Part II

PHYSICAL PROPERTIES

EVALUATION OF COMPOUNDS AND MATERIALS

Characteristics of a Houdresid Gasoline

R. K. SMITH, W. E. SCHORTMANN, and G. A. MILLS
Houdry Process Corp., Marcus Hook, Pa.

The conversion of residuum materials to gasoline and fuel oils has assumed increased importance with the development and commercial operation of the Houdresid process. Houdresid operation catalytically cracks residua to high quality gasoline and distillate products. Characteristically, residual stocks contain higher quantities of condensed ring hydrocarbons than distillate stocks generally charged to catalytic cracking. Detailed analyses have therefore been performed to determine the chemical composition of a gasoline from Houdresid operation. Relationships have been established between gasoline composition and product quality. For refinery operations, the comparison of Houdresid and Houdriflow gasolines is significant.

Analyses for hydrocarbon types became feasible through the combined techniques of silica gel adsorption and mass spectrographic analysis. Where possible, additional and more detailed tests have been used to corroborate the data obtained by such direct analyses.

Extensive use has been made of silica gel analysis by other workers in the field. Bates and others (*1*) utilized it to analyze thermal and catalytic gasolines with regard to paraffin, naphthene, olefin, and aromatic content. Rossini and others (*4*) used it in conjunction with extensive distillation to obtain the hydrocarbon type composition and also detailed data about the occurrence of specific paraffins and naphthenes. Neither of these groups attempted to differentiate among olefin types. In 1949, Rampton (*6*) effected olefin skeletal analysis by using the conventional silica gel adsorption technique in conjunction with mild hydrogenation. Although information is not available concerning the source of the catalytic gasoline which he studied, the summary data are presented below.

Sample	Shale Gasoline	Thermal Gasoline	Fluid Cracked Gasoline
Paraffins	37	31	10
Naphthenes	9	26	8
Aromatics	11	26	30
Olefins	31	8	34
Cyclic olefins	12	9	18

Cyclic olefins are reported here, apparently for the first time. In Rampton's samples, they represent from one fourth to one half of the total olefin contents. In other respects, there appears to be no fundamental difference between the above analyses and those previously reported. More recently, Headington and others (*5*) developed a mass spectrographic technique which permitted analyses similar to those above to be made in only a few man-hours, rather than the 200 required by Rampton's technique. Study of a gasoline from fluid catalytic cracking by the latter group indicated that 6% of cyclic olefins were present, representing about 15% of the total olefins in the gasoline fraction.

The use of the mass spectrographic technique at Houdry has been extended so that hydrocarbon type analyses have been made on several whole gasoline fractions. The presence of cyclo-olefins is detected directly by the identification of mass fragments corresponding to formulas of C_nH_{2n-2}. Combining this procedure with the standard procedure for PONA analysis using the FIA silica gel method, (ASTM-D1319) a comprehensive picture is obtained.

Conventional methods have been used to determine the characteristics of gasoline quality for the Houdresid and Houdriflow gasoline. The octane-boiling point relationships for Houdry fixed bed catalytic cracking were presented by Broom (*2*) in 1941. At that time, no marked variation in octane number (L-3 method then used) with boiling point of the gasoline fraction was observed. As this test had many of the characteristics of the current ASTM Motor method, the influence of olefins, which are found to be concentrated in the front end, was not so pronounced as when the ASTM Research method is used. The octane number of the gasoline discussed by Broom is markedly lower than current gasoline octane numbers.

The data reported here were obtained on two gasolines obtained, respectively, from catalytic cracking of a gas oil and a wide range residuum from the same crude source. These were obtained from successive operation of a single commercial unit using the same lot of catalyst. A mixed Louisiana, East Texas, and Mid-Continent crude was processed. The 50 to 90% gas oil fraction was charged under

Houdriflow conditions for production of one gasoline. The second gasoline sample was produced from the wide range 50 to 100% residuum fraction under Houdresid conditions. This process has been described by Dart and others (*3*).

Table I. Inspection Data for Charge Stock

Source	Crude from Mid-Continent, Texas, and Louisiana	
	50–100% residuum	50–90% gas oil
Gravity, °API	26.9	31.0
Distillation, vacuum assay °F. at 760 mm		
Initial boiling point	650	650
50%	804	750
End point	1066	935
Recovery, %	84	94
Sulfur, wt. %	0.47	0.30
Ramsbottom carbon wt. %	3.0	0.10
Nickel, p.p.m.	4.6	< 1.
Vanadium, p.p.m.	6.1	< 1.
Iron, p.p.m.	9.4	

Inspection data of the residuum charge are given in Table I. Certain characteristics of the product gasoline are shown below. In this paper all Research octane numbers refer to ASTM-D908.

