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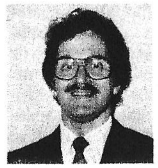

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Novel Catalyst and Process to Upgrade Heavy Oils

Pilot plant results show promise for hydroconversion process wherein free radical cracking reactions are controlled using trace amounts of catalyst generated in situ in the feed.

Roby Bearden and Clyde L. Aldridge, Exxon Research and Development Laboratories, Baton Rouge, La.

The projected worldwide shortage of conventional crude oil has focused attention on technology for upgrading such abundant heavy alternate feedstocks as tar sands bitumen, tar belt crudes, and vacuum residua. At present, coking is the most widely used primary upgrading process for these alternate feeds. While there is no problem in processing these heavy feeds by coking, there is the inherent drawback that a significant fraction of the feed is converted to gas and coke at the expense of potentially more valuable liquid products. In some cases the coke yield can amount to 20 wt-% or more. Moreover, the coke obtained from these heavy feeds is often of poor quality, i.e., rich in heteroatom impurities.

In the early 1970's we began work on a new approach to heavy feed hydroconversion, which has led to an attractive process alternative to coking. This process, based on the concept of catalytically controlled thermal cracking, operates with throwaway quantities of a novel micron-sized catalyst and provides yields of distillable liquid products of about 100 vol-% on feed.

Process Catalyst Formed in Situ

We refer to our process as M-coke hydroconversion wherein M-coke stands for micrometallic coke. This is a term describing the novel catalysts that we produce, i.e., micron-sized particles which comprise a catalytic metal sulfide component combined with a carbonaceous component.

In the process, the catalysts are formed *in situ* in the reactor liquid from compounds of catalytically active metals that are soluble in, or easily dispersed in, the feed. The catalyst forms immediately under the process conditions used; and the required catalyst concentration on feed, expressed in terms of the catalyst metal, is quite low.

For example, as little as 100 parts/million by wt. (0.1 g/kg) of our preferred catalyst metal, molybdenum, can be used to obtain up to 95% conversion of vacuum residua to products comprising largely naphtha, distillate, and gas oil. Thus, external catalyst preparation steps involving solids impregnation and drying are not required and the amount of catalyst used is sufficiently small that catalyst recovery and recycle steps are not essential.

In the course of the hydroconversion reaction, greater than 90% of feed nickel and vanadium contaminants are transformed into oil insoluble compounds, likely metal sulfides. These compounds, which deposit on the M-coke catalyst, may act as supplementary catalyst materials.

Since there is no bed of catalyst in the reactor, at least in the traditional sense, there is no problem with bed plugging when high-particulate content feeds are processed, e.g., clay containing Athabasca bitumen. Furthermore, with these micron-sized catalysts, deactivation resulting from pore diffusion limitations and from metals deposition, a common problem with conventional supported catalysts, is not a problem.

Aside from the catalytic role, the micron-sized, highly dispersed M-coke particles serve as nucleation sites for the small amount of coke formed in the hydroconversion reaction. In this manner fouling of reactor surfaces is prevented.

The hydroconversion reaction consists of contacting the feed containing the M-coke catalyst with hydrogen at temperatures ranging from 400°C to 454°C under total reactor pressures ranging from 6.9 MPa to 17.2 MPa. Liquid hourly space velocity is chosen in accordance with the level of conversion desired, the nature of the feed and the temperature and pressure used.

One very significant feature of the process is the use of vacuum distillation to recover oil products from the reactor product mixture, which contains catalyst along with coke and products of demetallization. This is made possible by the uniquely low catalyst concentration used and the very effective suppression of coke formation attained, which results in a low overall solids content. Thus, even at high conversion levels, the concentration of solids in the reactor effluent is sufficiently low that recovery of products by distillation does not lead to formation of an unmanageable, high solids content vacuum tower bottoms.

If desired a portion of the vacuum tower bottoms fraction can be recycled to the hydroconversion zone. The catalyst contained in the bottoms remains active and the bottoms can be further converted. However, in the once-through high conversion mode that is possible with this technology, it is anticipated that the small volume of unconverted bottoms, containing catalyst and demetallization products therein, may be burned for process heat or used to generate hydrogen.

