

Absolute Hydrogen Determination in Coal-Derived Heavy Distillate Samples* R. J. Kottenstette, D. A. Schneider and D. A. Loy, Dept. 6212 and 1812, Sandia National Laboratories, P.O.Box 5800, Albuquerque, NM 87185.

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Introduction

Coal liquefaction involves the use of recycle oils to mix slurry feed materials, and transfer hydrogen to coal as it is digested at high temperatures. Hydrogen donating abilities of recycle oils can be measured using Proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) Spectroscopy [1], liquefaction testing [2] and dehydrogenation tests [3]. This paper will describe the absolute determination of total organic elemental hydrogen by $^1\text{H-NMR}$ of small (less than one gram) heavy distillate samples produced for research purposes. A comparison will be made between a conventional combustion method and the NMR spectroscopic method.

Organic elemental hydrogen analysis is routinely performed with an automated analyzer having a high temperature combustion zone that is connected to a detector which measures the response of the product water. This technique has its historical roots in the experiments of Lavoisier [4] who in the 1770's burned alcohol and other combustible organic compounds in oxygen to gravimetrically determine the product water and carbon dioxide. Quantitative recovery and measurement of the combustion products were demonstrated by Berzelius and Liebig in the early 1800's. The work of Pregl [5] at the turn of this century advanced this technique to a high degree with the introduction and perfection of microchemical techniques (sample sizes in the milligram range). With the advent of instrumental electronics, automated microanalysis gradually replaced the gravimetric techniques mainly because of increased analysis speed. Modern automated organic elemental analysis consists of combusting the sample in the presence of a solid oxidant and sweeping the products into a thermal conductivity or infrared detector [4,5]. An alternative technique for the detection of hydrogen is to react the product water with carbonyldiimidazole to generate a quantitative amount of carbon dioxide which is measured by a coulometric titration [6].

The development of Proton Nuclear Magnetic Resonance Spectroscopy has led to the description and qualitative classification of hydrogen in organic compounds. These techniques have been especially helpful in describing hydrogen as it is classified into aliphatic, aromatic and hydroaromatic groupings [1,2,3]. In addition, low resolution proton $^1\text{H-NMR}$ has been successfully used to determine absolute amounts of hydrogen in a variety of petroleum fractions [7,8]. Our technique involves simple integration of high resolution $^1\text{H-NMR}$ spectra with careful attention given to sample preparation and spectral integration.

Experimental

Materials

Heavy distillate samples from Run 262 at the Wilsonville Advanced Coal Liquefaction Pilot Plant were supplied from CONSOL inc. The samples came from the V1074 stream and had an approximate boiling range of 650°F to 1050°F. The samples were hydrotreated in a laboratory scale trickle-bed reactor at 365°C. 1,2,3,6,7,8 hexahdropyrene (H_6Py) and deuterated chloroform (99.96%D) were purchased from Aldrich, naphthyl dibenzyl methane (NBM) was acquired from TCI America, acetanilide was obtained from Perkin Elmer and paraffin oil was purchased from LECO corporation.

Procedure

Combustion Analysis - Hydrogen amounts were determined with a Perkin Elmer model 2400 CHN analyzer. The combustion temperature was set at 925°C and the reduction tube was set at 640°C. Since the heavy distillate samples are viscous, the "standard" tin capsules could be used to contain the samples. Careful attention was paid to sample size since larger samples (>3mg) often lead to incomplete combustion or an "overload" condition which gives erratic hydrogen results. The analyzer is conditioned before sample analysis by running successive external standard samples until the hydrogen output stabilizes (usually one to two samples). The conditioning samples always show a lower than expected hydrogen value if they are preceded by a blank determination. External standards for the combustion technique include acetanilide, paraffin oil, and NBM.

