

HYDROGEN INCORPORATION IN RESIDUUM CONVERSION

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Introduction

In the last ten years there has been a large increase in residuum hydroconversion capacity in the United States and overseas. This expansion was derived from the expectation that the spread in market values between the high sulfur fuel oil and the light transportation fuels would increase to support the large investments required for these conversion facilities.

The reason for residuum conversion is simple--increasing the hydrogen-to-carbon ratio (H/C) and lowering the molecular weight generates marketable distillate products. Figure 1 illustrates this qualitatively. It shows a Stangeland (1) chart for pure paraffins, aromatics, and a number of petroleum fractions. The residuum is located to the right at higher carbon numbers. From a knowledge of the boiling points of pure paraffins and polycyclic aromatics, extra guidelines are drawn to represent approximate boiling points. This chart is very useful because it shows the extent to which carbon number must be reduced or hydrogen added to generate the desired light stocks. To correct this hydrogen imbalance, various residuum conversion processes either add hydrogen or reject carbon. A partial list of conventional residuum conversion options is shown in Table I. Thermal and extractive processes generally reject carbon while hydroconversion schemes add hydrogen.

Residuum Hydroconversion

The choice of residuum conversion process depends on the unique set of circumstances for each refinery, for example, feedstocks, existing equipment, and capital constraints. If the objective is to produce a distillate product slate, then hydroconversion can serve as an efficient process for conversion of lower value hydrocarbon feedstocks and heavy residuum to high quality distillate products.

Figure 2 shows a residuum hydroconversion refinery in its basic form is shown in Figure 2. The residuum feedstock is partially converted to C₄-1000°F distillate liquids and C₁-C₃ gas. The hydrogen necessary for the operation is supplied from an outside source. The hydroconversion reaction system may be thermal, catalytic, or may consist of a series of thermal and/or catalytic steps. Operating conditions, nature of the catalysts, and various processing schemes

Encl. - Tables I-IV
Figure 1 (RE 832399)
Figures 2-6

(for example, "recycle") all affect and define the process severity. The process severity in turn affects conversion, product slate, volumetric expansion, and hydrogen consumption.

It should be noted that the operating conditions, catalysts, and processing techniques vary considerably among the commercial hydroconversion processes; but as shown in Figure 3, both the total hydrogen consumed and the residuum conversion increase invariably with increasing process severity. Figure 3 represents hydrogen consumption and conversion data for Arabian Light residuum processing at different sulfur levels (2). This representation is based on Chevron-designed catalysts operating at conditions capable of giving run lengths of at least six months. For maximum conversion, operation at high severities is required.

In this paper, we use total conversion to distillates and the hydrogen consumed by the process as relative measures of process severity. Admittedly, these are relative definitions, but they allow evaluation of hydroconversion processes in general without regard to the details unique to each process (e.g., catalyst, reactor type, temperature, etc.). For a given example, referring to Figure 3, the relative hydrogen consumed at hydrocracking conversion depends upon the desired S specification of the product. Because we are only interested in the relative hydrogen consumed, knowledge of the specific process details are not necessary.

Under the usual hydroconversion conditions (elevated temperatures and pressure, high hydrogen-to-feed ratios, and high activity catalysts), many reactions with hydrogen proceed simultaneously. These include: hydrocracking, aromatization, hydrogenation, condensation, hydrodesulfurization, hydrodenitrification, deoxygenation, demetalation, and isomerization. However, these reactions do not all occur at equal ratios. Judicious selection of catalysts and processing conditions favor one or more of these reactions over others. One can learn more about the relative impact of these reactions by studying the stoichiometry of hydrogen incorporation.

Stoichiometry of Hydrogen Reactions

We used the same analytical approach as Finseth et al. (3) in formulating the hydrogen/residuum reactions. Finseth and his colleagues were interested in coal conversion chemistry and the role of hydrogen during coal liquefaction. However, the same approach with some modifications can be used to study the role of hydrogen during residuum conversion. The fact that it is difficult to understand the molecular level mechanisms of hydrogen incorporation should not preclude understanding the overall chemistry.