Finally, there is no apparent feed limitation. In small continuous pilot plant studies this technology has been successfully applied to heavy crude conversion *(1)*, coal liquefaction *(2)*, oil plus coal co-conversion *(3)* and gas oil hydrocracking *(4)*.

Hydroconversion Mechanism

The conceptual M-coke hydroconversion mechanism, shown in Figure 1, is viewed as primarily a thermally induced free radical cracking reaction of heavy materials such as asphaltenes and resins (reaction R-1). M-coke and hydrogen control the reaction by hydrogenating these free radicals to yield oil (reaction R-2) rather than allowing free radical coking reactions (e.g. polymerization) to occur via reaction R-3.

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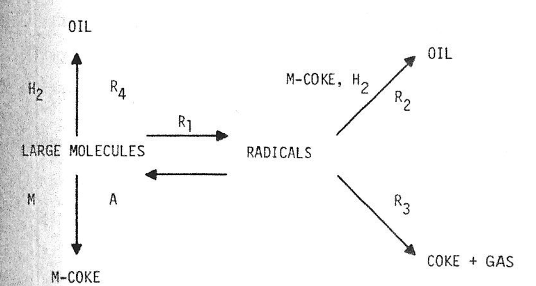

R_1, THERMAL CRACKING
R_2, RADICAL HYDROGENATION (INHIBITION)
R_3, CONDENSATION, POLYMERIZATION (COKING)
R_4, CONVENTIONAL HYDROCONVERSION
A, CHEMICAL INTERACTION

Figure 1. Conversion mechanisms. R_1 = thermal cracking. R_2 = radical hydrogenation (inhibition). R_3 = disproportionation, polymerization (coking). R_4 = conventional hydroconversion. A = chemical interaction.

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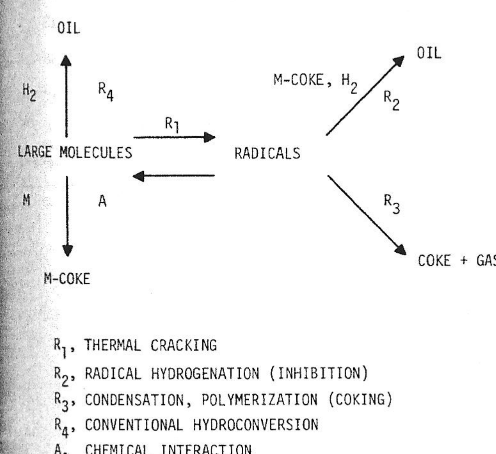


Figure 1. Conversion mechanisms. R_1 = thermal cracking. R_2 = radical hydrogenation (inhibition). R_3 = disproportionation, polymerization (coking). R_4 = conventional hydroconversion. A = chemical interaction.

massive amounts of catalyst and depend more upon direct catalytic attack on the molecules (Reaction R-4). M-coke is formed in the feed by a chemical reaction between the precursor and a portion of the feed to form the metal/coke combination (Reaction A).

It should be noted that some portions of heavy feeds, particularly some of the coke precursors or Conradson carbon materials may not be amenable to direct conversion by thermal cracking followed by hydrogenation and may require some hydrogen input via reaction R-4 before cracking occurs. Thus, to obtain high conversion levels the M-coke catalyst must be active for reaction R-4 as well as R-2. This requirement led us to select molybdenum as the preferred M-coke metal over a number of others which proved active for reaction R-2, but which showed relatively poor activity for R-4.

A key factor in M-coke hydroconversion is the small particle size of the catalyst and the high population of catalyst particles obtained per unit volume of reacting oil, even at quite low concentrations of catalysts. The reason this is important is that in a liquid-phase free radical cracking reaction occurring at high temperature, the reactive free radical intermediates must be engaged immediately and hydrogenated to prevent the formation of coke and incompatible, polymeric oils.