Proton NMR - A Bruker AM 300 FT-NMR spectrometer was used to determine hydrogen mass percents. Heavy distillate samples were prepared in CDCl_3 at a concentration of 30.0 mg per 1.0 mL of solvent. External standard samples (H_6Py) were prepared at concentrations ranging from 0.5 mg to 45.0 mg per 1.0 mL of solvent to generate a calibration curve. All samples were weighed in 20 mL sample vials; CDCl_3 was introduced with a syringe. Solutions were immediately capped, mixed thoroughly, and transferred to 5 mm NMR tubes with Pasteur pipettes. Spectra were acquired with a total time of 2.36 seconds between 20 degree RF pulses. At low external standard concentrations (0.5 mg-30 mg), 512 scans per sample were acquired to improve signal to noise ratios. It was found that the number of scans could be reduced from 512 to 64 for distillate samples and more concentrated external samples (30 mg to 45 mg). H_6Py standard samples of 30.0, 37.7, and 45.0 mg/mL were prepared and analyzed daily for distillate analyses. CDCl_3 acts as a de facto internal standard having a chemical shift of 7.27 ppm; the samples are integrated between 10.5 and 0.5 ppm. Before integrating the spectra, the baseline curvature is corrected using a spline-fit algorithm incorporated in the Bruker software. Area counts due to the CDCl_3 of approximately 0.2 are considered negligible compared to the output for a 30 mg H_6Py standard (arbitrarily set to give 100.0 area counts). NBM was also analyzed to check the accuracy of the method.

Results and Discussion

Previous tests in our laboratory showed that heavy distillate samples acquired less than 1 wt% additional hydrogen during catalytic hydrogenation even under the most favorable of conditions. Therefore, determining hydrogen concentration changes on the order of 0.3 to 1.0 wt% has become necessary. Analyses for hydrogen in our laboratory (using the CHN analyzer) have been deemed acceptable if the precision of the analysis was $\pm 0.3\text{wt}\%$. This was not acceptable when trying to detect the small hydrogen increases in the hydrotreated distillates.

Figure 1 shows a linearity plot of area (detector response) vs. absolute hydrogen content of a wide variety of model compounds and a known heavy distillate. The data in Figure 1 shows the calibration curve constrained through the origin. This curve illustrates that a one-point calibration (such as is commonly used in automated CHN analyses) would underestimate the hydrogen in samples such as acetanilide (6.71% H) and overestimate the amount of hydrogen in paraffin oil (13.63% H). A one point calibration becomes especially inaccurate if the standard has a hydrogen content much different than the sample to be analyzed. Since the recommended sample weight for the combustion analysis should fall in the narrow range between one and three milligrams, the difficulty in establishing a linear calibration curve is compounded. One solution to this dilemma is to plot the raw data against a wide range of known hydrogen standards. This is the method illustrated in Figure 2, in which the calibration curve is not constrained through the origin. This linear regression curve-fit has a correlation coefficient of 0.994 and provides a more reliable basis for analysis of samples within the range of the calibration curve (hydrogen content between 6.71% and 13.63%).

Figure 3 shows a four point calibration curve of area vs. hydrogen content for different amounts of hexahydropyrene in deuterated chloroform as analyzed with the ^1H -NMR technique. This curve has excellent linearity over its range giving a linear regression correlation coefficient of 0.9999. The ^1H -NMR technique requires only one type of standard at different concentrations rather than multiple standards for the combustion technique. The X-axis in Figure 3 is an order of magnitude larger than the corresponding axis for the combustion technique since a typical sample weight for the ^1H -NMR analysis is ten times larger (30 mg vs. >3 mg) than for the microcombustion technique. The Y-axis presents the integrated area in arbitrary units with the 30mg/mL H_6Py standard assigned a value of 100.0.

Table 1 shows the analytical results and uncertainties for a series of heavy distillate samples and model compounds typically used in coal liquefaction research. Hydrogen concentration is presented as the average of four runs for the combustion analyses and the average of three determinations for the ^1H -NMR analyses. The theoretical hydrogen content is shown for the two model compounds, H_6Py ($\text{C}_{16}\text{H}_{16}$) and NBM ($\text{C}_{22}\text{H}_{25}$). The distillate samples were taken at different times "on-stream" with the highest hydrogen content being for the sample taken after one hour when the catalyst was the freshest. Hydrogen content decreases with time on-stream until at ten hours the reaction temperature was raised by 10°C to increase the rate of hydrogenation. Indeed this sample showed a slight increase of 0.1 wt% hydrogen. In general the absolute hydrogen analyses for the two methods are remarkably close with the largest difference between the averages being no more than 0.16%. The standard deviations are larger for the ^1H -NMR determinations in general with the exception of the H_6Py sample which gave a very low (0.05%) standard deviation. Figure 4 is a parity plot comparing the results from the two

techniques. Again the correlation coefficient from a linear regression gave a good linear fit, thus the two techniques compare well, at least in the range of hydrogen concentrations studied.