As Finseth, hydrogen/residuum reactions are classified into six categories:

1. Hydrogenation and dehydrogenation.
2. Hydrocracking and (its reverse) condensation.

3. Isomerization and hydrogen exchange.
4. Desulfurization.
5. Denitrification and deoxygenation.
6. C₁-C₃ gas production.

This grouping is done basically to generalize the stoichiometries of very high number of reactions. Once the stoichiometry is established then it is possible to devise a technique which discriminates among these six hydrogen reaction routes.

We used ¹H and ¹³C NMR to determine the hydrogen distribution during hydrogenation/dehydrogenation reactions. We have seen only aromatization as the dehydrogenation reactions. Hydrogenation consumes one hydrogen atom for every carbon reduced. For example, if a residuum sample containing 25 aromatic, 75 aliphatic carbons is hydrogenated to 20 aromatic, 80 aliphatic carbons, ¹³C NMR should detect the change in aromaticity from 25% to 20%.

The second category of reactions, cracking/condensation, is more difficult to determine. No satisfactory method is available to count the number of cracking reactions occurring during residuum conversion. However, if all of hydrogen involved in the other five categories of reactions are accounted for, then we can calculate the hydrogen consumed due to cracking by difference.

The total change in hydrogen content can be determined by classical elemental analysis.

The third class of reactions, isomerization/exchange, does not affect net hydrogen incorporation. Therefore it is not considered here.

The remaining three categories are basically bond scission reactions eliminating heteroatoms and forming C₁-C₃ gases. Gas production is easily measured and analyzed with commonly available analytical instruments. Since two hydrogens are incorporated for every molecule of C₁-C₃ formed (mostly due to alkyl chain cracking reactions), these gas analyses provide a good estimate of hydrogen consumed in gas formation.

It is difficult to quantify accurately hydrogen consumed due to heteroatom (S, N, O) removal due to the multiplicity of reactions. For simplicity, we assume sulfur in the residuum occurs as thiophenic. Therefore, two hydrogen atoms are incorporated into the residuum for each sulfur removed.

We also assume nitrogen as pyrrolic and oxygen as a mixture of carboxylic and phenolic. Therefore, one hydrogen atom is incorporated into the residuum for each N or O removed.

Even though carboxylic acid amides and other compounds have been detected in residua (4), the above assumptions should not affect the calculations significantly because no residua studied contained more than 2% N, O. Furthermore, probably any deviations in

stoichiometry due to very large number of reactions involving heteroatoms tend to cancel each other and are therefore self-correcting.

Coking reactions produce insoluble organic material which is not accounted for in the above analysis, primarily reducing the amount of measurable aromaticity of the processed products. In hydroconversion, these levels were all under 1%, and generally less than 0.5%. These levels should have little affect on the calculations.

Therefore, using ^1H and ^{13}C NMR, as well as elemental analysis and quantitative gas analysis, one can determine the net hydrogen incorporated due to each of the six categories of reactions. Furthermore, if these determinations are coupled to process parameters, they greatly enhance the understanding of residuum conversion chemistry and hydrogen utilization. With these goals in mind, we conducted residuum hydroconversion experiments at different process severities and analyzed both the liquid and gas products as well as the feed extensively using the technique described here.

Experimental

Three California residua (designated A, B, and C) were obtained by single-plate distillation of the corresponding crude.

The ^{13}C NMR and ^1H NMR spectra were recorded on either a Bruker CXP 300 or WH-90 spectrometers. The samples were prepared as dilute solutions in deuterated chloroform with tetramethylsilane as reference. Integrations were performed by the spectrometers, and the ratios were calculated by hand. The NMR spectra were interpreted by the method of Young and Gayla (5). No olefins were observed in spectra. Gadolinium tris(1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) was added as a relaxation agent to ensure accurate integration of the aromatic region. The aromatic region was integrated between 110-180 ppm. The aliphatic region was integrated between 0-60 ppm. Each were calculated as percentage of the total integrated area (minus the solvent peaks).

Total aromatic content of liquid is adjusted for the composition of the gas.

