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*A METHOD OF ESTIMATING THE
AMOUNT OF HYDROGEN
REQUIRED TO UPGRADE
RESIDUAL OILS AND TARS*

B. I. PARSONS

FUELS RESEARCH CENTRE

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A METHOD OF ESTIMATING THE AMOUNT OF HYDROGEN REQUIRED
TO UPGRADE RESIDUAL OILS AND TARs

by

B.I. Parsons*

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ABSTRACT

The hydrogen required to refine (by hydrogenation) a high-residuum oil is the sum of the hydrogen involved in four separate processes: (a) the hydrogen added to the residuum material to lower the specific gravity and improve hydrocarbon quality, (b) the hydrogen consumed in the removal of impurities, and the hydrogen removed from the system in the course of processing by the formation of (c) gases and (d) coke. In the following article a method is described for estimating the amount of hydrogen required in each step. The results of general (nominal) calculations for feed stocks of specific gravity 1.04, 0.98, 0.963 and 0.936 are presented in graphical form. Major factors taken into account in the calculations are the volume yield and specific gravity of the liquid product and the composition of the gases formed. Interpolation of the graphs for the preparation of estimates of hydrogen requirements for particular feed stocks and products is easy and quick. A typical application of the method to the processing of whole-crude and coker distillates from the Alberta Bituminous Sands Deposits is discussed.

* Research Scientist, Fuels Research Centre, Mines Branch,
Department of Energy, Mines and Resources, Ottawa, Canada.

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UNE MÉTHODE POUR ÉVALUER LA QUANTITÉ
D'HYDROGÈNE REQUISE POUR AMÉLIORER LES
PÉTROLES ET BITUMES À RÉSIDUS LOURDS

par

B.I. Parsons

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RÉSUMÉ

La quantité d'hydrogène requise pour raffiner (par l'hydrogénation) un pétrole à résidus lourds se mesure à la quantité totale consommée dans quatre procédés individuels: a) l'hydrogène ajouté aux résidus pour abaisser le poids spécifique et améliorer la qualité de l'hydrocarbure, b) l'hydrogène consommé dans l'élimination des impuretés, et l'hydrogène éliminé du système au cours du traitement par c) la formation de gaz et d) la production de coke. L'auteur décrit une méthode qui permet d'évaluer la quantité d'hydrogène requise à chaque étape. Les résultats des calculs généraux (nominiaux) relatifs aux bruts d'alimentation pour des poids spécifiques de 1.04, 0.98, 0.963 et 0.936 sont présentés sous une forme graphique. Les principaux facteurs dont l'auteur a tenu compte dans les calculs sont le rendement volumétrique et le poids spécifique du produit liquide, et la composition des gaz formés. Il est facile et rapide de procéder à l'interpolation des graphiques et ainsi évaluer les quantités d'hydrogène requises pour des bruts d'alimentation et des produits particuliers. L'auteur donne aussi un exemple d'application de la méthode au traitement de brut entier et de distillats de cokéfaction provenant des sables bitumineux de l'Alberta.

* Préposé aux recherches scientifiques, Centre de recherche sur les combustibles, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

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INTRODUCTION

A large part of the program of research in petroleum at the Mines Branch has been concerned with the refining and upgrading of residual oils and tars. Bench-scale experimental work on the hydrogenation of coal and heavy tars was begun in 1932. A process for the separation of the bitumen from the Alberta tar sands deposits was developed in 1948-49(1), and an experimental coking plant for the production of coker distillates from the bitumen (and other residual crude oils) was operated in 1949-51(2). More recently, high-pressure liquid- and vapour-phase hydrogenation pilot plants have been constructed for the hydrogen-refining of both coker distillates and vacuum bottoms from residual oils (3, 4, 5, 6).

At almost every stage in the development of processing skill, however, the "cost of the hydrogen required" has been proposed as an economic barrier for commercial application. Until very recently, it has been difficult to assess this economic specter because process yields and product qualities have not been established accurately enough to provide a firm basis for estimates. Some experimental results and analyses are now available and the purpose of the following article is to indicate a scheme (provided in graphical form) whereby rapid estimates of hydrogen requirements can be obtained, taking into account both the yield and quality of product and the composition of the gases formed. The calculations provide a method for comparing the hydrogen requirements for various hydrogenation processes under widely differing reaction conditions.

Interest in hydrogen refining (hydrogenation) has increased considerably in the past ten years. This is due, very largely, to progress in the equipment and technology of hydrogenation processing itself, and also to progress in the manufacture of hydrogen and in the recovery of sulphur. Engineering developments in low-temperature (predominately liquid-phase) processes have resulted in the production of high-quality jet and diesel fuels in good yield (6, 7). The capability and cost of producing hydrogen from natural gas, or from naphtha fractions, have been improved so much that the advertised price for hydrogen is now as low as 22 cents per 1000 standard cubic feet (8). Greater industrial experience in the recovery of sulphur from H_2S , and the rising value of sulphur on the world market (9), continue to provide additional incentive for the hydrogen treatment of low-grade oils. The current market value of the sulphur contained in the Alberta bitumen is 30.5 cents per barrel of separated bitumen (10).

THE BASIS OF THE CALCULATIONS

The total amount of hydrogen required to upgrade a high-residuum petroleum feed stock is the sum of the hydrogen involved in four separate and distinct processes:

1. Constituent hydrogen - that which must be added to the residuum material to improve the hydrocarbon quality, i.e. reduce the specific gravity and the average molecular weight.

2. Refining hydrogen - that which is consumed in the process of removing impurities such as sulphur, nitrogen, etc.

3. Hydrogen in gases formed - in the course of treatment, gases (methane, etc.) are formed which have the effect of reducing the hydrogen content of the product. The type of gases produced varies considerably with the process used, i.e. hydrocracking or catalytic hydrogenation, and the amount of gas varies with the severity with which the process is operated.

4. Hydrogen in the tars and coke formed - the amount (weight) of hydrogen involved in the tar and coke formed in processing is usually quite small* for most catalytic hydrogenation processes and is generally neglected. It is significant sometimes in cases of non-catalytic (thermal) hydrogenation.

To calculate the amount of hydrogen required in the above processes, one must be able to determine, or assume, the composition (percent hydrogen, carbon, sulphur, etc.) of (a) the starting material, (b) the product, (c) the gases formed and (d) the coke produced (if applicable), and must also have some working knowledge of the yield of liquid product to be expected from the processes used. The first two factors -- the compositions of the starting material and of the product -- determine the amount of hydrogen required to accomplish the chemistry of the process, and the last three factors -- the compositions of the gases and coke formed and the yield of liquid product -- establish the hydrogen losses along the way. The estimates of the hydrogen required for the chemical transformations, the improvement of hydrocarbon quality and the removal of impurities, are based essentially on analytical measurements. These can, with today's technology, approach 1% accuracy or better.