Figure 5 shows an analysis of hydrogen distribution according to three broad categories. Alkyl protons are defined as alkyl α , alkyl β , and gamma having $^1\text{H-NMR}$ chemical shifts of 2.5-2.0, 1.4-1.0, and 1.0-0.5 ppm respectively. Condensed aromatic and uncondensed aromatic hydrocarbons have chemical shifts of 10.5-7.15 and 7.15-4.7 ppm, respectively. Hydroaromatic hydrogens are defined as cyclic α and cyclic β protons with proton shifts of 4.7-2.5 and 2.0-1.4 ppm respectively. Results in Figure 5 illustrate the additional benefit of the $^1\text{H-NMR}$ technique. The $^1\text{H-NMR}$ spectrum can quantitatively analyze the hydrogen species in a heavy distillate sample (not possible with combustion elemental analyses). These proton distributions can then be used to evaluate the quality of a liquid (in our case for hydrogen donation purposes).

Conclusion

Elemental hydrogen determinations giving sample repeatability of less than 0.1 wt% at the 10 wt% level have not been demonstrated with either the combustion or the $^1\text{H-NMR}$ technique. However, excellent correlation has been achieved between the combustion method and the $^1\text{H-NMR}$ method, giving results for model compounds which are quite good (see Table 1). A refinement of the combustion analysis has been shown by improving the calibration procedure from the typically used single point calibration. Small differences in hydrogen content were noted for a series of hydrotreated heavy distillate samples. In addition the absolute determination of hydrogen by $^1\text{H-NMR}$ can also yield information about the relative amounts of aromatic, alkyl and hydroaromatic protons. The $^1\text{H-NMR}$ technique can also be applied to evaluate absolute hydrogen content when a rapid combustion technique is not immediately available.

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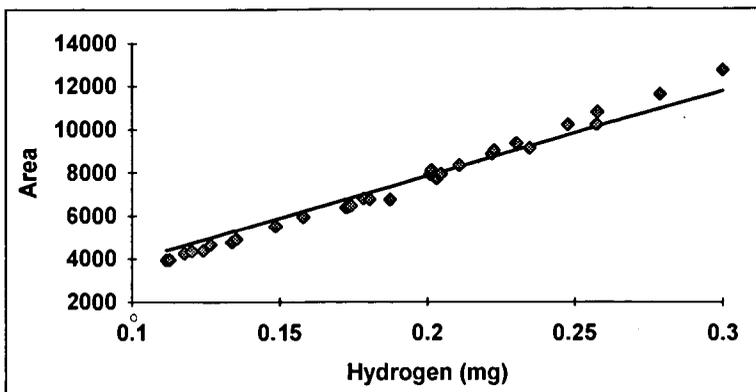


Figure 1. Calibration Curve for Combustion Elemental Hydrogen Analysis (forced through zero, $r^2=0.971$)

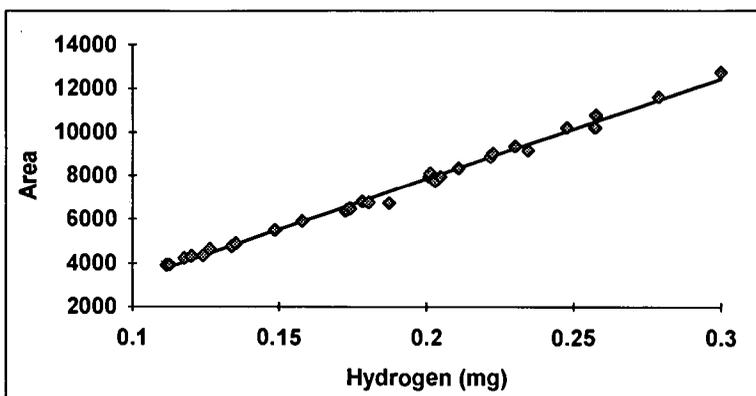


Figure 2. Calibration Curve for Combustion Elemental Hydrogen Analysis ($r^2 = 0.994$)