Catalyst Dispersion is High

In this regard it is interesting to compare, as seen in Table 1, the catalyst dispersion attainable in oil with M-coke to that calculated for a typical expanded bed reactor, which configuration is used in some commercial heavy feed hydroconversion processes. As shown, the M-coke system provides several orders of magnitude more catalyst particles per cm³ of oil in the reactor liquid phase than does an expanded bed process; even though the amount of M-coke catalyst in the reactor is only a fraction of that in the expanded bed. Moreover, the distance between catalyst particles is much less in the M-coke process than in the expanded bed.

In the final analysis, it is this inter-particle distance that we consider important in determining the efficiency of a catalytically controlled free radical hydroconversion reaction. It would be expected that as the distance between particles decreases the control over thermal reactions would increase; i.e., the ability to intercept and hydrogenate free radical intermediates that would otherwise form coke and incompatible oils would increase. Accordingly, at least in theory, the M-coke system would be expected to provide better operability under severe thermal conditions than could be obtained in an expanded bed.

Though no direct comparison of M-coke and expanded bed conversion performance has been made, we have found M-coke process operability in our small continuous pilot plants to be exceptionally good. This is true even when operating at high (90+%) once-through conversion of bottoms. In a commercial plant this should translate into a high service factor.

TABLE 1. M-COKE PROVIDES HIGH CATALYST PARTICLE CONCENTRATION

	Vol-% catalyst in reactor	Catalyst size, mm	Particles per cm³ of oil	Distance between particles, cm
M-Coke	~1	0.001-0.003	10^8-10^{10}	~0.001
Expanded bed	~40	~0.8 × 3	~250	~0.040

The excellent coke inhibiting activity attainable with small concentrations of highly dispersed M-coke catalysts is illustrated by the plot in Figure 2. The plot shows coke yield as a function of M-coke metal (molybdenum in this case) on feed for the high temperature hydroconversion of Cold Lake crude. As can be seen, a concentration of molybdenum on feed as low as 0.04 g/kg has a significant impact on coke suppression, and at 0.1 g/kg molybdenum, coke yield is dropped to an easily manageable level of less than 1 wt-% on feed. In the range of 0.15 to 1 g/kg molybdenum, coke yield reaches a minimum and is then seen to increase slowly with increasing molybdenum concentration. This increase does not reflect a breakdown in the coke inhibition associated with hydroconversion, but does reflect an increase in the catalytic coke associated with the formation of increasing amounts of M-coke catalyst. Clearly, molybdenum concentrations on feed as low as 0.1 g/kg suffice to bring hydroconversion related coking reactions under control.

Catalyst Formation and Characteristics

As previously stated, M-coke catalysts are formed *in situ* in the hydroconversion feeds at hydroconversion conditions from oil soluble or oil dispersible metal compounds. A literature search in this general area turned up a number of references on the use of oil soluble metal compounds in hydroprocessing applications.

For example, Zorn *(5)* conducted hydroconversion tests using oil-soluble metal salts of 1,3-diketones as catalysts as early as 1932. More recently, Gatsis and Gleim *(6, 7, 8)* evaluated numerous oil soluble metal-organic and inorganic compounds as catalysts for heavy oil hydroconversion. Also, Stolfa *(9)* has proposed a homogeneously catalyzed black oil conversion process using as catalyst a small amount (e.g. 1 g/kg on feed) of a Group V, VI, or VIII metal phthalocyanine. Further, in the related field of catalytic coal hydroliquefaction, there are examples wherein oil soluble metal compounds *(10)* and oil dispersible metal compounds *(11)* have been used as catalyst precursors. However, to our knowledge, no one has previously proposed and worked out a viable heavy petroleum feed hydroconversion process using trace amounts of an oil soluble or oil dispersible catalyst precursor.

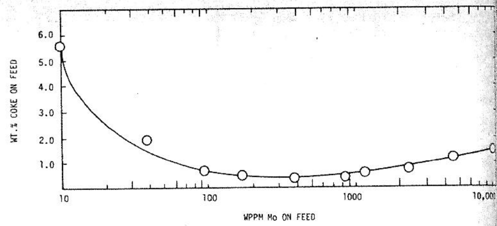


Figure 2. Coke suppressing activity of molybdenum M-coke. Feed is Cold Lake crude. Hydroconversion in batch runs. Conditions: 438°C, 1 hr, 17.2 MPa average reactor pressure. Note: 10 WPPM (parts/million by wt.) = 0.01 g/kg.