Elemental analyses were performed by Chevron Research Company Analytical Department. C,H were done by Carlo Erba, N by either Mettler (Dumas) or Dohrmann (ASTM D 3431), S by Dohrmann (ASTM D 3120), and metals by either X-ray fluorescence or inductively coupled plasma emissions. Boiling point distribution was determined by thermogravimetric analysis (TGA). Gas composition was determined by gas chromatography.

Hydroconversion Experiments

Hydroconversion experiments were conducted in a flow reaction system using the heavy residua from California crudes. Inspections of these residua are given in Table II. These residua are very rich in nitrogen, sulfur, and metals. Arabian Heavy 730°F+ oil

is included for comparison. They represent a big challenge for the refining industry in the coming decades.

These feedstocks were processed at different severities using different sets of operating variables such as temperature, pressure, residence time, hydrogen circulation rate, and catalyst. Total hydrogen consumption varied from 600-2100 SCF/bbl of feed. Residuum conversion (1000°F+/1000°F-) ranged from 50-95%. Hydrogen consumption, 1000°F+ conversions, and the percent aromatic carbon are summarized in Table III.

Hydrogenation, Cracking, and Process Severity

The number of hydrogen atoms incorporated per 100 carbon atoms is compared in Figure 4 for Residuum A, 850°F+ cut point at three different conversion levels (Table III: Runs 2A, 2B, and 2C). With increasing process severity, the number of hydrogen atoms consumed due to cracking and gas formation reactions appears to increase linearly. The bulk of the hydrogen is used to cap the ends of cracked fragments. Since two hydrogens are incorporated for every molecule of C₁-C₃ gas formed, it is natural that hydrogen consumed in gas formation reactions also increases with increasing conversion. On the other hand, the net number of hydrogens involved in aromatic saturation remains constant in all three experiments. This may be due to all three experiments were at high levels of 1000°F+ conversion. At these high conversion levels, incremental conversion probably comes from cracking off alkyl branches from already hydrogenated species.

In Figure 5, hydrogen incorporation into Residuum A 850°F+ is compared to that of Residuum A 650°F+. As shown in Tables II and III, 850°F+ is more aromatic and contains more heteroatoms. Due to its hydrogen deficient nature relative to the 650°F+, the 850°F+ consumes more hydrogen at roughly equal process severities. Comparing Experiments 1A to 2C in Figure 5, we see that cracking reactions consume more hydrogen with 650°F+ compared to the 850°F+. With regard to hydrogenation, this order is reversed, probably because some of the hydrogen deficient species in the 850°F+ have to be hydrogenated before they crack. Due to the high conversion, the number of hydrogens involved in capping the cracked fragments far exceeds the hydrogens involved in net aromatic saturation.

In Figure 6, we compare two hydroconversion experiments conducted with Residuum B 650°F+. Experiment 3A was a thermal treatment of the feedstock, while the Experiment 3B included a catalytic treatment. The effect of these process differences is very apparent in Figure 6. The number of hydrogens incorporated due to net hydrogenation reactions is negative (-1.8/100 carbons) during Experiment 3A. This suggests that at this particular processing condition, aromatization of the residuum is occurring, and it is providing some of the hydrogen consumed for cracking and other hydrogen consuming reactions. During Experiment 3B, under different processing conditions, there is no net aromatization (indicated by the number of

hydrogens incorporated in hydrogenation). In fact, aromatic saturation is the dominant reaction in this case, consuming more hydrogen than cracking. Figure 6 is a good example of how this technique can be used as a sensitive test of the effect of processing conditions on different reaction pathways.