It is in the region of the "yield" and "gas losses" that much uncertainty has arisen. Until very recently there has been little information

* Not insignificant from the viewpoint of catalyst activity, but small in terms of the total weight of feed and products.

available on the processes that have been proposed, and one has been placed in the position of having to assume the worst. During the past few years, however, several publications indicating yields and losses in hydrogenation processes for upgrading residual oils have appeared, notably reports on the "H-oil" process (11), the catalytic hydrotreating of shale oil in the U.S. (12), the Gulf HDS process (13), the German "Combi" liquid-phase process (14), as well as publications originating in the Mines Branch (5, 6, 7). All of these reports indicate the volume yield of liquid product to be in the region of 98-102% under mild reaction conditions, i.e. low temperature and low space velocity. Good conversion rates and low coking rates have been observed at reaction temperatures of 410-430°C and a space velocity of one or less, at medium pressures in the range 2000-3000 psi. Considerably higher pressures are required to minimize the coking rate and extend catalyst life at elevated temperatures.

To simplify matters, and also to ensure consistency in the calculations, the "yields", "losses" and "chemical analyses" upon which the present hydrogen consumption estimates are based are those originating in the research at the Mines Branch on the hydrogenation of whole-crude (7), and coker distillates (5), derived from the bituminous sands deposits at Mildred Lake, in Alberta. Sufficient data will be supplied in the graphical presentation of the estimates to permit the reader to interpolate the results for feed stocks in the specific gravity range 1.04 to 0.93. The procedures and factors taken into account in calculating the amounts of hydrogen required in each step of the process are outlined briefly below. A detailed sample calculation is shown in Appendix 1.

Constituent Hydrogen

An accurate estimate of the amount of hydrogen which must be added to the feed stock to improve the hydrocarbon quality can be obtained, using the results of hydrogen analyses made on both feed and products, as follows:

$$\begin{array}{rcl}
 \boxed{\begin{array}{c} \text{Constituent} \\ \text{Hydrogen Required} \\ \text{(lb/bbl processed)} \end{array}} & = & \boxed{\begin{array}{c} \text{Weight of} \\ \text{Products Formed} \\ \text{From One Barrel} \\ \text{of Feed} \\ \text{(lb)} \end{array}} \quad \times \quad \boxed{\begin{array}{c} \text{Fraction} \\ \text{Hydrogen} \\ \text{in} \\ \text{Product} \end{array}} \\
 & - & \boxed{\begin{array}{c} \text{Weight of One} \\ \text{Barrel of Feed} \\ \text{(lb)} \end{array}} \quad \times \quad \boxed{\begin{array}{c} \text{Fraction} \\ \text{Hydrogen} \\ \text{in Feed} \end{array}}
 \end{array}$$

Rarely, however, are all the analyses readily available. For estimating purposes, the engineer usually has only the constituent analysis of the raw feed

stock and assumes a series of "hypothetical" products of varying quality. It has been our experience (4) that the equation

$$\% \text{ H}_2 = 26 - 15d, \quad (1)$$

where d is the specific gravity of the oil,

provides a remarkably accurate estimate of the hydrogen content for products from many upgrading processes, both thermal and hydrogenating type. The equation was originally proposed by Cragoe (15) for application to pure hydrocarbon systems, but a comparison of calculated and measured hydrogen contents of oils containing as much as 2.5% combined sulphur and nitrogen indicates general agreement within the reproducibility of the hydrogen analyses. The impurity content of the oil need only be taken into account when calculating the carbon content corresponding to equation (1), as follows:

$$\% \text{ carbon} = \boxed{100 - \% \text{ H}_2} - \boxed{\% \text{ sulphur and nitrogen in oil}} \quad (2)$$

Refining Hydrogen

The amount of hydrogen required to remove impurities, such as sulphur and nitrogen, from the feed stock are also calculated, using the constituent analyses of the feed and product; for example, for sulphur removed as H_2S :

$$\begin{aligned} &\boxed{\text{Weight Sulphur Removed (lb/bbl processed)}} = \boxed{\text{Weight of One Barrel of Feed (lb)}} \times \boxed{\text{Fraction Sulphur in Feed}} \\ &\quad - \boxed{\text{Weight of Products Formed From One Barrel of Feed (lb)}} \times \boxed{\text{Fraction Sulphur in Product}} \\ &\boxed{\text{Hydrogen Required to Remove S as H}_2\text{S (lb/bbl processed)}} = \frac{\text{Weight of Sulphur Removed (lb)}}{\text{Molecular Wt. Sulphur}} \times \text{Molecular Weight of Hydrogen} \\ &= \frac{\text{Weight of Sulphur Removed (lb)}}{16} \end{aligned}$$

Similar equations can be set up for the hydrogen required to remove N as NH_3 , or O as H_2O .

As in the case of the calculation of the "constituent hydrogen", however, analyses of the products are usually not available and it becomes necessary to assume reasonable values for the concentration of sulphur and nitrogen in order to proceed. The graph shown in Figure 1 is offered as a guide to the concentration of sulphur remaining in oil products formed from feed stocks containing 4.0-4.5% sulphur in low- and medium-pressure hydrogenation processes (5, 7).

The hydrogen required to remove nitrogen and oxygen from high-residuum crude oils can frequently be neglected in the calculation of "refining hydrogen", because the amounts involved are usually small and tend to be compensated for as hydrogen lost in gas formation in the course of treatment. For example, the nitrogen content of whole-crude from the Alberta bitumen is approximately 0.5% by weight. The hydrogen required to completely remove this amount from one barrel of feed is 0.38 lb or 68 std cu ft. If the nitrogen removed is neglected in the estimate of the hydrogen required for refining purposes, it appears as a weight loss in the carbon balance, and is assumed to be part of the weight of gases formed, such as CH_4 or C_2H_6 , involving approximately 0.43 lb of hydrogen or 78 std cu ft. By neglecting the nitrogen removed in the refining process, an overestimate occurs in the overall amount of hydrogen required (in this case, 10 cu ft).

Hydrogen in Gases Formed

To calculate the amount of hydrogen removed from the system by the formation of gases, it is necessary to know (or be able to make a reasonable estimate of) the amount of gas formed, and its composition. The calculations here are more dependent on experimental, operational information than those described in previous sections the upper and lower limits of the yield of liquid product must be known to be able to calculate the amount of gas formed, and analyses (typical) are needed to establish the composition. It is particularly important to have information regarding the yield and composition of the gases for calculations involving hydrocracking processes. The amount of hydrogen removed from the system by the formation of gases in hydrocracking is frequently equal to, and sometimes considerably greater than, that required to upgrade the hydrocarbon quality of the liquid product.

