mention that given d1 = 40 s, the NMR method gave the hydrogen content for this diesel 13.10 wt%. As the diesel is free from olefin, there has been no signal between 4 and 6 ppm.

Mangala crude

The Mangala crude 1 (entry 33, Table 3) and Mangala crude 2 (entry 27, Table 4) have been subjected to NMR analysis to estimate the hydrogen content in them. Both the samples showed excellent correlation between the hydrogen estimated by the developed NMR method

(13.66 and 12.94 wt%, respectively) and the ASTM D5291 combustion method (13.80 and 12.98 wt%, respectively) (see Additional file 1).

Distribution of the H content calculated by NMR and ASTM D5291 combustion methods

The distribution of the H content estimated by NMR and ASTM combustion methods is shown in Fig. 2. Region A indicates a wide variation in H content while regions B and C show good correlation between both methods. Region B, consisting primarily middle distillates, and region C, consisting higher boiling fractions (CLO, VGO, etc.), behave differently in terms of deviation from ASTM D5291 combustion method. While the NMR-derived H content shows little higher values than ASTM method in the former case, it shows less H content for the latter. Alternatively, samples with less aromatics (light and middle distillates) gave higher hydrogen and samples with more aromatics (heavier cuts) provided less hydrogen content

Table 3 H in petroleum fractions by ¹H NMR (d1 = 20 s, scan = 16) and ASTM D5291 methods

No.	Sample	H, by NMR (HMDSO) ^a	H, by combustion	Diff (%)	H, by NMR (dioxane) ^b
1	Crude 1 C5-95 ^d	14.80	–	–	14.81
2	Crude 1 95-149 ^d	14.63	11.51	27.1	14.67
3	Crude 1 149-250 ^d	14.01	13.77	1.8	14.05
4	Crude 1 250-369 ^d	13.41	13.30	0.8	13.44
5	Crude 2 C5-95 ^d	14.72	–	–	14.73
6	Crude 2 95-149 ^d	14.88	11.43	30.2	14.88
7	Crude 2 149-250 ^d	14.21	13.71	3.6	14.02
8	Crude 2 250-369 ^d	13.57	13.41	1.2	13.55
9	Crude 3 C5-95 ^d	15.55	–	–	15.56
10	Crude 3 95-149 ^d	14.68	11.49	27.8	14.68
11	Crude 3 149-250 ^d	14.31	13.83	3.5	14.31
12	Crude 3 250-369 ^d	13.53	13.39	1.0	13.55
13	Crude 4 C5-95 ^d	15.00	–	–	15.21
14	Crude 4 95-149 ^d	14.59	11.69	24.8	14.69
15	Crude 4 149-250 ^d	14.27	13.83	3.2	–
16	Crude 4 250-369 ^d	13.15	13.22	–0.5	–
17	Crude 5 C5-95 ^d	15.09	–	–	15.21
18	Crude 5 95-149 ^d	14.54	11.89	22.3	14.59
19	Crude 5 149-250 ^d	13.95	13.55	3.00	–
20	Crude 5 250-369 ^d	13.16	13.21	–0.3	–
21	Crude 6 C5-95 ^d	15.35	–	–	15.53
22	Crude 6 95-149 ^d	14.67	12.05	21.8	14.74
23	Crude 6 149-250 ^d	13.89	13.54	2.6	–
24	Crude 6 250-369 ^d	13.17	13.03	1.1	–
25	Crude 7 C5-95 ^d	15.07	–	–	15.14
26	Crude 7 95-149 ^d	14.72	11.97	23	14.96
27	Crude 7 149-250 ^d	14.45	13.87	4.2	–
28	Crude 7 250-369 ^d	13.07	13.11	–0.3	–
29	Crude 8 C5-95 ^d	15.85	–	–	15.88
30	Crude 8 95-149 ^d	15.38	11.51	33.6	15.38
31	Crude 8 149-250 ^d	14.82	13.92	6.5	–
32	Crude 8 250-369 ^d	13.55	13.47	0.6	–
33	Mangala crude 1 ^d	13.65	13.80	–1.1	13.71
34	(Gasoline range) ^e	13.45	11.91	12.5	13.43
35	(Gasoline range) ^e	13.37	11.93	11.8	13.41
36	Diesel Std	13.19/13.10 ^c	13.11	0.6	13.19
37	HR OHCU mixed feed ^f	12.45	11.78	5.7	12.32
38	HR OHCU test feed ^f	12.42	11.99	3.6	12.56
39	MRU2 Pdt VGO ^e	12.13	11.99	1.2	12.13
40	PR OHCU test feed ^f	12.07	11.63	3.8	11.86
41	MRU2 feed VGO ^e	11.52	11.69	–1.5	11.49
42	VGO HT ^f	11.07	11.82	–6.3	11.09
43	HR OHCU furfural extract ^f	10.79	10.67	1.1	10.71
44	MRU10 LCO feed ^e	9.70	9.98	–2.8	9.70