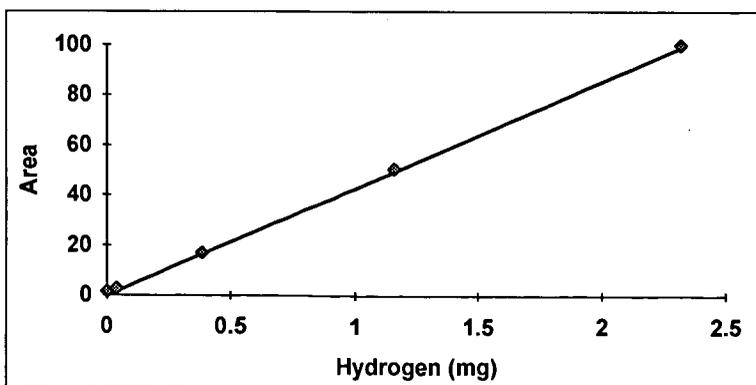


Figure 3. Calibration Curve for Proton NMR Hydrogen Analysis using Hexahydroindole ($r^2 = 0.999$)

Table 1. Comparison of Combustion and NMR Hydrogen Data for Flow Reactor Product (Heavy Distillate)

Sample	%H Theory	%H Combustion	Std. Dev.	%H NMR	Std. Dev.
V1074	NA	9.66	0.23	9.68	0.12
Reactor Feed	NA	8.57	0.11	8.42	0.21
1 Hour	NA	9.33	0.06	9.34	0.37
2.5 Hour	NA	8.97	0.11	9.04	0.27
7 Hour	NA	8.81	0.06	8.94	0.30
10 Hour (+10°C)	NA	8.92	0.14	9.04	0.20
H6Py*	7.74	7.74	0.17	7.75	0.05
NBM**	6.87	6.98	0.10	6.83	NA

* 1,2,3,6,7,8 Hexahydropyrene. ** Naphthyl Dibenzyl Methane

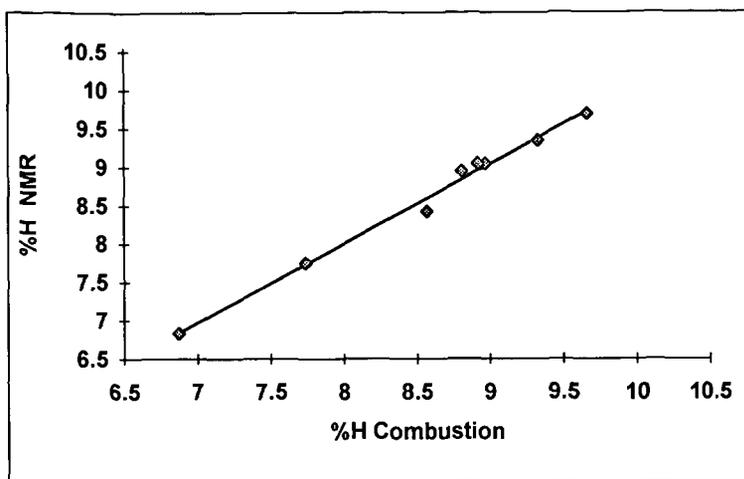


Figure 4. Comparison of Combustion Analysis with NMR Analysis ($r^2 = 0.993$)

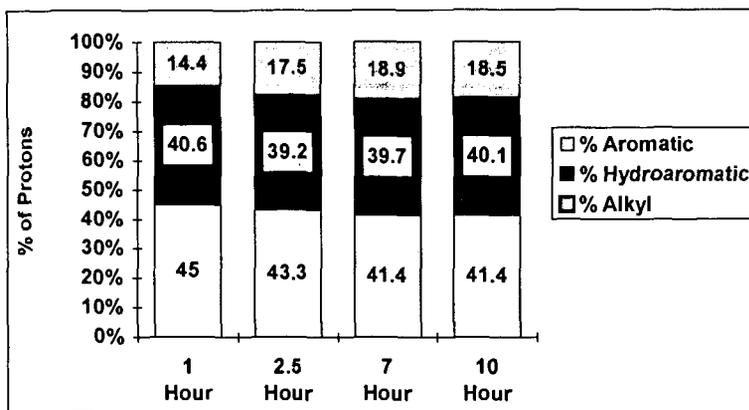


Figure 5. Hydrogen Distribution in Heavy Distillate Sampled at Intervals from Flow Reactor (Proton NMR)