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CANMET

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THE CANMET HYDROCRACKING PROCESS

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1. WHY UPGRADE BITUMEN FROM OIL SANDS AND HEAVY OIL?

Because of the increasing demand for oil, it is important for Canada to develop its oil sands and heavy oil deposits as rapidly as possible. More than 1000 billion barrels of bitumen are estimated to be in the reserves of oil sands and heavy oil in western Canada. Such quantities exceed the known world reserves of conventional oil by a wide margin. However, only a small fraction of Canada's bitumens are considered to be recoverable at unit costs comparable to the present international price of oil. While current estimates vary widely, the pilot trials presently underway using "in situ" recovery methods suggest that recoveries could be 150 billion barrels.

Bitumen, as separated from oil sands, for example, contains many materials which would cause serious operational difficulties in a conventional refinery, e.g., 0.5 to 1.0% fine clay mineral matter, 300 to 500 parts per million of chemically bound nickel, vanadium and iron, 4 to 5% sulphur, 1% oxygen, and 0.4 to 0.6% nitrogen (Table 1). Such contaminants would foul and poison normal catalytic reactor systems very quickly. Further, a typical bitumen contains 50 wt % pitch (material boiling above 525^{o}C) and as a consequence, possesses a high viscosity and cannot be transported by pipeline. It is necessary, therefore, to subject the bitumen to an upgrading process to reduce viscosity, and pitch, sulphur and metals content, in order for it to meet pipelining and refinery requirements. Once the pitch has either been removed or converted to distillable hydrocarbon material, little difficulty is encountered in subsequent, secondary catalytic hydrogenation steps. Distillable fractions derived from the bitumen are easily refined in conventional, fixed-bed reactors under conditions suited to the particular boiling range of the feedstock.

2. HOW CAN BITUMEN BE UPGRADED TO REFINERY FEEDSTOCK?

The pitch fractions can be converted to distillate oils either by thermal coking or by hydrocracking. Both approaches are in commercial use today.

Thermal Coking - Carbon Removal

This type of process involves subjecting bitumen by itself to high temperatures, converting part of the bitumen to coke and the remainder to distillate products and gas. The large pitch molecules are split into smaller fragments which are stabilized by extracting hydrogen from other molecules which are thus converted to coke. A re-distribution of hydrogen thus takes place but the hydrogen content of the total product remains unchanged.

The disadvantage of this type of process is that it produces a minimum of 16-18 wt % coke which limits the maximum liquid yields to 74-76 wt %, together with 7-8 wt % gases (Fig. 1).

The coking process is the basis for the present upgrading methods in use by Great Canadian Oil Sands Ltd. (Delayed Coking) and Syncrude (Fluid Coking). Exxon has developed a process they call Flexicoking which is an extension of Fluid Coking.

Delayed Coking is a batch process and involves heating the bitumen in wide diameter coking drums. When all the distillate has been driven off, the drums are opened and the coke removed. Fluid Coking is a continuous process in which bitumen is cracked in a fluidized bed of hot coke which is circulated between an external heater and the reactor. Coke is continuously withdrawn from the system. Flexicoking is a modification of this process in which the excess coke is gasified after withdrawal (Fig. 2).

A fourth variation of the purely thermal processes, called the Eureka Process, has been developed by Kureha of Japan. This involves thermally cracking bitumen in the presence of steam. Instead of coke, about 30 wt % pitch is produced by this method.

Hydrocracking - Hydrogen Addition

This involves heating bitumen with hydrogen under pressure (Fig. 3). The large pitch molecules are still broken into smaller fragments, however these fragments are stabilized by the gaseous hydrogen instead of by extracting hydrogen from other hydrocarbon molecules as in the coking process. Thus, hydrogen is added to the bitumen and the hydrogen content of the total product is increased.

By using this type of process, all bitumen recovered from the oil sand deposit or heavy oil field is potentially available for conversion to marketable hydrocarbon products, and the yield of distillate is substantially higher. Typically, distillate yields of 85 wt % with about 8 wt % gas and 7 wt % pitch can be achieved (Fig. 1 and 4).