Table 3 H in petroleum fractions by 1H NMR (d1 = 20 s, scan = 16) and ASTM D5291 methods (Continued)

45	ATF biojet-1 ^e	14.57	12.21	19.3	14.57
46	ATF biojet blend (UOP) ^e	14.95	12.33	21.1	14.96
47	ATF biojet blend (Jat) ^e	14.63	12.35	18.5	14.63
48	Kerosine Std	14.83	12.55	18.2	14.98
49	Std HSD-PQM	14.26	13.79	3.4	14.24
50	High diesel feed ^e	12.80	12.87	-0.5	12.81

Samples were recorded in neat CDCl₃ using ^aHMDSO and ^bdioxane as internal reference

^cd1 = 40 s

^dCrude oil

^ePilot plant (PP)

^fRefinery

by the NMR method. Careful analysis of Fig. 2 in combination with Tables 3 and 4 clearly indicates that low boiling fractions or composites having low boiling range products gave greater variation in H content by NMR and ASTM 5291 methods.

Repeatability and reproducibility in H content for crude oil samples

The accuracy of the NMR method is heavily dependent on the accuracy of the weight taken for reference compound as well as for the sample chosen. The H content for some of the crude oil fractions and few model compounds have been estimated three times with variable amount of HMDSO and samples under the same experimental condition. Table 5 shows that in the case of C5-95 samples variations in the repetitions are much greater (RSD = 0.254) than those of 149-250 samples (RSD = 0.089). Octadecane

and some other model compounds show excellent repetition (RSD of ~0.033).

The reproducibility of the developed proton NMR method has been established and found to be satisfactory when some of the samples were recorded by two different operators following the same experimental conditions, sometimes in two different spectrometers as well.

Variation in H content with integration

The NMR method is sensitive to the values of integration taken for the different region of the spectrum. Though the mean of the three integration values was taken for each spectrum, to determine the relative standard deviation of different integral values, several (8) integrations have been taken after baseline and drift correction for few model compounds as well as for some fractions. RSD in integration values found for model compounds is 0.025 and for fractions is 0.139.