Several metals have shown useful activity as M-coke hydroconversion catalysts. The list includes copper, cobalt, nickel, iron, titanium, manganese, tungsten, vanadium, chromium, and molybdenum. Of these, molybdenum is preferred based on overall effectiveness in promoting attractive conversion in terms of boiling point conversion, Conradson carbon conversion, and hydrodesulfurization. This can be seen from the hydroconversion results given in Table 2, where molybdenum is compared with representative metals from the list.

Several oil-soluble or dispersible compounds of molybdenum, ranging from micronized molybdenum trioxide to molybdenum naphthenate, were tested as precursors. As shown in Table 3, activity varied widely with precursor chosen. Fortunately, for reasons of economy, aqueous phosphomolybdic acid was found to be equivalent to more expensive forms of molybdenum, e.g., the naphthenate and hexacarbonyl compounds. Further, we found that the activity of aqueous phosphomolybdic acid could be substantially enhanced by modification with phosphoric acid to give a phosphorous to molybdenum atom ratio of 0.5 to 3.5 *(12)*.

TABLE 2. MOLYBDENUM MOST ATTRACTIVE OF M-COKE METALS TESTED

Batch hydroconversion runs
Heavy crude feed
Conditions: 438°C, 1 hr, under 17.2 MPa avg. reactor pressure
Screening basis: 0.7 to 0.8 g/kg metal on feed

	None	Iron	Molybdenum	Vanadium	Chromium	Manganese	Titanium
Desulfurization, %	33	40	66	50	56	39	43
Conradson carbon conversion, %	50	51	60	50	51	53	58
Coke yield, wt-% on feed	6.0	2.8	0.5	0.4	0.3	1.8	0.5

TABLE 3. COMPARISON OF MOLYBDENUM M-COKE PRECURSORS

Batch hydroconversion runs
Heavy crude feed
Conditions: 438°C, 1 hr, 17.2 MPa avg. reactor pressure
Screening basis: 0.35 g/kg Mo on feed

	None	Micronized MoO_3	MoS_2 Powder	$Mo(CO)_6$	Molybdenum Naphthenate	PMA*	PMA*/H_3PO_4
Solvent or dispersing medium	—	Water	None	None	None	Water	Water
Desulfurization, %	33	36	33	50	50	48	61
Conradson carbon conversion, %	50	47	44	51	53	51	56
Coke yield, wt-% on feed	6.0	4.2	4.6	0.4	0.4	0.3	0.1

* PMA = Phosphomolybdic Acid

Continuous Pilot Plant Results

The hydroconversion results discussed below were obtained in small continuous pilot plants in once-through operation. The heavy feeds that were run included Athabasca tar sand bitumen, Cold Lake crude and a light Arabian vacuum residuum. Feedstock properties are given in Table 4. Molybdenum M-coke was used as catalyst in all of these tests. Process conditions included temperatures in the range of 400°C to 443°C, and pressures between 6.9 and 17.2 MPa. Overall, continuous operation was smooth and run lengths of up to three months were obtained prior to voluntary shutdown.

The conversion potential of the M-coke process is clearly seen from Figure 3 which shows a correlation between 566+°C boiling point conversion and Conradson carbon conversion for each of the three feeds. With Cold Lake Crude, these conversions were carried to 95% and 90%, respectively. Of interest, all three feeds fit the same correlation line. This similarity is considered to reflect the strong contribution of thermal cracking to the conversion mechanism and also suggests an underlying commonality of the heavy components of these feeds.

Desulfurization was found to increase with increasing 566+°C conversion, but there was some variation in behavior among the three feeds. At 90% conversion, desulfurization values ranged from 70 up to 77%. At this level of desulfurization, sulfur in most of the distillable product fractions still exceeds specification values. Consequently, some downstream product cleanup by catalytic hydrotreating will be required.