	Houdresid	Houdriflow
Research octane Nos. clear	91.5	92.0
S, wt. %	0.070	0.063
N, wt. %	0.015	0.015

CHEMICAL ANALYSIS OF HOUDRESID GASOLINE

Distribution of Hydrocarbon Types in Cracked Gasolines. Detailed analyses of the paraffin-naphthene fractions, aromatic fraction, and olefin fractions have been performed on both the Houdresid and Houdriflow gasolines. During the early phases of the research and development work on residuum processing, mass spectrographic analysis of the product gasolines indicated the presence of compounds with an empirical formula of C_nH_{2n-2}. The class of compounds may include cyclic olefins, such as cyclohexene, diolefins, alkyl acetylenes, or bicyclic naphthenes. Analysis by infrared and measurement of maleic anhydride values eliminated conjugated diolefins and alkyl acetylenes from consideration. Bicyclic naphthenes were assumed to be absent throughout the C_6 to C_9 regions of the gasoline boiling range. By elimination, the presence of cyclic olefins was deduced.

Full range gasolines have been fractionated to provide 40° to 50°F. cuts for analysis and evaluation of quality characteristics of each fraction.

Composition of Gasoline Samples

Charge Stock Type of Unit	Residuum Houdresid	Gas Oil Houdriflow
Aromatics, vol. %	27	25
Paraffins, vol. %	16	16
Naphthenes, vol. %	8	8
Olefins		
Acyclic, vol. %	36	38
Cyclic, vol. %	13	13

Analyses of the fractions from Houdriflow and Houdresid gasolines are presented in Figure 1. Similarities in composition are evident over the entire boiling range. In this lower range, the Houdriflow analysis shows more naphthenes than would have been anticipated. The reason for this is not clear.

Previous analyses (*1,4*) of catalytic gasolines from Houdry fixed bed units had not revealed the presence of cyclic olefins. In general, olefins were determined by bromine number, chromatographic analysis using silica gel, or other chemical tests which were incapable of differentiation between olefins and cyclic olefins.

Paraffin-Naphthene Analysis of Houdresid Gasoline. A sample of Houdresid gasoline has been analyzed for paraffins and naphthenes following acid absorption to remove aromatic and unsaturated materials. The paraffin-naphthene raffinate was distilled in a 100-plate column into 2% cuts. Each cut was subsequently analyzed by mass spectrometry to determine the individual compounds present. The final data obtained by this procedure are presented in Table II. The paraffin-naphthene fraction represented 28.2% of the gasoline. Analysis indicated that 70% of the fraction was paraffinic; the remainder was naphthenic. Of the individual

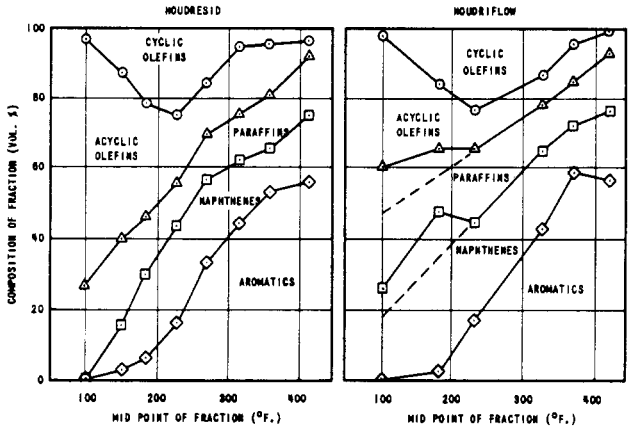

Figure 1. Catalytically cracked gasolines

Composition vs. boiling range for Houdresid and Houdriflow operations

paraffins identified, methyl alkanes constituted the largest single class, comprising 42% of the paraffin fraction. *n*-Alkanes represented 24% of the paraffin fraction, while unidentified higher boiling isomers and dimethyl alkanes made up the rest.

The naphthene composition is characterized by relatively small quantities of nonsubstituted naphthenes. About 1% of the naphthenes are cyclopentane and cyclohexane. This is to contrast to nearly 14% identified as dimethyl cyclopentanes and cyclohexanes. Higher boiling naphthenes were determined but individual isomers could not be identified owing to the lack of spectroscopic reference materials.