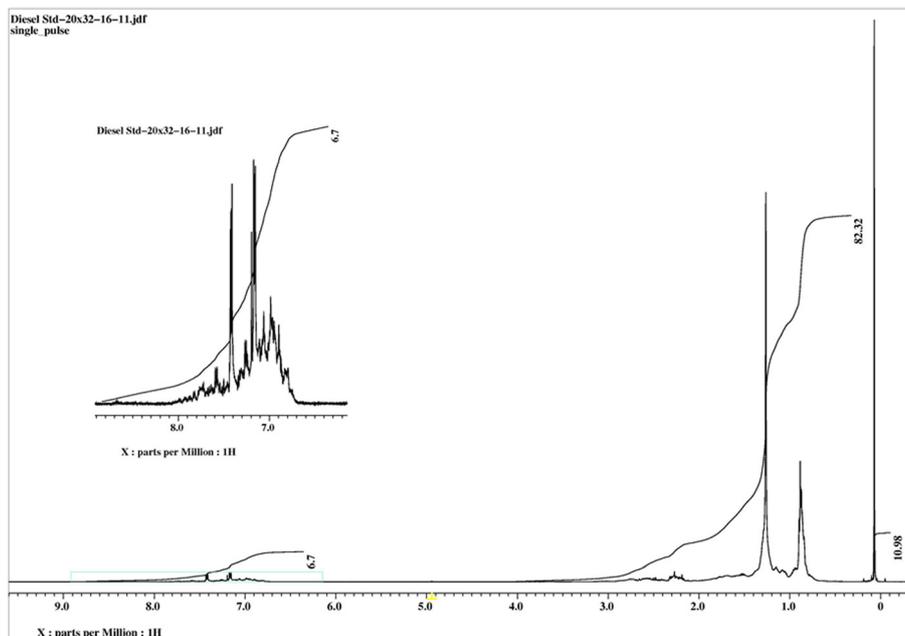


Fig. 1 1H NMR spectrum of #2 diesel oil with HMDSO

Table 4 Composite samples: new NMR method vs combustion method

No.	Sample ^a name	H, by NMR	H, by combustion	Diff (%)
1	Feed crude 9	10.83	11.13	-2.7
6	Feed crude 9 (after 2 months)	10.54	11.03	-4.4
2	Pdt at rxn 380 °C (from crude 9)	12.24	11.51	6.3
3	Pdt at rxn 400 °C (from crude 9)	12.87	11.97	7.2
4	Pdt at rxn 420 °C (from crude 9)	13.08	11.91	9.8
5	Feed crude 10	11.88	11.57	2.7
7	Pdt at rxn 380 °C (from crude 10)	12.22	11.59	5.4
8	Pdt at rxn 400 °C (from crude 10)	12.40	11.96	3.7
9	Feed crude 11	11.50	11.55	-0.4
10	Pdt at rxn 400 °C (from crude 11)	12.95	11.88	9.0
11	Pdt cut IBP-70 °C (1)	15.95	-	-
12	Pdt cut IBP-70 °C (2)	15.84	-	-
13	Cut C5-140 (1)	15.10	-	-
14	Cut C5-140 (2)	14.51	-	-
15	Base case Pdt	14.20	14.41	-1.5
16	Diesel case Pdt	14.10	13.89	1.5
17	Pdt cut 70-200 °C (1)	13.74	12.21	12.5
18	Pdt cut 140-330 °C	13.36	12.93	3.3
19	Pdt cut 70-200 °C (2)	13.34	12.08	10.4
20	Pdt cut 330-400 °C	12.54	13.01	-3.4
21	Pdt cut 200+ °C	12.52	12.31	1.7
22	Exit Pdt	12.26	11.15	10.0
23	Pdt cut 400-480 °C	11.36	11.45	-0.8
24	Pdt cut 480+ °C	10.14	10.24	-1.0
25	VGO feed + 10 %LGO	11.43	11.86	-3.6
26	Pdt at MRU	10.36	10.58	-2.1
27	Mangala crude 2	12.94	12.98	-0.3

^aSamples are not conventional boiling fractions, either a mixture of several boiling range products or direct product from MRU/MFU/PP

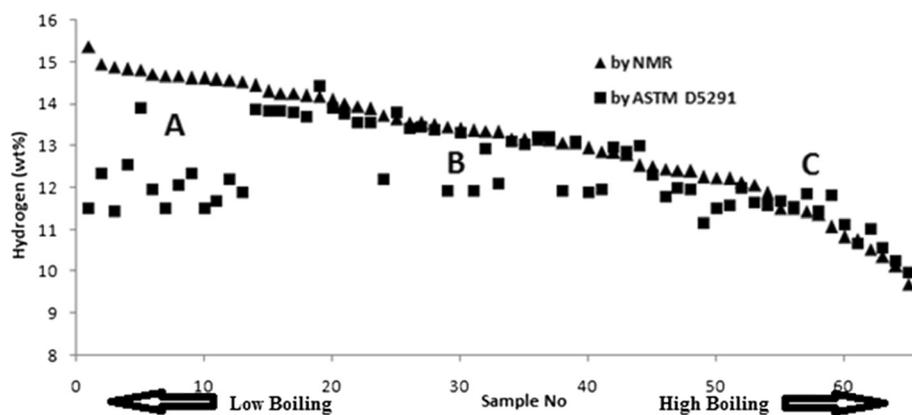
**Fig. 2** Distribution of H content by NMR and ASTM methods

Table 5 Repeatability in ¹H NMR method

Sample name	No. of Exp	H content (wt%)
Crude 1 C5-95	1	14.8
	2	15.18
	3	14.88
Crude 2 C5-95	1	14.72
	2	15.28
	3	14.89
Crude 3 C5-95	1	15.55
	2	15.18
	3	15.69
Crude 4 C5-95	1	15.00
	2	15.38
	3	15.49
Crude 1 149-250	1	14.05
	2	14.19
	3	13.91
Crude 5 149-250	1	13.95
	2	14.02
	3	14.09
Crude 7 149-250	1	14.45
	2	14.40
	3	14.55
Crude 4 149-250	1	14.27
	2	14.35
	3	14.41
Octadecane	1	15.23
	2	15.26
	3	15.24
Diesel Std	1	13.19
	2	13.14
	3	13.26
Ethylbenzene	1	8.72
	2	8.84
	3	8.73
Propylbenzene	1	10.09
	2	10.03
	3	10.11
Tetralin	1	8.94
	2	9.04
	3	8.98
Isooctane	1	16.02
	2	16.01
	3	16.02

Table 5 Repeatability in ¹H NMR method (Continued)