Finally, the important issue of liquid yield is addressed in Table 5. The data represents operation at 90-92% conversion of 566+°C components, once-through, for the Cold Lake crude and Arabian vacuum residuum feedstocks. As shown, the yield of total C_4+ liquid was very high (~105 vol-% on fresh feed) for both feedstocks as was the yield of C_4−566°C distillable liquids, which ranged from 98.1

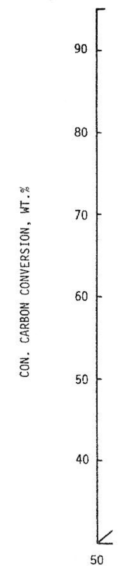
TABLE 4. FEEDSTOCK PROPERTIES

	Arabian Vacuum Residuum	Cold Lake Crude	Tar Sand Bitumen
Initial, b.p., °C	505	454	325
Wt-% 566°C+	90	67	45
Wt-% Conradson Carbon	21.2	20.0	12.7
Wt-% Asphaltenes	7.4	19.2	10.4
Wt-% Sulfur	4.0	5.4	4.3
Nickel, g/kg	0.016	0.090	0.057
Vanadium, g/kg	0.077	0.260	0.171
Wt-% Particulates	nil	~0.1	0.4-1.0

TABLE 5. PROCESS YIELDS AND SELECTIVITIES

Continuous pilot plant data, operation at 90-92%, 566+°C conversion

	Cold Lake Crude	Arabian Vacuum Residuum
Yields, vol-% on fresh feed:		
Total C_4+ Liquid	104.7	105.8
C_4−566°C Liquid	99.5	98.1
C_5−188°C Naphtha	28.9	22.5
188°C-343°C Distillate	47.8	35.4



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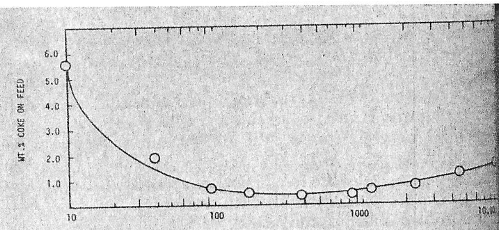

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The conversion potential of the M-coke process is clearly seen from Figure 3 which shows a correlation between 566+°C boiling point conversion and Conradson carbon conversion for each of the three feeds. With Cold Lake Crude, these conversions were carried to 95% and 90%, respectively. Of interest, all three feeds fit the same correlation line. This similarity is considered to reflect the strong contribution of thermal cracking to the conversion mechanism and also suggests an underlying commonality of the heavy components of these feeds.

Desulfurization was found to increase with increasing 566+°C conversion, but there was some variation in behavior among the three feeds. At 90% conversion, desulfurization values ranged from 70 up to 77%. At this level of desulfurization, sulfur in most of the distillable product fractions still exceeds specification values. Consequently, some downstream product cleanup by catalytic hydrotreating will be required.

Finally, the important issue of liquid yield is addressed in Table 5. The data represents operation at 90-92% conversion of 566+°C components, once-through, for the Cold Lake crude and Arabian vacuum residuum feedstocks. As shown, the yield of total C_4+ liquid was very high (~105 vol-% on fresh feed) for both feedstocks as was the yield of C_4-566°C distillable liquids, which ranged from 98.1

TABLE 4. FEEDSTOCK PROPERTIES

	Arabian Vacuum Residuum	Cold Lake Crude	Tar Sand Bitumen
Initial, b.p., °C	505	454	325
Wt-% 566°C+	90	67	45
Wt-% Conradson Carbon	21.2	20.0	12.7
Wt-% Asphaltenes	7.4	19.2	10.4
Wt-% Sulfur	4.0	5.4	4.3
Nickel, g/kg	0.016	0.090	0.057
Vanadium, g/kg	0.077	0.260	0.171
Wt-% Particulates	nil	~0.1	0.4-1.0

TABLE 5. PROCESS YIELDS AND SELECTIVITIES

Continuous pilot plant data, operation at 90-92%, 566+°C conversion

	Cold Lake Crude	Arabian Vacuum Residuum
Yields, vol-% on fresh feed:		
Total C_4+ Liquid	104.7	105.8
C_4-566°C Liquid	99.5	98.1
C_4-188°C Naphtha	28.9	22.5
188°C-343°C Distillate	47.8	35.4