Hydrocracking can be carried out with or without a catalyst. All commercially operating processes involve passing a mixture of hydrogen and oil through a cobalt-molybdenum catalyst either in an ebullated bed or a fixed bed. Both H-oil and LC Fining processes employ an ebullated bed in which the catalyst is kept in suspension by the flow of fluid through the reactor. Such processes only work well at relatively high pressures (2500 psi) and when operated at high pitch conversions, solids tend to deposit on the relatively expensive catalyst causing rapid deactivation and thus higher catalyst replacement costs.

Processes involving a fixed catalyst bed include Exxon Residfining and the Gulf HDS process. They also suffer from problems of catalyst deactivation due to solids deposition and fouling.

3. WHY THE CANMET PROCESS?

In keeping with the Federal Government's policy of making full use of Canada's natural resources, the main thrust of CANMET's effort has been to improve the hydrogen addition or hydrocracking process. Most of the work has been aimed at:

(i) increasing liquid yields by operating at higher pitch conversions;
(ii) reducing operating pressures and thus decreasing the high capital and operating costs associated with high pressure processes; and
(iii) eliminating the need for expensive catalysts by substituting a cheaper processing aid.

The result has been the development of the CANMET process.

4. WHAT IS THE CANMET PROCESS?

During the past 40 years CANMET has carried out many hydrocracking bench-scale studies, and during the past 10 years extensive work has been done involving a 1-barrel-per-day pilot plant (Table 2). It was with the use of this pilot plant that the CANMET process was developed.

A simplified flow diagram of the pilot plant is shown in Fig. 5. Bitumen is mixed with hydrogen under pressure and the mixture pumped up a long heated tubular reactor where the hydrocracking takes place. The products leave the top of the reactor and are separated into a light oil, a heavy oil and a gas fraction, which are collected separately. The gas is purified by removal of hydrocarbons and hydrogen sulphide and recycled to the reactor after addition of make-up hydrogen.

All process variables and parameters are recorded and controlled, and the liquid and gaseous products extensively analysed. In this way, CANMET has established a substantial data base concerning the influence of operating conditions on product yields and properties as well as on plant operability.

The main problem with using a purely thermal hydrocracking process, especially at low pressures, is the deposition of coke and other solids in various parts of the system which can cause blockages and plant shutdowns. CANMET has overcome these problems by developing cheap throw-away additives and by modifying the processing scheme. A measure of the success of these developments is the ability of the pilot plant to run continuously for up to 3 weeks with no solid deposits or other operating problems.

It should be pointed out that this process is not a radical departure from previous practice and that presently developed high pressure hydrocracking technology can be employed in plant design and construction.

5. WHAT CAN THE CANMET PROCESS DO?

(a) Flexibility of Operation

The amount of pitch converted can easily be controlled by alterations in reactor temperature and bitumen feed rate. Thus, if process fuel (e.g., coal) supply is interrupted, more pitch can be produced to make up the deficit.

(b) High Liquid Yields

The CANMET process can produce 85% distillate, compared to 75 wt % for coking processes. Because the CANMET process can operate at higher pitch conversions than catalytic processes, higher liquid yields can also be obtained in this case.

(c) Trouble-Free Operation

Extended pilot plant runs indicate that the process will operate continuously without coke deposits.

(d) Low Pressure Operation

The operating pressure can be reduced to 1500 psi by the use of cheap throw-away additives developed by CANMET. This will allow a reduction in both operating and capital costs.

(e) Hydrogen Consumption

Less hydrogen is added to the pitch fraction of the product than with catalytic hydrocracking, although the pitch has a higher sulphur content. Thus more hydrogen goes where it is wanted, e.g., in the distillate fraction.

(f) Feedstock Flexibility

The Process can use a variety of feedstocks including the more refactory in situ bitumen. The pilot plant has been run successfully with Athabasca bitumen, Cold Lake in situ bitumen and Lloydminster residuum.