Furfural	1	3.91
	2	3.92
	3	3.90

Hydrogen for composite samples

Hydrotreating crude oil is associated with catalytic hydro-desulfurization, hydro-deoxygenation, hydro-denitrogenation, hydrogenation of aromatics, saturation of olefins, etc. In conventional hydrocracking and hydrotreating processes, the hydrogenation of aromatic compounds play a crucial role. As heavy residual compounds are normally aromatic in nature, therefore, the complete or partial saturation of these compounds, by hydrogen addition, is an important step in their cracking into smaller, more valuable compounds. In order to achieve good hydrogenation efficiency, reactions need to take place at a favorable lower temperature range for which expensive noble metal catalysts are usually used. Products of hydrotreating expected to have more hydrogen than the feed. Moreover, products collected from micro reactor units (MRU) of PP operating at different temperatures should have different H contents. Conventionally, the products collected from MRU operating at a higher temperature gives product with a higher H content. Here, we present, in Table 4, a case of differential hydrogen content of the products at different temperatures by NMR method and the corresponding hydrogen content calculated by ASTM D5291 combustion method (entry 1-10).

The hydrogen content of several other composite cut samples have also been estimated by NMR method, and the results are compared with conventional ASTM D5291 method (entry 11-27). It can be concluded from Table 4 that some of these composite samples gave hydrogen contents which varied ± 5 % while estimated by NMR and combustion methods. In few cases, the variation is large. Given the fact that the products are a mixture of different boiling range fractions, the variation is reasonable.

Estimation of ethanol and H/C and O/C ratio for ethanol-blended gasoline and oxy-diesel

For reformulated gasoline and oxy-diesel, the percentage of ethanol and thus the H/C and O/C ratio could easily be determined by the described method without any additional experimentation (see Additional file 1).

Experimental

The experimental details are discussed in Additional file 1.

Conclusions

A simple and highly reliable spectroscopic method has been developed for the estimation of hydrogen content in all petroleum products irrespective of their origin, composition,

boiling range, etc. The method is applicable to a wide range of petroleum products such as naphtha, kerosene, diesel, gas oils, vacuum gas oils, and the residua as well as for reformulated gasoline and oxy-diesel. HMDSO, as an internal reference standard, has been introduced for quantitative calculation of hydrogen content and oxygenates in petroleum brands. The internal standard alone serves as a frequency and quantitative reference for proton NMR. The ^1H NMR-based method is also applicable to low boiling fractions and compounds containing very low hydrogen content. In most of the model compounds, the NMR method delivers hydrogen close to its theoretical values. In addition to hydrogen content, the developed method can directly be used to estimate the ethanol content/oxygen content in blended gasoline or oxy-diesel.

Additional file

Additional file 1: This file includes experimental details along with correlation curves for T1 measurements, few relevant spectra, and a representative estimation of ethanol content.

Abbreviations

CHNS: carbon hydrogen nitrogen sulfur; FCC: fluidized catalytic cracking; HSD: high speed diesel; HVGO: heavy vacuum gas oil; IBP: initial boiling point; LVGO: light vacuum gas oil; MFU: micro flow unit; MRU: micro reactor unit; MS: motor spirit; PP: pilot plant; RSD: relative standard deviation; VR: vacuum residue.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

SM designed and executed the whole work and drafted the manuscript. The acquisition, analysis, and interpretation of data have been carried out by SM and RK. VB and MBP conceived of the study and participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

Acknowledgements

We acknowledge the IOCL R&D Centre for granting permission to publish this paper. Also, we gratefully acknowledge Ms. Suman Mukherjee of Analytical Division for her support in recording the CHNS combustion data.