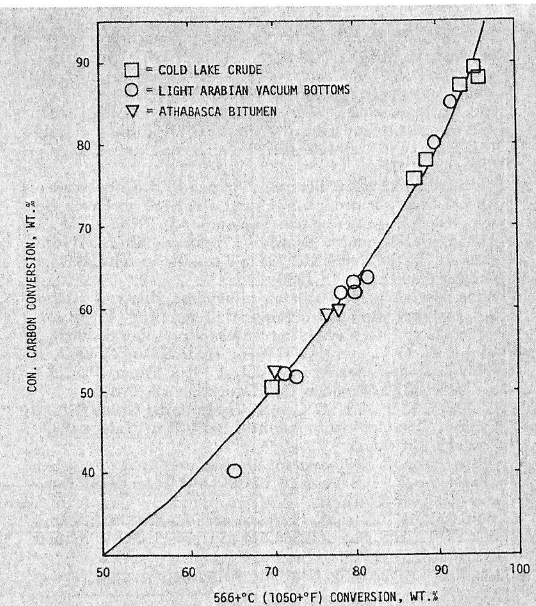

Figure 3. Conradson carbon conversion vs. 566+°C conversion (continuous pilot plant data). Catalyst is molybdenum M-coke, 0.1 g/kg Mo on feed.

vol-% with Arabian vacuum residuum to 99.5 vol-% with Cold Lake crude.

Furthermore, the distillable liquids were fairly light in that the combined naphtha and 188-343°C distillate accounted for a major portion of the C_4-566°C products. Though not illustrated here, product selectivity can be varied at a given conversion level. This can be accomplished through control over reactor conditions and catalyst concentration as well as process configuration, e.g., once-through versus recycle operation.

The M-Coke process concept has proved technically sound over several years of small pilot plant operations. Currently, a technical and economic assessment is being made by Exxon Research and Engineering to determine future development steps required to bring this technology to commercial application.

Conclusions

A new concept in heavy feed upgrading based on catalytically controlled free radical reactions has been successfully demonstrated in small, continuous pilot plant tests.

Catalyst is formed *in situ* in heavy feeds from oil soluble or dispersible metal compounds under hydroconversion conditions and is made up of micron sized particles, which contain a metal component and a carbonaceous component. These catalysts, which we call M-coke, are effective for control of coke forming reactions at quite low concentrations. As little as 0.1 g/kg metal based on oil feed suffices.

Several metals have given catalysts with useful activity. However, molybdenum M-coke is preferred based on overall effectiveness.

The process provides excellent 566+°C and Conradson carbon conversion, substantial removal of heteroatom impurities and yields of distillable liquids of about 100 vol-% based on fresh feed. Both once-through and recycle modes of operation appear technically feasible.

Finally, there is no feedstock limitation with respect to asphaltene content, metals content, or the presence of particulate matter such as clay. #

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Low Sulfur Products from High Sulfur Crude Oil

Four refinery process schemes are compared on bases of product quality product yield, and the capital investment requirements

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Current projections of petroleum products consumption in the USA show an increase in the percentage of light, clean products and a decrease in the percentage of residual fuel oil. At the same time, pollution restrictions are requiring the production of petroleum products with low sulfur levels. To further aggravate the refining industry's problems, the world supply of crude oil is expected to become gradually heavier and higher in sulfur in future years.

In this article, four refinery process schemes for converting high sulfur crude oils to low sulfur products are compared. The refinery schemes are similar except for the handling of the atmospheric resid where the following variations are used:

1. Atmospheric resid HDS (hydrodesulfurization), vacuum distillation, delayed coking, and gas oil FCC (fluid catalytic cracking).
2. Vacuum distillation, "Flexicoking," FCC feed HDS, and gas oil FCC.
3. Amospheric resid HDS, and heavy oil catalytic cracking.
4. Atmospheric resid HDS, vacuum distillation, solvent deasphalting, and gas oil FCC.

Other cases could have been included; those based on processes such as H-oil, LC-fining, fluid coking, vacuum resid HDS, delayed coking of high-sulfur vacuum resid, visbreaking, and partial oxidation of coke or pitch. We fe however, that the four cases selected included a good cro section of product distributions and available technologie for converting high-sulfur resid to low-sulfur products.