Aromatic Analysis of Gasolines. As a further means of characterization of gasoline samples, data concerning the occurrence of various aromatics have been compiled.

Aromatic Components of Gasoline

Charge Stock Type of Unit	Residuum Houdresid	Gas Oil Houdriflow
Benzene, vol. %	0.5	0.7
Toluene, vol. %	2.3	3.1
C_8 aromatics, vol. %	7.4	7.2
C_9 aromatics, vol. %	9.2	8.0
Higher aromatics, vol. %	7.8	6.0

The table indicates very little difference in either the quantity of aromatics or the molecular weight distribution between the gasolines.

Olefin Content of Gasolines. The olefin portion of Houdresid gasoline was found to contain cyclic olefins. Analyses of various cuts of a Houdresid and Houdriflow

Table II. Analysis of Paraffin-Naphthene Fraction[a]

Houdresid gasoline, 24% of whole gasoline

Paraffins		Naphthenes	
Compound	%	Compound	%
Iso-pentane	0.3	Cyclopentane	0.1
n-Pentane	1.0	Methylcyclopentane	0.1
2,3-Dimethylbutane	1.0	1,2-Dimethylcyclopentane	0.2
2-Methylpentane	4.7	1,3-Dimethylcyclopentane	0.1
3-Methylpentane	2.0	1,1,2-Trimethylcyclopentane	0.2
n-Hexane	1.4	Other trimethylcyclopentanes	0.2
2,2,3-Trimethylbutane	0.1	1-Methyl,2-ethylcyclopentane	0.4
3,3-Dimethylpentane	0.1	Propylcyclopentane	0.1
2,3-Dimethylpentane	0.8	Higher boiling cyclopentanes	10.8
2,4-Dimethylpentane	0.7		
2-Methylhexane	5.2	Cyclohexane	0.2
3-Methylhexane	3.7	Methylcyclohexane	2.9
Ethylpentane	0.5	1,1-Dimethylcyclohexane	0.5
n-Heptane	1.6	1,2-Dimethylcyclohexane	0.2
2,4-Dimethylhexane	0.8	1,3-Dimethylcyclohexane	1.2
2,5-Dimethylhexane	1.4	1,4-Dimethylcyclohexane	2.0
3,3-Dimethylhexane	0.1	Ethylcyclohexane	0.5
2,3-Dimethylhexane	0.3	Higher boiling cyclohexanes	6.4
Ethylhexane	0.4		
2-Methylheptane	3.3	Polynaphthenes (C_8 to C_{12})	3.3
3-Methylheptane	3.1		
4-Methylheptane	1.4	Endocyclic naphthenes (C_{11})	0.1
n-Octane	1.4	Total	29.5
2,4-Dimethylheptane	0.8		
2,5-Dimethylheptane	1.6		
2,6-Dimethylheptane	0.2		
4-Ethylheptane	0.6		
2-Methyloctane	2.0		
3-Methyloctane	3.6		
4-Methyloctane	1.7		
n-Nonane	1.7		
C_{10} branched chain	7.3		
n-Defane	3.2		
C_{11} branched chain	3.8		
n-Undecane	3.3		
C_{12} branched chain	2.2		
n-Dodecane	3.2		
	70.5		

[a]The whole gasoline, after depentanization, was extracted with several treats of sulfuric acid. The subsequent raffinate was distilled through a 100-plate column into 2% cuts and the individual cuts were analyzed by mass spectroscopy.

gasoline indicate that these materials attain a maximum in the C_8 region as shown in the following summary table.

Distribution of Cyclic Olefins

Cyclic Olefins, Vol. % of Cut	Houdresid Gasoline	Houdriflow Gasoline
150–205° F.[a]	21	15
205–250°	26	23
250–300°	16	13
300–345°	5	4

[a]Approximate cut points used for purposes of comparison. Again, no substantial differences are observed between gasoline from Houdresid and that from Houdriflow operations.

Nonhydrocarbon Components of Houdresid Gasoline. Sulfur and nitrogen contents of Houdresid gasoline are related to those of the charge. For the Houdresid gasoline analyzed here, the observed values are 0.07% of sulfur and 0.015% of nitrogen. Analysis of cuts obtained from this gasoline indicate that the sulfur content is not more than 0.07% in fractions boiling lower than 400° F. (Figure 2). Nitrogen analyses indicate that a marked increase in nitrogen content occurs at 300° F. (Figure 3). No attempt has been made to identify individual compounds or types of compounds containing nitrogen.