Received: 24 February 2015 Accepted: 18 June 2015

Published online: 03 July 2015

References

- Abu-Dagga F, Ruegger H (1988) Evaluation of low boiling crude oil fractions by NMR spectroscopy. Average structural parameters and identification of aromatic compounds by 2D NMR spectroscopy. *Fuel* 67:1255–62
- Allen DTNMR (1985) Characterization and property estimation in heavy fuels. Preprints: Division of Petroleum Chemistry. *Am Chem Soc* 30(2):270–3, Published by ACS, Washington, DC, USA
- ASTM D-3701 (1992) Standard test method for hydrogen content of aviation fuels by low resolution nuclear magnetic resonance spectroscopy. ASTM, West Conshohocken
- ASTM D-4808 (1992) Standard test methods for hydrogen content of light distillates, middle distillates, gas oils, and residua by low resolution nuclear magnetic resonance spectroscopy. ASTM, West Conshohocken
- ASTM D-5291 (1996) Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants. ASTM, West Conshohocken
- ASTM D-7171 (2011) Standard test method for hydrogen content of middle distillate petroleum products by low-resolution pulsed nuclear magnetic resonance spectroscopy. ASTM, West Conshohocken
- Bansal V, Kapur GS, Sarpal AS, Kagdiyal V, Jain SK, Srivastava SK, Bhatnagar AK (1998) Estimation of total aromatics and their distribution as mono and global di-plus aromatics in diesel-range products by NMR spectroscopy. *Energy Fuels* 12:1223–1227
- Bansal V, Krishna GJ, Chopra A, Sarpal AS (2007) Detailed hydrocarbon characterization of RFCC feed stocks by NMR spectroscopic techniques. *Energy Fuels* 21:1024–1029
- Bansal V, Kumar R, Krishna GJ, Patel MB, Sarpal AS, Basu B (2014) Transferable hydrogen by ^1H nuclear magnetic resonance spectroscopy—vital structural aspects of petroleum heavier ends (370–660 °C) feed stocks. *Fuel* 118:148–155
- Barni R, Zanini S, Riccardi C (2012) Characterization of the chemical kinetics in an O₂/HMDSO RF plasma for material processing. *Adv Phys Chem Artic ID* 205380:1–6
- Gautier S, Quignard A (1995) Low resolution ^1H NMR: the ultimate tool for accurate determination of hydrogen content in petroleum products. *Revue de l'Institut Francais du Petrole* 50:267
- Gillet S, Delpuech JJ, Valentin P, Escalier JC (1980) Optimum conditions for crude oil and petroleum product analysis by carbon-13 NMR spectroscopy. *Anal Chem* 52:813–817
- Government to take a call on ethanol price soon (November 21, 2011). The Hindu, New Delhi
- Kennedy GJ, Kohout FC, Moy EA Jr (1998) Improved hydrogen determination in petroleum streams using a bench top pulsed NMR analyzer. *Energy Fuels* 12:812–817
- Khadim MA, Wolny RA, Al-Dhuwahi AS, Al-Hajri EA, Al-Ghamdi MA (2003) Determination of hydrogen and carbon contents in crude oil and petroleum fractions by NMR spectroscopy. *Arabian J Sci Eng* 28(2A):147–162
- Kodibagkar VD, Cui W, Merritt ME, Mason RP (2006) Novel ^1H NMR approach to quantitative tissue oximetry using hexamethyldisiloxane. *Magn Reson Med* 55:743–748
- Kodibagkar VD, Wang X, P-Torres J, Gulaka P, Mason RP (2008) Proton imaging of siloxanes to map tissue oxygenation levels (PISTOL): a tool for quantitative tissue oximetry. *NMR Biomed* 21:899–907
- Kvalheim OM, Aksnes DW, Brekke T, Eide MO, Sletten E, Telnaes N (1985) Crude oil characterization and correlation by principal component analysis of C-13 NMR spectra. *Anal Chem* 57:2858–64
- Mirotnichnik K, Kantzas A, Starsud A, Aikman M (2001) A new method for group analysis of petroleum fractions in unconsolidated porous media. *J Can Pet Tech* 40:38–44
- Poveda JC, Molina DR (2012) Average molecular parameters of heavy crude oils and their fractions using NMR spectroscopy. *J Petroleum Sci Eng* 84–85:1–7
- Removal of reformulated gasoline oxygen content requirement (national) and revision of commingling prohibition to address non-oxygenated reformulated gasoline (national) (February 22, 2006). U.S. Environmental Protection Agency
- Sarpal AS, Kapur GS, Mukherjee S, Jain SK (1997) Estimation of oxygenates in gasoline by ^{13}C NMR spectroscopy. *Energy Fuels* 11(3):662
- Sarpal AS, Kapur GS, Bansal V, Jain SK, Srivastava SK (1998) Direct estimation of aromatic carbon content of base oils by ^1H NMR spectroscopy. *Petroleum Sci Tech* 16:851–68
- Smirnov MB, Melikhov VA, Frolov Ye B, Parenago OP (1992) ^1H NMR study of unsaturated compounds in distillate fractions of olefin-containing crude oils. *Petroleum Chem (English translation of Neftekhimiya)* 32:441–7
- Srivastava SP (1982) Quantitative measurement of the percentage of aromatic carbons in petroleum crudes by carbon-13 NMR spectroscopy. *J Chem Tech Biotech* 32:614–6
- Young DC, Galya LG (1984) Determination of paraffinic, naphthenic, and aromatic carbon in petroleum derived materials by carbon-13 NMR spectroscopy. *Liquid Fuels Tech* 2:307–326