(g) Thermal Stability

The Process can operate without problems of thermal run-away and development of hot spots, problems which can occur with catalytic hydrocracking.

(h) All By-products are Usable or Saleable

Hydrocarbon gas can be used as a process fuel; hydrogen sulphide can be converted to sulphur; and the pitch can either be gasified and burned for process fuel, or used in the production of metallurgical coke.

A unique feature of the CANMET hydrocracking process is that it produces a pitch which can be used to improve the quality of borderline metallurgical coals.

(i) Sulphur Removal

The CANMET process can remove approximately 60% of the sulphur originally present in the bitumen.

(j) Product Distribution

The yields of naphtha and middle distillate fractions are higher in the CANMET process compared to the coking processes.

6. TECHNOLOGY PACKAGE

Approximately 40 professional and technical experts are employed in bitumen and heavy oil upgrading. The following facilities have been used by CANMET for the development of hydrocracking and the evaluation of feedstocks and products:

(1) A one-barrel-per-day pilot plant is in operation. Another one-barrel-per-day plant is under construction, with modern data acquisition system.

(2) Catalyst development facilities and four bench-scale high pressure flow reactors.

(3) A six-barrel-per-day continuous vacuum distillation column for preparation of feed and distillates.

(4) Analytical laboratories.

(a) Development Studies

A comprehensive data bank has been developed using both bench scale equipment and the 1-barrel-per-day hydrocracking pilot plant. Many short runs (8-16 hours each) have been carried out to obtain optimum operating conditions and product qualities and yields. However, long runs (21 days each) were necessary to evaluate deposit accumulation and to eliminate operating problems. The pilot plant has been operating for more than 4000 hours each year for the last two years (Fig. 6). The graph shows significant increase in operating hours during recent years.

The pilot plant data base contains information on the effect of process variables such as pressure, feed rate, temperature, gas rate and additives. Eight patent applications have been filed so far and additional patent applications are being processed. Over 60 reports have been published on heavy oil hydrocracking by scientists in CANMET. However, the recent improvements which resulted in successful development of the CANMET process are being patented and are not available in published literature.

(b) Secondary Refining Studies

The CANMET process is essentially a first-stage in an upgrading scheme. Further refining of the product needs to be done to meet synthetic crude specifications. A pilot hydrotreating unit is operating to evaluate secondary refining of the products. Data on operating conditions and hydrogen consumption have been accumulated for the hydrotreating of different product cuts (naphtha, light gas-oil and gas-oil) using commercial catalysts.

(c) Support Studies

The technology package has been strengthened by the support studies which give data for economics, design, scale-up, product qualities and product handling.

(i) Process and Scale-up Costs - two studies have been completed, one comparing several upgrading processes such as H-oil, Flexicoking, Eureka and Resid-fining, and the other comparing the CANMET process with Flexicoking.

Optimum Hydrogen Generation and Utilization of By-product Pitch - the cost of generating hydrogen has a strong impact on the economics of the hydrocracking process. A paper study has been done to evaluate pitch for producing hydrogen.

Data for Modelling - data has been accumulated on heat of reaction, vaporization, reactor voidage and solubilities of hydrogen and hydrogen sulphide to help develop a model for the CANMET hydrocracking process.

Corrosion Studies - corrosion-resistant materials are required because hydrogen, hydrogen sulphide and naphthenic acids are present at high pressures and temperatures, and the heavy oil contains erosive mineral matter. Materials for valve stems and reactors have been evaluated.

(ii) Product Evaluation and Analytical Studies - compatibility of different product streams is important because of the possibility of phase separation occurring during the transportation of the product blend. Methods have been developed to determine compatibility.

Characterization of Hydrocracked and Hydrotreated Products - a determination of hydrocarbon types in the products has been carried out. Improved analytical methods have been developed.

Sulphur and Nitrogen Compounds - the types of sulphur and nitrogen compounds have been identified in bitumen and hydrocracked products.

Analytical Studies of Mineral Matter and Solids in Reactor and Products - microscopic and petrographic studies of these materials have helped to improve the CANMET process.