In the present work, the estimates of the hydrogen required for processing are based upon the results of investigations of low- and medium-pressure catalytic hydrogenation of whole-crude and coker distillates derived from the Alberta bituminous sands deposits. The yield of liquid product (C_5 and up) with this type of feed stock falls in the range 96 to 106% by volume, depending upon the reaction conditions selected, and the gases formed are

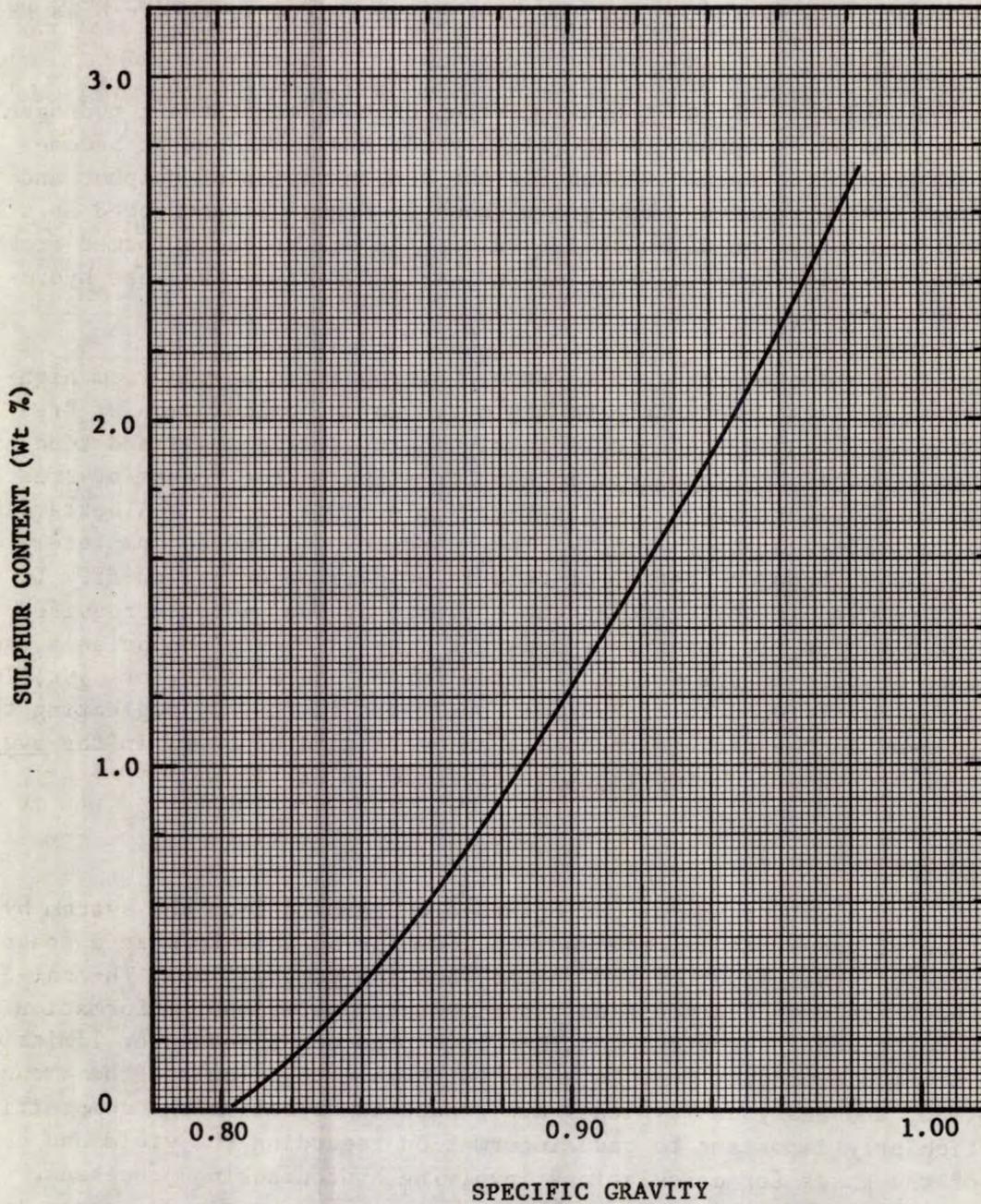


FIGURE 1 - The concentration (for estimating purposes) of sulphur remaining in oil products formed from high-sulphur, low-grade feed stocks in low- and medium-pressure hydrogenation processes.

usually methane, ethane, propane, and butane. Small amounts of unsaturated hydrocarbons are sometimes detected in the gases formed but their total rarely exceeds 5% by volume. For most purposes, amounts of unsaturated hydrocarbons up to 5% have only a marginal effect on the calculations. Typical "Off-Gas" analyses for two catalyst systems investigated at the Mines Branch (6) are shown in Table 1.

The calculation of the hydrogen associated with the gases formed is made in two steps. In the first step, the amount of carbon lost in processing and attributable to gas formation is estimated:

$$\begin{array}{rcc}
 \boxed{\begin{array}{c} \text{Weight of} \\ \text{Carbon in} \\ \text{One Barrel} \\ \text{of Feed} \end{array}} & - & \boxed{\begin{array}{c} \text{Weight of Carbon} \\ \text{in Liquid Product} \\ \text{Formed From One} \\ \text{Barrel of Feed} \end{array}} & = & \boxed{\begin{array}{c} \text{Total Weight of} \\ \text{Carbon Lost Per} \\ \text{Barrel Processed} \end{array}} \\
 \\
 = & & \boxed{\begin{array}{c} \text{Weight of Carbon} \\ \text{in Gases Formed} \\ \text{Per Barrel} \\ \text{Processed} \end{array}} & + & \boxed{\begin{array}{c} \text{Weight of Carbon} \\ \text{in Coke Formed} \\ \text{Per Barrel Processed} \\ \text{(if significant)} \end{array}}
 \end{array}$$

As mentioned previously, the amount of coke and tars formed in most catalytic hydrogenation processes is quite small in relation to the total amount of carbon in a barrel of feed. It can, therefore, usually be neglected and the total amount of carbon lost in processing can be assumed to be as the result of gas formation.

In the second step of the calculation, a "factor" is prepared by which to multiply the carbon loss to obtain the associated weight of hydrogen taking into account the constituent analysis of the gas.

TABLE 1

Typical Analyses of Gases Formed in the
Hydrogenation of Residual Oils (6)

Constituent	Over Cobalt Molybdate Catalyst		Over Iron Sulphate On Carbon Catalyst	
	Volume %	Weight %	Volume %	Weight %
Methane	30.4	14.4	65.1	43.1
Ethane	24.0	21.2	15.8	19.6
Propane	28.2	36.6	10.5	19.1
Butane	13.4	23.0	4.8	11.5
Unsaturated H.C. (average C ₃)	3.9	4.8	3.8	6.7

The general equation is:

$$\text{Hydrogen Factor} = \frac{A_H}{A_C} \sum_{C_1}^{C_i} f_i \frac{(\text{NH})_i}{(\text{NC})_i}, \quad (3)$$

where A_H is the atomic weight of hydrogen (1.00),

A_C is the atomic weight of carbon (12.0),

f_i is the fraction (by weight) of the constituent present,

$(\text{NH})_i$ is the number of atoms hydrogen in constituent, and

$(\text{NC})_i$ is the number of atoms carbon in constituent.