Figures 1 through 4 show overall block flow diagram and refinery product balances for the four cases. The cru oil processed is a mixture of 25% light Arabian, 35% hea Arabian, and 40% Kuwait. The amount of crude oil pr cessed in each case was based on producing 8744 cub meter per calendar day (55,000 BPCD) of motor gasoli The other refinery products were allowed to fluctuate.

Table 1 shows a comparison of the yields from the fo process schemes. The liquid products recovery as a pe cent of crude is as follows: Case 1, 94.5; Case 2, 96.0; Ca 3, 98.0; Case 4, 96.7. Case 3, with atmospheric resid HD and heavy oil cat cracking, has the highest overall liqu recovery. With the cost of crude oil and petroleum pr ucts escalating at a rapid rate, this incremental liquid r covery will become increasingly valuable.

The most important product qualities to be compar are the octane numbers of the motor gasoline pool and t cetane number of the diesel fuel. Table 2 shows a compa son of these values, and it indicates that Case 3, with t heavy oil cat cracker, has a greater spread between F-1 a F-2 octanes on the gasoline pool and a lower ceta number on the diesel. The spread on the gasoline octa is caused by the higher percentage of olefins in the to pool. The lower diesel cetane number is the result of blending a larger volume of cat cracked light cycle oil into the diesel fuel product.

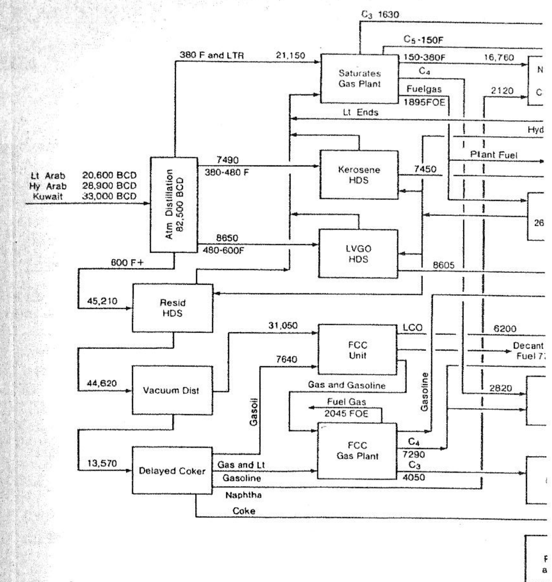

Figure 1. Long resid HDS (hydrodesulfurization)

Metric conversions for Figures 1-4:
1 BCD (bbl/calendar day) = 0.159 m³/day (0.159 kL/day)
1 MM SCF/CD (million std cu ft/calendar day) = 28,317 std m³/day
1 ST/CD (short ton/calendar day) = 0.907metric ton/day
1 LT/CD (long ton/calendar day) = 1.016 metric ton/day
°F = 1.8 × °C + 32

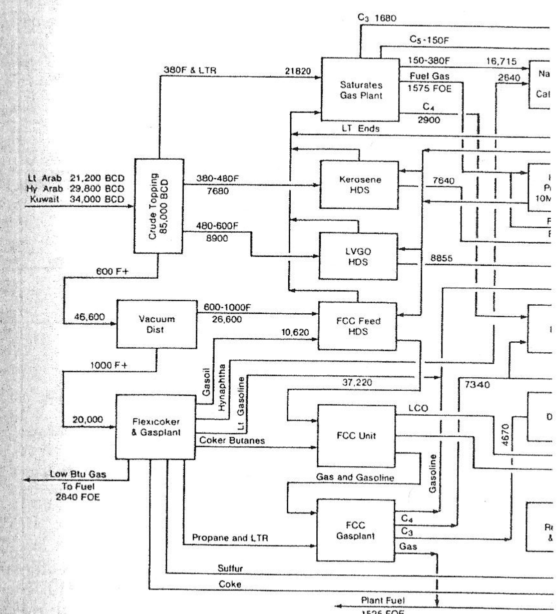

Figure 2. Flexicoking. Case

Curv cess ur charge