7. COSTS - CANMET PROCESS VS. FLEXICOKING

A cost study carried out by independent consultants, In-Situ Research and Engineering, Edmonton, Alberta, shows that the capital and operating costs for the CANMET process are comparable to Flexicoking, a coking process. In the case of surface mined Athabasca bitumen, where large amounts of low grade heat are required for hot water extraction plant, the Flexicoking Process was deemed to be slightly more economical than CANMET hydrocracking. However, for in situ steam stimulated bitumen and wet combustion produced bitumen, the CANMET hydrocracking process was found to be more cost effective. In these comparisons coal was used as the balancing fuel, enabling high liquid yields to be obtained.

The In-Situ economic study was carried out last year when the CANMET process was not fully developed. Now the process can be operated at lower pressures using CANMET's processing additives. These improvements will further enhance the economics of CANMET hydrocracking.

SUMMARY

The CANMET process offers several advantages over competing commercial processes:

1. <u>Greater Liquid Yields than for Coking Processes</u>

   About 10% more liquid yields can be obtained. This enables better use of the heavy oil reserves.

2. <u>Flexibility of Operation - Different Conversions and Different Feeds</u>

   The pitch (525^{0}F+) conversion can be varied easily by adjusting process variables. Very high conversions can be obtained without fouling of reactor and refractory feeds can be handled.

3. <u>Better Hydrogen Distribution in Products</u>

   Other commercial hydrocracking processes use expensive Co-Mo catalysts which unnecessarily increase the hydrogen content of the pitch fraction. CANMET process uses cheaper additives which distribute proportionally more hydrogen in the distillate fraction.

4. <u>No Catalyst Disposal or Regeneration Problem</u>

   CANMET process uses cheap throw-away additives, thereby eliminating catalyst disposal or regeneration problems. The additives end up in the pitch fraction and can be disposed of easily.

5. <u>Can Operate at Lower Reaction Pressures</u>

   Development of coke inhibiting additives results in successful operation at low pressures.

POTENTIAL FOR CANMET HYDROCRACKING PROCESS

CANMET process can be developed to handle coal slurries or coal-derived liquids using the same additives. This will result in an improved coal liquefaction process.

The CANMET process also has great potential for upgrading non-Canadian heavy-oil feedstocks (e.g., from Mexico, U.S.A., Venezuela and Europe), as well as for the treatment of conventional vacuum residua.

TABLE-I

PROPERTIES OF ATHABASCA BITUMEN AND CONVENTIONAL CRUDE OIL

		ATHABASCA BITUMEN	CONVENTIONAL CRUDE OIL
SPECIFIC GRAVITY 15/15°C		1.009	0.84 TO 0.9
SULPHUR	Wt %	4.48	0.1 TO 2.0
ASH	Wt %	0.59	NIL
C.C.R	Wt %	13.3	1 TO 2
VANADIUM	ppm (wt)	213	2 TO 10 (TOTAL METALS)
NICKEL	ppm (wt)	67	-
CARBON	Wt %	83.36	86
HYDROGEN	Wt %	10.52	13.5
NITROGEN	Wt %	0.43	0.2
VISCOSITY at 38°C	CSt	10,000	3 TO 7
PITCH (524°C+)	Wt %	51.5	1 TO 5

TABLE-2

HISTORY OF CANMET HYDROCRACKING

YEAR	ACTIVITY
1930	HYDROGENATION OF ATHABASCA BITUMEN
1933	LIQUEFACTION OF COAL, PEAT, CHAR AND BITUMEN
LATE 1930's	COAL LIQUEFACTION
LATE 1940's	VAPOUR PHASE HYDRODESULPHURIZATION OF DISTILLATE OILS AND COKER DISTILLATE
EARLY 1960's	HYDROCRACKING OF RESIDUUM
LATE 1960's	THERMAL AND CATALYTIC HYDROCRACKING OF ALBERTA BITUMEN
LATE 1960's TO PRESENT	PILOT PLANT HYDROCRACKING OF RESIDUUM, BITUMEN AND HEAVY OILS HYDROTREATING