Where the composition of the gases is unknown, an upper-limit estimate* of the hydrogen involved in gas formation can be made by assuming it to be entirely methane (CH_4). It is immediately obvious, of course, that the amount of hydrogen removed (per unit weight of gas formed) as methane is considerably greater than that as propane (C_3H_8) or ethylene (C_2H_4). For example, the hydrogen factors for the typical "Off-Gas" analyses shown in Table 1 are as follows:

(a) Gases formed over cobalt molybdate catalyst

methane:	$\frac{1.00}{12.0}$	x	0.144	x	$\frac{4}{1}$	=	0.048
ethane:	0.0834	x	0.212	x	$\frac{6}{2}$	=	0.053
propane:	0.0834	x	0.366	x	$\frac{8}{3}$	=	0.081
butane:	0.0834	x	0.230	x	$\frac{10}{4}$	=	0.048
unsaturates: (as C_3H_6)	0.0834	x	0.048	x	$\frac{6}{3}$	=	0.008

Hydrogen Factor is 0.238

* A "guess-timate".

(b) Gases formed over iron sulphate on carbon catalyst

methane:	$0.0834 \times 0.431 \times \frac{4}{1}$	= 0.145
ethane:	$0.0834 \times 0.196 \times \frac{6}{2}$	= 0.049
propane:	$0.0834 \times 0.191 \times \frac{8}{3}$	= 0.042
butane:	$0.0834 \times 0.115 \times \frac{10}{4}$	= 0.024
unsaturates: (as C_3H_6)	$0.0834 \times 0.067 \times \frac{6}{3}$	= 0.011

Hydrogen Factor is 0.271

The weight of hydrogen associated with a particular carbon loss is then:

Weight of Hydrogen Removed in Gas Formation Per Barrel Processed	=	Weight of Carbon Lost Per Barrel Processed	x	Hydrogen Factor
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RESULTS OF THE CALCULATIONS

Calculations were made for four separate feed stocks derived from the Alberta bituminous sands deposits:

- (a) whole-crude,
specific gravity = 1.012,
- (b) thermally treated (vis-break) whole-crude,
specific gravity = 0.980,
- (c) a typical coker distillate prepared from the
residuum fractions of the whole-crude,
specific gravity = 0.963, and
- (d) a typical coker distillate prepared from the
whole-crude (light ends not removed),
specific gravity = 0.936.

In the calculations for the whole-crude and the thermally treated whole-crude, it was assumed that liquid products of specific gravity 0.95, 0.90 and 0.85 were formed in 92 to 104% yield, and for the two distillate

feed stocks it was assumed that liquid products of specific gravity 0.90, 0.85 and 0.80 were formed in 94 to 106% yield. The sulphur contents of the products were read from the graph in Figure 1. Separate estimates were made with each feed stock, using four hydrogen factors:

- 0.33 - pure methane
- 0.30 - predominately methane and ethane
- 0.27* - typical off-gas from high-temperature hydrogen treatment processes
- 0.24* - typical off-gas from medium-pressure catalytic hydrogenation processes

The results of the calculations are shown in graphical form in Figures 2 to 5. The background scale-lines of the graphs have been left showing, to facilitate interpolation between the liquid products and hydrogen factors within the increments shown, linear interpolation is accurate to 1%.

A TYPICAL APPLICATION

General estimates of the hydrogen required for processing many feed stocks to a designated specific gravity can be obtained directly from the graphs shown in Figures 2 to 5. Interpolation between the lines shown in the Figures to products of intermediate specific gravity (or the interpolation of the entire Figure to a feed stock of intermediate specific gravity) is relatively easy and quick. It has been our experience, however, that once the general type of estimate has been prepared, the next step is to obtain estimates of hydrogen requirements for one particular process operating under various reaction conditions. This is only possible when some specific experimental results are available, i.e. product quality, yield, gas analysis, etc.** on which to base the calculations. As has been mentioned previously, such information has been published for the hydrogenation of whole-crude and coker distillates from the Alberta bituminous sands deposits, and the following procedure and calculations are presented to indicate how the graphs can be used to evaluate the hydrogen requirements of a process more fully.

The estimates shown in Figures 2 to 5 were prepared assuming that the feed material is passed only once through a fixed-bed reactor, i.e. a "single-pass" type of processing. The products are a mixture of hydrocarbons ranging from gasoline to lubricating distillates and some unreacted residuum. With conventional feed stocks (in the heavy fuel-oil class), where the object

* See Table 1, page 7.

** Alternatively, one can make use of an investigation with a similar type of feed stock to prepare reasonable assumptions of yields, etc.