Silica gel analysis had indicated that the sulfur compounds can be concentrated by an elution technique. Analysis of the concentrated fraction by mass spectroscopy indicates that methyl thiophene and alkyl thiacyclopentanes and thiacyclohexanes contribute the bulk of the sulfur.

Analysis of Gaseous Products from Houdresid Operations. As a matter of collateral interest to the analysis of Houdresid gasoline, brief mention may be made of the relative quantities of olefins and paraffins found in the C_3 and C_4 stream. The following table presents the quantities of propylene and butylenes as percentages of the C_3 and C_4 effluent, respectively. The data are obtained from two refinery surveys in order to compare residuum operation with conventional gas oil operation.

Operation	Olefin Contents, Vol. %	
	C_3	C_4
Houdresid	78	57
Houdriflow	79	59

Although these data show no difference between residuum and gas oil operation in so far as olefin concentrations are concerned, both streams are high in olefins.

Other data, obtained in the laboratory, on a completely different charge stock show 84% of olefins in the C_3 and C_4 streams in Houdresid operation compared with 59% of olefins in the same streams when conventional Houdriflow operation is used. From laboratory experience, greater quantities of gaseous olefins are produced in Houdresid compared to Houdriflow operation.

QUALITY CHARACTERISTICS OF HOUDRESID GASOLINE

The quality characteristics of Houdresid gasoline have been obtained on distillate fractions of the whole gasoline. For this purpose, a 10-plate distillation was performed which

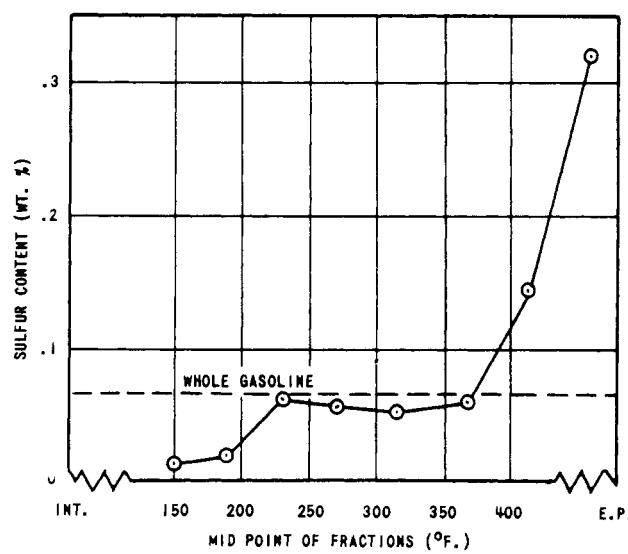

Figure 2. Sulfur contents of Houdresid gasoline

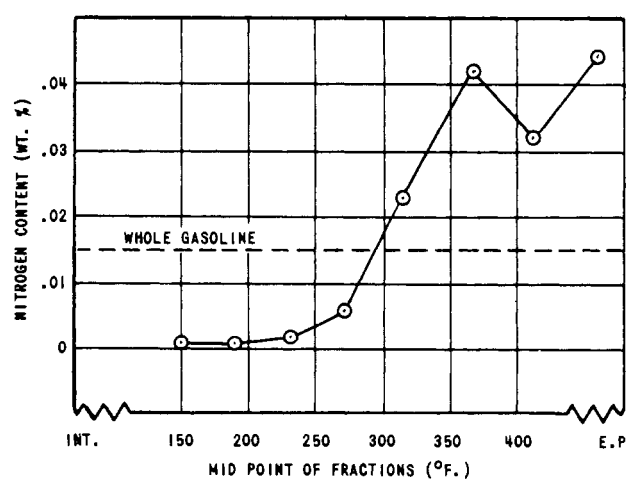

Figure 3. Nitrogen contents of Houdresid gasoline

separated the gasoline into nine fractions of 30° to 50°F. Each of these fractions was examined for quality characteristics. Sufficient quantities of each cut were made to permit determination of octane numbers, accelerated gum tests, and oxidation stability tests.