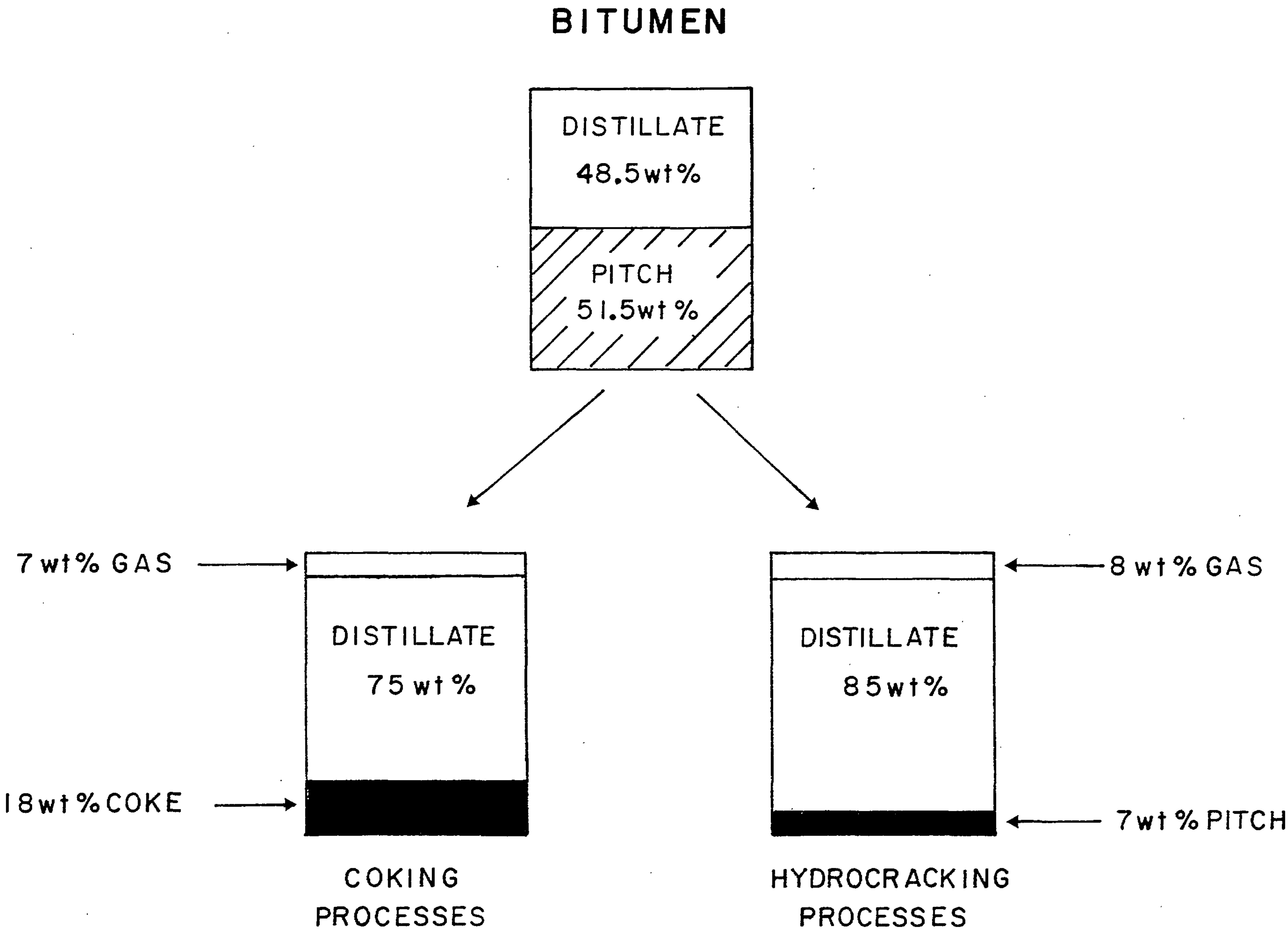

BITUMEN
DISTILLATE
48.5wt%
PITCH
51.5wt%
7wt% GAS
DISTILLATE
75 wt%
18wt%COKE
8 wt% GAS
DISTILLATE
85wt%
7wt% PITCH
COKING
PROCESSES
HYDROCRACKING
PROCESSES