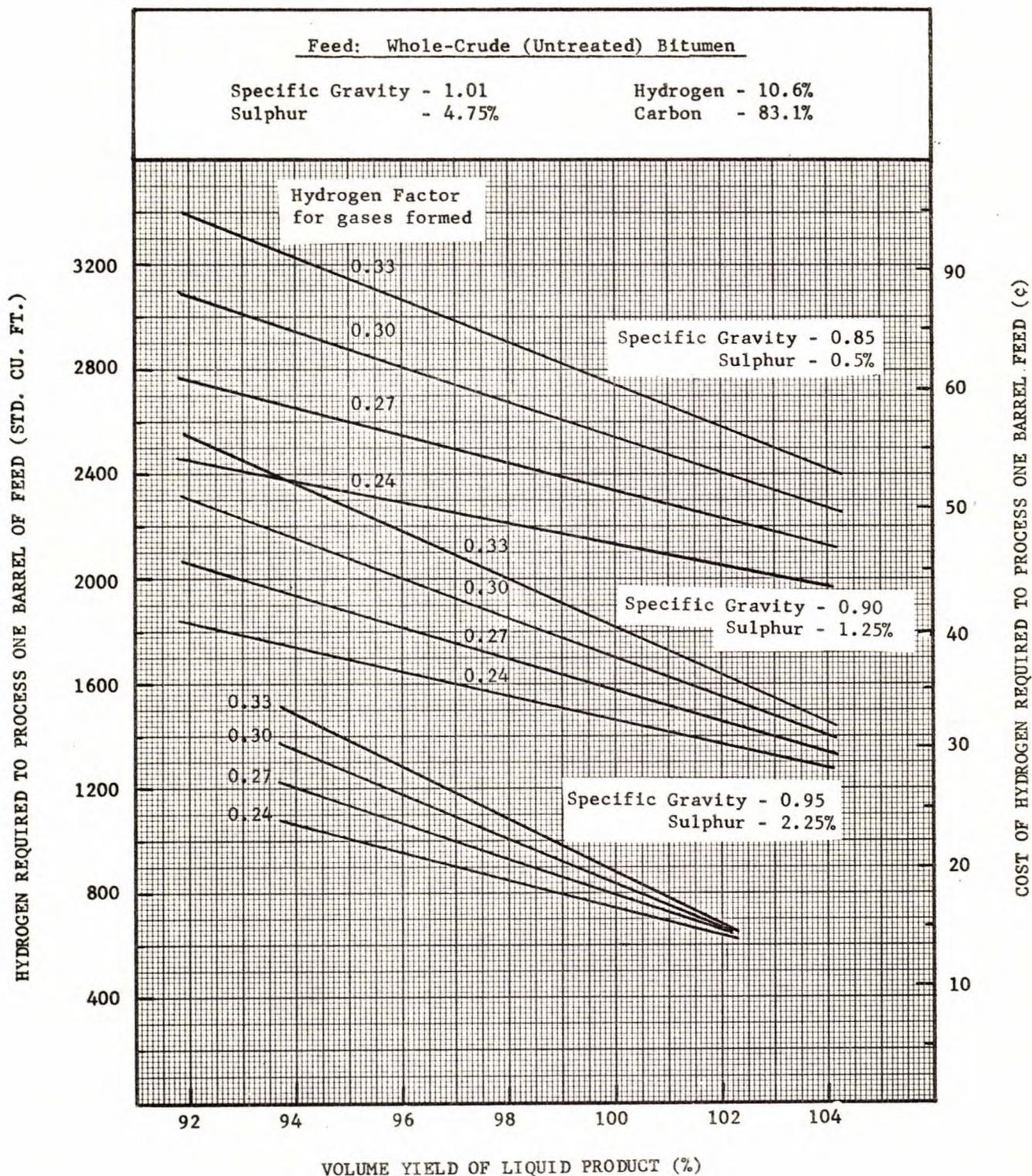


FIGURE 2 - The amount of hydrogen required to process whole-crude (untreated) bitumen, shown as a function of the specific gravity and volume yield of liquid product and the composition of the gases formed.

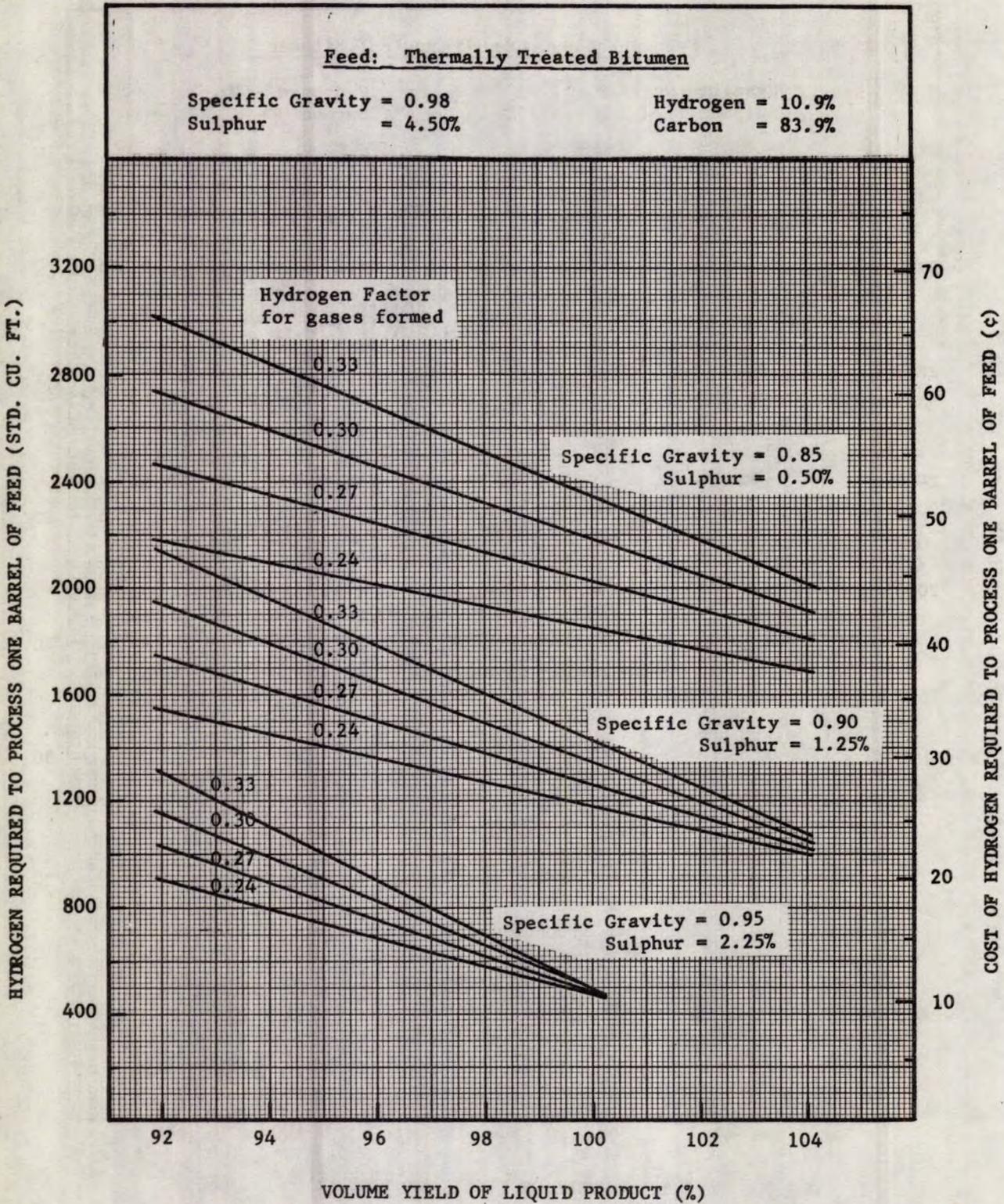


FIGURE 3 - The amount of hydrogen required to process thermally treated bitumen, shown as a function of the specific gravity and volume yield of liquid product and the composition of the gases formed.