This technique also reveals the sensitivity of hydroconversion to characteristics of the feedstock. In Table IV, comparing 1B to 4A, total number of hydrogens incorporated is roughly the same, 24 per 100 carbons. The gross hydrogen consumption is about the same, about 1600 SCF/bbl. However, the starting feedstocks are very different. In Experiment 4A, the feedstock was Residuum C 950°F+, which is very rich in aromatic carbon and hydrogen, but low in sulfur. (See Tables II and III.) On the other hand, the feed in Experiment 1B was Residuum A 650°F+, which is less aromatic but much higher in sulfur (relative to Residuum C 950°F+). Due to the hydrogen deficient nature of the Residuum C 950°F+, more of the hydrogen is consumed in hydrogenating the aromatic species than for Residuum A 650°F+. Since overall conversion is the same in both experiments, there was not that much difference in the number of hydrogens involved in cracking and gas make. However, substantially more hydrogen was used to remove sulfur from Residuum A 650°F+ compared to Residuum C 950°F+. Therefore, although the same number of hydrogens were involved in both experiments, the distribution of these hydrogen atoms were radically different.

Conclusions

This approach yields a detailed description of hydrogen incorporation during residuum hydroconversion. Character of the feedstock, processing conditions, and the catalyst all affect how hydrogen is incorporated into residuum matrix. The two dominant reaction routes are hydrocracking and hydrogenation.

Our data analysis suggests hydrogenation and hydrocracking reactions incorporate hydrogen equally at moderate process severities. At high severities, the bulk of the hydrogen is consumed by capping reactions of cracking fragments. Judicious selection of processing conditions favor one or the other.

The feedstock characteristics also influence hydrogen incorporation. With aromatic feedstocks, hydrogenation reactions compete equally with hydrocracking for hydrogen. With less aromatic feedstocks, hydrocracking dominates over hydrogenation reactions.

The technique we presented here is useful in relating these processing conditions to understanding of the overall chemistry and exploiting these processing conditions to tailor the process and the products to the desired product slate.

Acknowledgments

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References

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FIGURE 1
THE STANGELAND CHART FOR FUELS

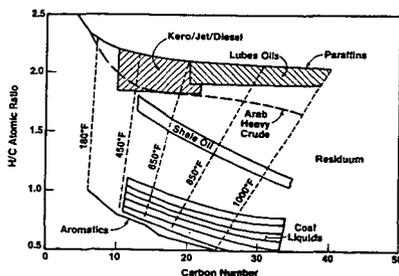


TABLE I
RESIDUUM
PROCESSING OPTIONS

Thermal Processes

- . Visbreaking
- . Delayed Coking
- . Fluid Coking
- . Steam Cracking
- . Partial Oxidation

Extractive Processes

- . Solvent Deasphalting

Catalytic Processes

- . Residuum FCC
- . Residuum Hydroconversion

TABLE II
INSPECTIONS OF FEEDSTOCKS

	Arabian Heavy	Residuum A	Residuum A	Residuum B	Residuum C
Cut Point, °F+	730	650	650	850	950
Gravity, °API	11	9.8	5	9	4.2
N, %	0.3	0.8	1.1	1.1	1.0
S, %	4.6	5.7	5.7	4.2	1.2
H, %	10.7	10.6	10.1	10.6	10.2
C, %	84.1	82.0	81.5	83.7	85.3
H/C	1.53	1.55	1.49	1.52	1.44
Ni, ppm	24	109	139	115	165
V, ppm	88	274	359	197	75
Fe, ppm	4	0	14	3	75
C ₇ Asphaltenes, %	8.4	12	15	10.1	7.6
Ramscarbon, %	14	13	16.8	13.7	20.2
1000°F+ Content, %	60	48	75	46	95

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TABLE III
HYDROCONVERSION EXPERIMENTS

Exp. No.	Identification	Total Hydrogen, % Wt	Aromatic Carbon, %	1000°F+ Conversion, %	H ₂ Consumed, SCF/Bbl of Feed
1	Residuum A 650°F+ (Feed)	10.6	22.5	-	-
1A	(Product)	12.7	20	95	2000
1B	(Product)	12.4	20.3	84	1530
2	Residuum A 850°F+ (Feed)	10.1	26.7	-	-
2A	(Product)	12.3	20.1	79	1660
2B	(Product)	12.3	20.4	82	1750
2C	(Product)	12.4	20.3	87	2050
3	Residuum B 650°F+ (Feed)	10.5	29.5	-	-
3A	(Product)	11.2	32	60	600
3B	(Product)	11.79	22.5	73	1100
4	Residuum C 950°F+ (Feed)	10.2	33	-	-
4A	(Product)	11.9	26	77	1600