Octane Numbers of Houdresid Gasoline. As shown in Figure 4, the octane number decreased as the boiling point of the fraction increased, except for a slight leveling effect in the middle of the boiling range. The decrease in octane number at the higher end of the boiling range may be due to the relatively large quantities of straight-chain paraffins

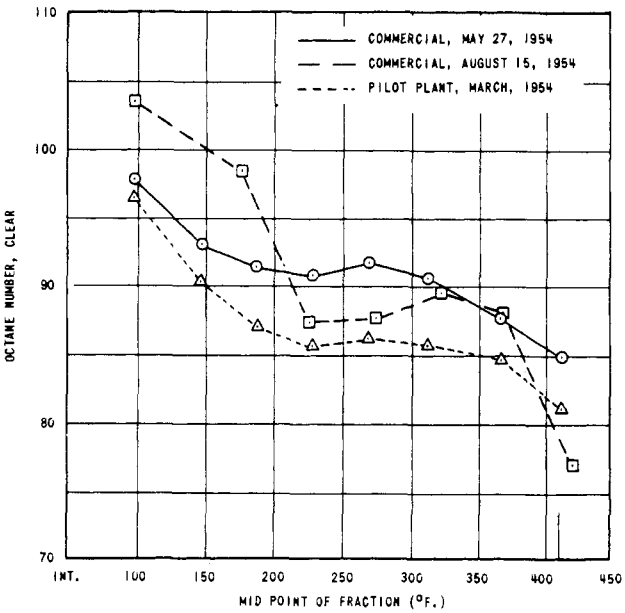

Figure 4. Octane rating vs. boiling range of Houdresid gasoline

which have been found in them. It is possible that this is due to a small amount of low boiling components in the charge which appear in the product gasoline. The following table presents the ratio of isoparaffins to normal paraffins throughout the gasoline boiling range. This ratio reaches at maximum for C_8 paraffins and decreases markedly in the C_{10} and C_{12} region.

Ratio of Isoparaffins to *n*-Paraffins in Houdresid Gasoline

Carbon No.	*i/n*
C_6	5.6
C_7	6.3
C_8	7.8
C_9	6.2
C_{10}	2.3
C_{11}	1.1
C_{12}	0.7

The C_{10} to C_{12} fraction represents 33% of the total paraffin fraction, or about 10% of the total gasoline. As the normal paraffins have octane values much less than zero, very small quantities depress the octane number of the fraction in which they are found.

Comparisons in Figure 5 of Houdresid gasolines with Houdriflow gasoline show that this Houdresid gasoline is fundamentally similar to the gasoline produced from gas oil cracking.

Stability of Houdresid Gasoline. The stability of Houdresid gasoline has been evaluated in the laboratory by the ASTM oxidation test (Method D-525) and the accelerated gum test. Results of the former showed an induction period of 9.2 hours, while 60 mg. of gum per 100 ml. were found in the latter. These values are essentially the same as corresponding data for other cracked gasolines from similar crude sources.

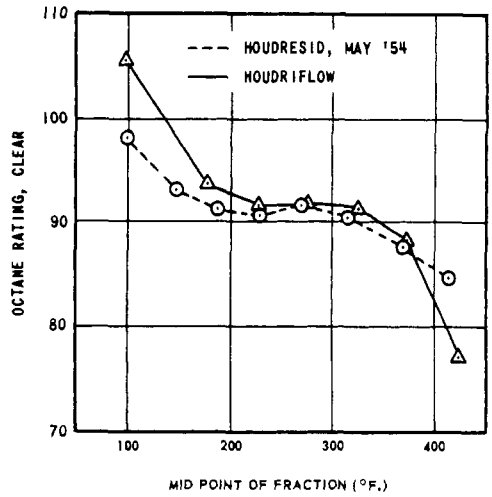

Figure 5. Octane rating vs. boiling range curves

ANALYSIS OF OLEFINS

Conventional techniques were used for the analysis of paraffins, naphthenes, and aromatics. The olefin analyses with regard to olefin type were based upon mass spectrographic data. To corroborate these data, additional analysis of the olefin fraction was performed.

The whole gasoline was split into two fractions by distillation, one boiling below and the other boiling above 130°C. Each fraction was then separated by silica gel chromatography into a paraffin-naphthene fraction, a paraffin-naphthene-olefin fraction, an olefin fraction, an olefin-aromatic fraction, and an aromatic fraction. The fractions containing olefins were then hydrogenated over 5% palladium on charcoal, to saturate the olefins. The remaining material was then analyzed by mass spectrometry in order to attain an over-all picture of the amount of cyclic and acyclic olefins. As shown in the following table, analysis of the olefin fraction by hydrogenation and mass spectrometric analysis is in agreement with direct mass spectrometric data on individual cuts of the whole gasoline.

Cyclic Content of Houdresid Olefins

	Analysis by Hydrogenation and MS Technique	Analyses by MS Technique of Individual Fractions
Cyclic structure, vol. %	31	27
Acyclic structure, vol. %	69	73

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