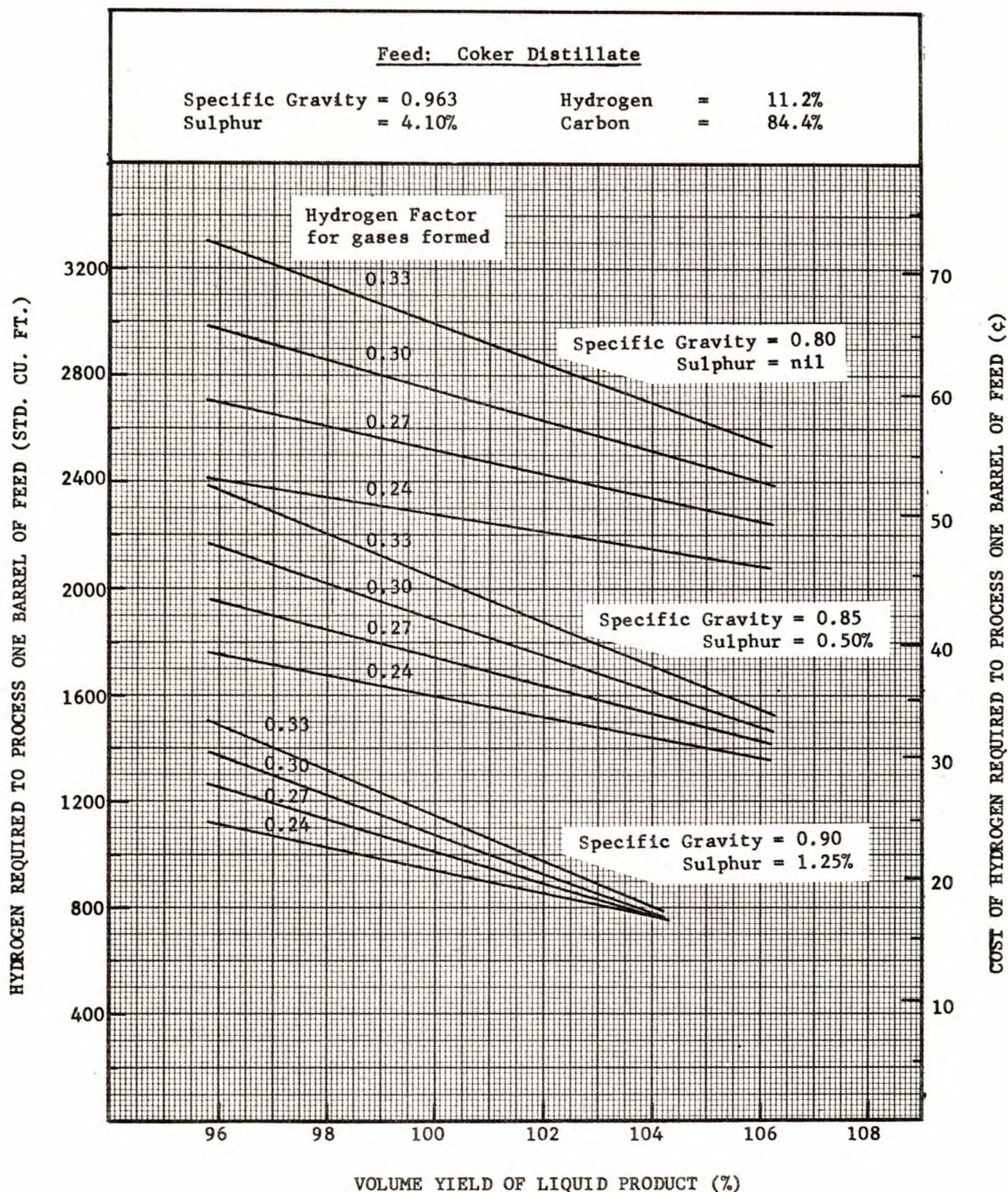


FIGURE 4 - The amount of hydrogen required to process a coker distillate (prepared from the residuum fractions of the whole-crude), shown as a function of the specific gravity and volume yield of liquid product and the composition of the gases formed.

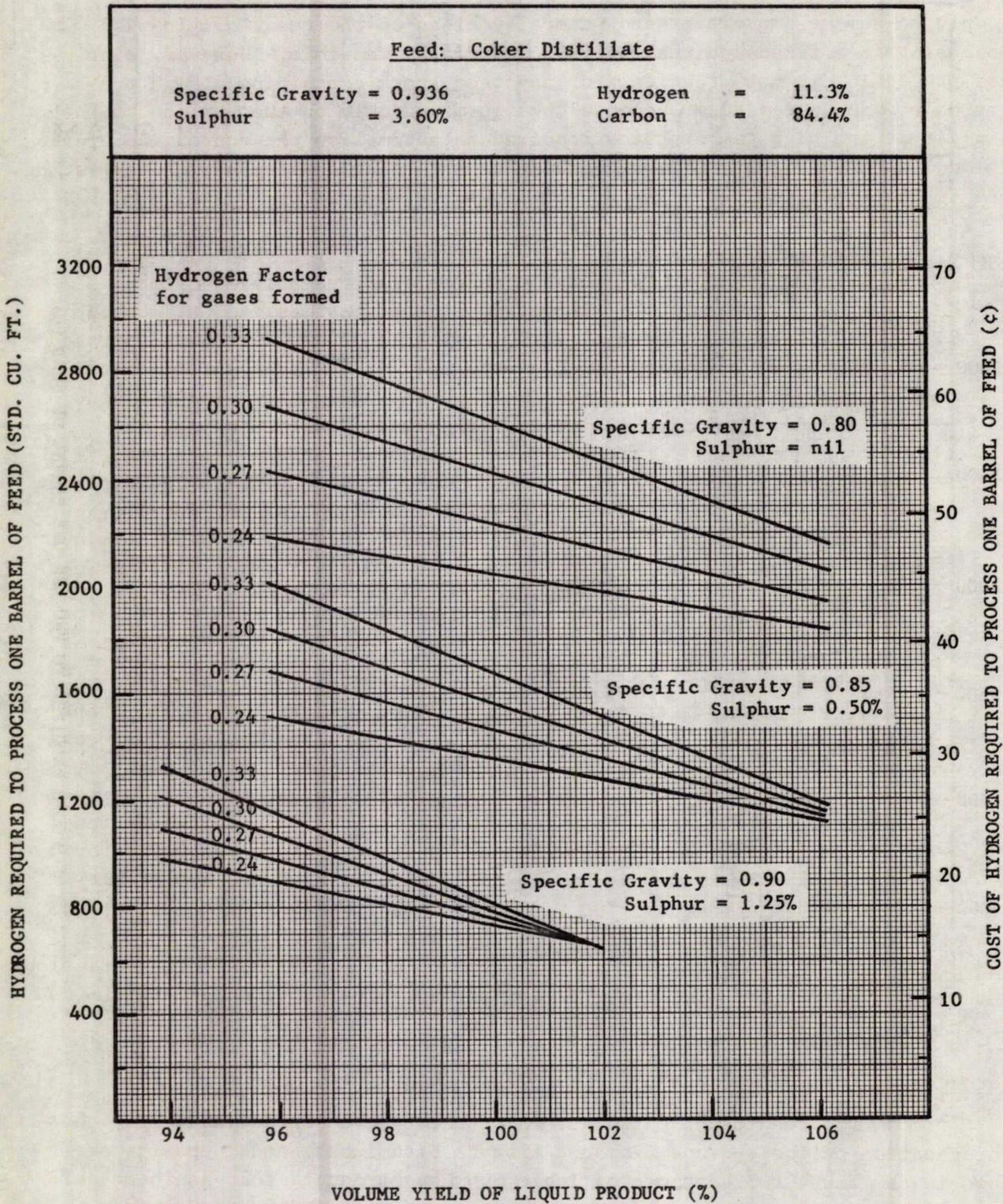


FIGURE 5 - The amount of hydrogen required to process a coker distillate (prepared from the whole-crude--light ends not removed), shown as a function of the specific gravity and volume yield of liquid product and the composition of the gases formed.

is only to remove impurities and generally clean up the feed, single-pass processing in a fixed-bed reactor is commercially feasible. However, single-pass processing is not practical for any feed stock containing a high proportion of vacuum residuum, because coke forms quickly on the surface of the catalyst at the high temperatures required to accomplish the conversion of the residuum material to distillable hydrocarbon in a single pass, and the operating life is too short.