TABLE IV
HYDROCONVERSION OF
RESIDUUM C 950°F+ VERSUS RESIDUUM A 650°F+

	Residuum C 950°F+	Residuum A 650°F+
Feed		
Aromatic C, %*	33.0	22.5
Aromatic H, %**	6.7	3.2
Experiment No.	4A	1B
H Atoms Incorporated/100 C		
Due to Cracking	9.9	11.9
Due to Hydrogenation	8.3	3.0
Due to C ₁ -C ₃	3.5	3.8
Due to Heteroatom Removal	2.4	6.0
Total	24.1	24.7

*From ¹³C NMR.

**From ¹H NMR.

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FIGURE 2
GENERALIZED DIAGRAM
RESIDUUM CONVERSION REFINERY

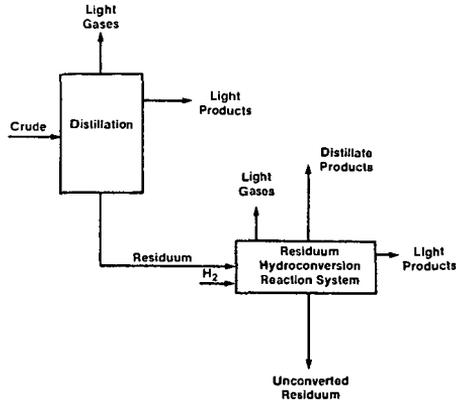
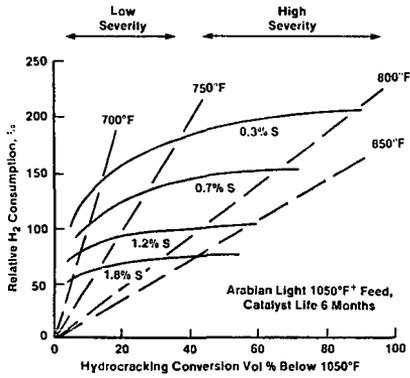


FIGURE 3
H₂ USAGE IN RESIDUUM PROCESSING*



*From A. G. Bridge, J. W. Scott, E. M. Reed, The Oil and Gas J, May 19, 1975

FIGURE 4
HYDROCONVERSION OF RESIDUUM A 850°F⁺

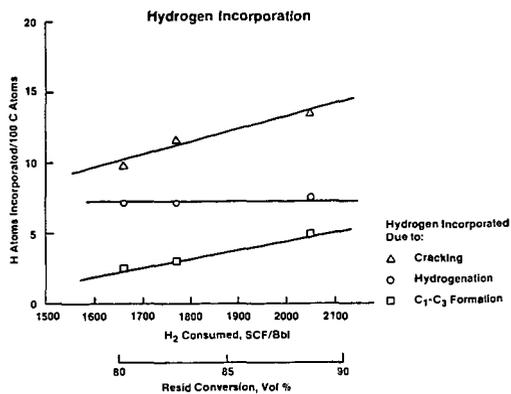


FIGURE 5
HYDROCONVERSION OF RESIDUUM A

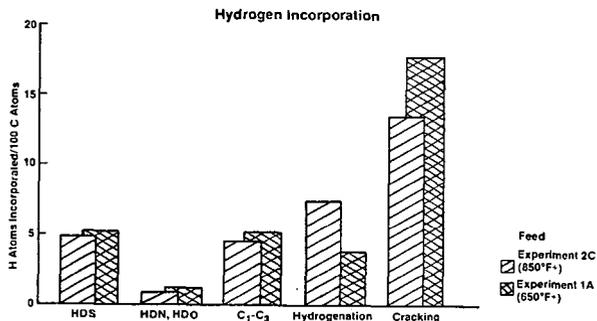


FIGURE 6
HYDROCONVERSION OF RESIDUUM B 650°F⁺
Thermal Treatment Versus Catalytic Treatment