Two processes for catalytically hydrogenating vacuum residuum in the liquid phase at low and medium temperatures are presently in commercial use on a small scale, (a) the "H-oil" process at Cities Service Oil Company's Lake Charles Refinery in Louisiana (11), and (b) the "Combi" process operated by Scholven Chemie A.G. in Germany (14). In the "H-oil" process, the heavy feed stocks are hydrogenated in an ebullated cobalt molybdate catalyst bed. The "Combi" process uses a conventional liquid-phase reactor and a finely powdered iron-carbon black catalyst. Both engineering arrangements achieve a high level of conversion, partly by removing the lighter hydrocarbon fractions as they are formed (leaving the heavier oils in the catalyst bed for a longer period of time) and also by distilling the lighter fractions from the product in a separate step and recycling the heavy ends. Such systems process essentially all (90%+) of the feed material to a product distilling below a designated end-point temperature.

To use the graphs shown in Figures 2-5 to estimate hydrogen requirements for any system where the residuum material is virtually all transformed to distillable oil, it is necessary only to assume a series of processing steps in which the heavier fractions are recycled. For calculating purposes, select (arbitrarily) an end-point temperature for the product and recycle all fractions distilling above the designated end-point until the feed has been (virtually) completely processed. The total hydrogen required for processing is then the sum of the hydrogen consumed in each cycle. Where estimates are being prepared for only slightly varying reaction conditions, it is advisable to compare the figures on the basis of the production of a standard volume of product. Any differences are then attributable to variations in the yield and in the amount of gas formed under the different reaction conditions.

Hydrogenation of Whole-Crude

The results of calculations of the type described above for the hydrogenation of whole-crude from the Alberta bituminous sands deposits are shown in the first two sections of Table 2. The "product" that has been selected for the comparison has an end-point temperature of 740°F. Consider Section 1 - for the hydrogenation of whole-crude at 797°F (425°C) and 2000 psi: In Cycle No. 1, one barrel of feed (specific gravity = 1.01) is processed to form 1.02 barrels of oil (specific gravity = 0.90). Distillation analysis of the oil (7) indicates 53% by volume distills below 740°F, and 47% by volume

(0.489 barrel) is to be recycled in Cycle No. 2. The specific gravity of the recycle oil is generally less, say 0.98, than that of the whole-crude, because of the presence of larger amounts of hydrocarbons distilling in the lubricating oil range. In Cycle No. 2, 0.489 barrel of feed (specific gravity 0.98) is processed to form 0.499 barrel of oil (specific gravity 0.90). The process is repeated until, after four cycles, 0.993 barrel of product distilling below 740°F has been prepared, requiring 2282 cubic feet of hydrogen at a cost of 50.2 cents.

The results of calculations for the same system operating at a lower temperature are shown in the second section of Table 2. In the first cycle, one barrel of feed (specific gravity 1.01) is processed to form 1.02 barrels of product (specific gravity 0.940). Distillation analysis of this product indicates only 40% by volume distilling below 740°F and 60% by volume (0.612 barrel) to be recycled in Cycle No. 2. To produce the same volume of product as in the case of the high-temperature experiment, seven cycles are required. The hydrogen consumption, however, is only 1679 cubic feet, at a cost of 36.9 cents.

It is immediately apparent from such a comparison that, while considerably more recycling of the feed stock is required at low temperatures, much less hydrogen is consumed . . . for the production of an equal volume of product. This is due primarily to the fact that the amount of gas formed is smaller at lower temperatures. Experimental analyses (7) indicate that the compositions of the products (distilling below 740°F) were essentially the same and that both contained less than 0.1% sulphur. Similar calculations can be made for other changes in reaction conditions.

Hydrogenation of a Coker Distillate

The results of calculations made for the catalytic hydrogenation of a coker distillate derived from the whole-crude are shown in Sections 3 and 4 of Table 2. Unfortunately, it is not possible to compare these results directly with those obtained for the processing of the whole-crude, because the reaction conditions used in the two investigations were not exactly equal. The catalysts used were the same, but the space velocity used in the investigation with the coker distillate was greater (2.0) compared to that used with the whole-crude (0.5); and the distillate feed stock was not preheated over catalyst packing and consequently the reaction temperatures used were somewhat higher. In addition, the coker distillate contained approximately 14% by volume of light fractions (gasolines and light gas-oils), whereas the whole-crude had been topped to remove all light ends.

The presence of the light fractions in the coker-distillate feed stock has a profound effect on the overall hydrogen requirements for processing. The low-molecular-weight hydrocarbons tend to crack and to form gases readily at the high reaction temperatures needed to hydrogenate and refine the residuum. This tendency is greatest at low pressures . . . as illustrated in

TABLE 2

Hydrogen Requirements for the Conversion of Whole-Crude and Coker Distillates from the Alberta Bituminous
Sands Deposits to Liquid Product, Distilling below 740°F by Hydrogenation over Cobalt Molybdate Catalyst

Cycle No.	Specific Gravity, 60/60°F		Hydrogen Factor for Gas Formed	Volume of Feed in Cycle (bbl)	Volume Yield (%)	Volume of Product in Cycle (bbl)	Liquid Product Distilling Below 740°F			Recycle Oil		Hydrogen Required to Process			
	Feed	Product					Yield (%)	Vol. in Cycle (bbl)	Cumulative Vol (bbl)	Yield (%)	Vol. in Cycle (bbl)	Nominal per Single Pass (cu ft/bbl)	Volume per Cycle (cu ft)	Cumulative Volume (cu ft)	Cumulative Cost at 22¢/1000 (cents)
<u>Section 1: Whole-crude hydrogenation at 797°F (425°C) and 2000 psi (reference 7)</u>															
1	1.01	0.90	0.24	1.000	102	1.020	53	0.541	0.541	47	0.489	1370	1370	1370	30.1
2	0.98	0.90	"	0.489	"	0.499	"	0.264	0.805	"	0.235	1090	533	1903	41.9
3	0.98	0.90	"	0.235	"	0.240	"	0.127	0.932	"	0.113	"	256	2159	47.5
4	0.98	0.90	"	0.113	"	0.115	"	0.061	0.993	"	0.054	"	123	2282	50.2
<u>Section 2: Whole-crude hydrogenation at 761°F (405°C) and 2000 psi (reference 7)</u>															
1	1.01	0.94	0.24	1.000	102	1.020	40	0.408	0.408	60	0.612	790	790	790	17.4
2	0.98	0.94	"	0.612	100	0.612	"	0.245	0.653	"	0.367	610	373	1163	25.6
3	0.98	0.94	"	0.367	"	0.367	"	0.147	0.800	"	0.220	"	224	1387	30.5
4	0.98	0.94	"	0.220	"	0.220	"	0.088	0.888	"	0.132	"	134	1521	33.5
5	0.98	0.94	"	0.132	"	0.132	"	0.053	0.941	"	0.079	"	81	1602	35.2
6	0.98	0.94	"	0.079	"	0.079	"	0.032	0.973	"	0.047	"	48	1650	36.3
7	0.98	0.94	"	0.047	"	0.047	"	0.019	0.992	"	0.028	"	29	1679	36.9
<u>Section 3: Coker-distillate hydrogenation at 797°F (425°C) and 1000 psi (reference 5)</u>															
1	0.963	0.90	0.27	1.000	99.5	0.995	45	0.448	0.448	55	0.547	1040	1040	1040	22.9
2	0.963	0.90	"	0.547	"	0.544	"	0.245	0.693	"	0.299	"	569	1609	35.4
3	0.963	0.90	"	0.299	"	0.297	"	0.134	0.827	"	0.164	"	311	1920	42.2
4	0.963	0.90	"	0.164	"	0.163	"	0.073	0.900	"	0.090	"	171	2091	46.0
5	0.963	0.90	"	0.090	"	0.090	"	0.041	0.941	"	0.049	"	94	2185	48.1
6	0.963	0.90	"	0.049	"	0.049	"	0.022	0.963	"	0.027	"	51	2236	49.2
<u>Section 4: Coker-distillate hydrogenation at 842°F (450°C) and 3000 psi (reference 5)</u>															
1	0.963	0.85	0.27	1.000	103	1.030	64	0.659	0.659	36	0.371	1580	1580	1580	34.8
2	0.936	0.85	"	0.371	101	0.375	"	0.240	0.899	"	0.135	1300	586	2166	47.7
3	0.936	0.85	"	0.135	"	0.136	"	0.087	0.986	"	0.049	"	213	2379	52.3
4	0.936	0.85	"	0.049	"	0.050	"	0.032	1.018	"	0.018	"	77	2456	54.0

section 3 of Table 2. In the first cycle, one barrel of feed (specific gravity 0.963) is processed at medium temperatures and low pressure (1000 psi) to form 0.995 barrel of product (specific gravity 0.90). After six cycles, only 0.963 barrel of product have been formed (with only 0.027 barrel of recycle oil remaining) requiring 2236 cubic feet of hydrogen at a cost of 49.2 cents.

Better yields of liquid product and less gas formation occur at higher pressures. Typical results for medium-pressure, high-temperature hydrogenation are shown in Section 4 of Table 2. Under these conditions 1.018 barrels of product are formed in four cycles, requiring 2456 cubic feet of hydrogen at a cost of 54¢. This represents a net gain (approximate) of 2.3 gallons (U.S.) of liquid product per barrel processed. From the viewpoint of the yields, as well as the cost of the hydrogen involved in processing, it would appear that the full-range coker distillates can only be treated successfully at quite high operating pressures, in the region of 10,000 psi (5). At the comparatively low pressures used in the experiments forming the basis for the calculations shown in Table 2, i.e. at 1000 and 3000 psi, more hydrogen is required to produce a unit volume of liquid product from the full-range coker distillate than from the whole-crude, in spite of the higher (initial) hydrogen content of the distillate feed stock. The results show that, at low and medium pressures, 2200-2400 cubic feet of hydrogen are required to form a barrel of liquid product distilling below 740°F from the full-range distillate, compared to only 1700-2000 cubic feet to form a barrel of similar product from the whole-crude. The amount of hydrogen consumed in the production of the liquid product is of the same order in both cases. The difference is due mainly to the formation of gases.

The results of the calculations shown in Table 2 are intended only to indicate how the general method of estimating hydrogen requirements can be applied in an experimental investigation. They should not, and cannot, be construed as unequivocal evidence in favour of the direct hydrogenation of the whole-crude versus the refining of a coker distillate. There are too many other factors involved, over and above the cost of the hydrogen, which must be taken into account in making such a decision. The calculations do demonstrate, however, the importance of minimizing gas formation at every possible stage in the refining scheme. This can be accomplished by a) processing at low temperatures (minimum severity) and b) distilling the feed stocks and recycle oils and treating the residuum and heavy gas-oil fractions separately from the low-boiling hydrocarbons.

One of the principal reasons put forward for the preparation of a coker distillate in preference to the treatment of the whole-crude is that a large part of the clay and mineral matter remaining from the separation of the crude from the sand is retained in the coke. The life of the catalysts used in conventional fixed-bed hydrogenation reactors would be greatly improved by removing, or reducing, the amount of mineral matter present. How-

ever, recent reports of engineering developments in liquid-phase hydrogenation processes (11) indicate that feed stocks containing comparatively large amounts of clay and mineral matter can now be processed successfully using ebullated-bed reactors. More extensive recycling would undoubtedly be required to process the residuum from the whole-crude (and catalyst cost would definitely be greater, because of the mineral matter), but the coking step would be eliminated from the overall refining scheme and the volume of marketable oil from a unit volume of whole-crude would be increased correspondingly. If necessary, the concentration of mineral matter could be reduced by subjecting the separated bitumen to a relatively mild thermal treatment (vis-breaking) and a centrifuging step, instead of coking.

In the preparation of estimates of the costs involved in refining a coker distillate, one must remember to include the value of the hydrocarbon material destroyed in the course of manufacturing the distillate. Some of the coke produced, of course, can be used as a source of "in-plant" heat, but experimental evidence available to date indicates that more coke will be formed than will be required for heat generation, including that required for the separation of the oil from the sand. The time is also rapidly approaching when air pollution regulations will preclude the release of the large amounts of fly-ash and sulphur present in the coke into the atmosphere. Many of the pollution and production problems could be minimized by using the "off-gases" formed in the course of processing as the principal source of plant heat and manufacturing the hydrogen required from high-purity natural gas.

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APPENDIX - Sample Calculations

(All weights in pounds;
all gas volumes in standard cubic feet)

Feed stock: Whole-crude from the Alberta Bituminous Sands Deposits (16)

Specific gravity = 1.012
Hydrogen content = 10.6%
Carbon content = 83.1%
Sulphur content = 4.75%
Nitrogen content = 0.4% (neglected, see page 5)

Weight of one barrel* of feed	=	Weight of barrel spec. grav. = 1.000	x	Specific gravity of feed
	=	350.3	x	1.012
	=	355 lb		

Weight of hydrogen in one barrel feed stock = 355 x 0.106
= 37.63 lb

Weight of carbon in one barrel feed stock = 355 x 0.831
= 295 lb

Weight of sulphur in one barrel feed stock = 355 x 0.0475
= 16.9 lb

Product Assume specific gravity of product = 0.900
volume yield = 102%
sulphur content = 1.25%
and the Hydrogen Factor = 0.240.

Using equation (1), % H₂ = 26 - 15d,

the hydrogen content of the product = 26 - 15 x 0.900
= 12.5%,

and the carbon content = 100 - (Hydrogen) - (% sulphur)
= 100 - 12.5 - 1.25
= 86.25%.

* The "barrel" is the traditional unit of measure for liquid feeds in refinery practice (17). It is defined as 42 gallons (U.S.), which is the estimated average content of the nominal 45-gallon (U.S.) drum.

Hydrogen required to process one barrel of bitumen	=	Weight of hydrogen in product	-	Weight of hydrogen in feed	+	Weight of hydrogen in H ₂ S formed	+	Weight of hydrogen in gases formed
	=	40.2	-	37.6	+	0.81	+	4.22
	=	7.7 lb						

Volume of hydrogen required to process one barrel = $\frac{\text{Weight of hydrogen required}}{\text{density of hydrogen}}$

= $\frac{7.7}{0.00561}$
= 1370 standard cu ft.

Cost of hydrogen required to process @ 22¢/1000 std cu ft = 30¢

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