FIGURE-I

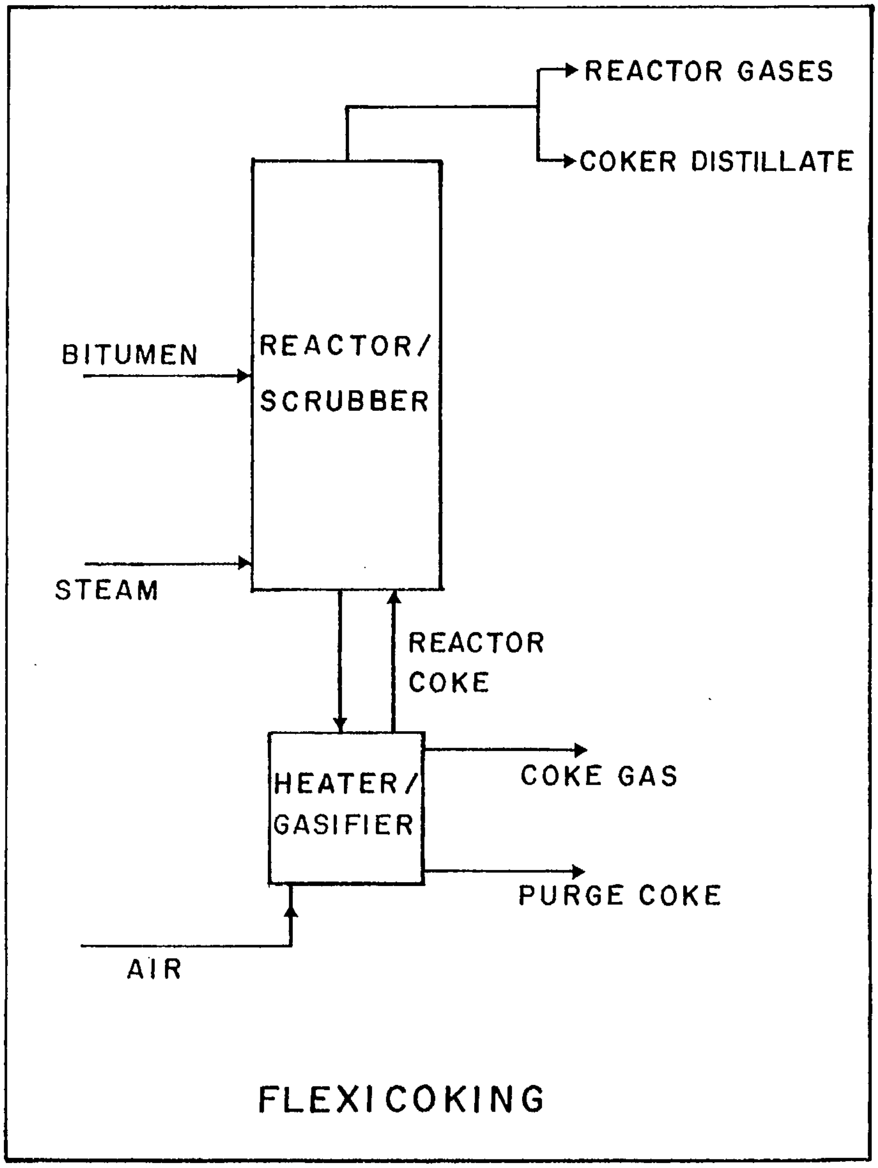

REACTOR GASES
COKER DISTILLATE
BITUMEN
REACTOR/
SCRUBBER
STEAM
REACTOR
COKE
HEATER/
GASIFIER
COKE GAS
PURGE COKE
AIR
FLEXICOKING

FIGURE-2

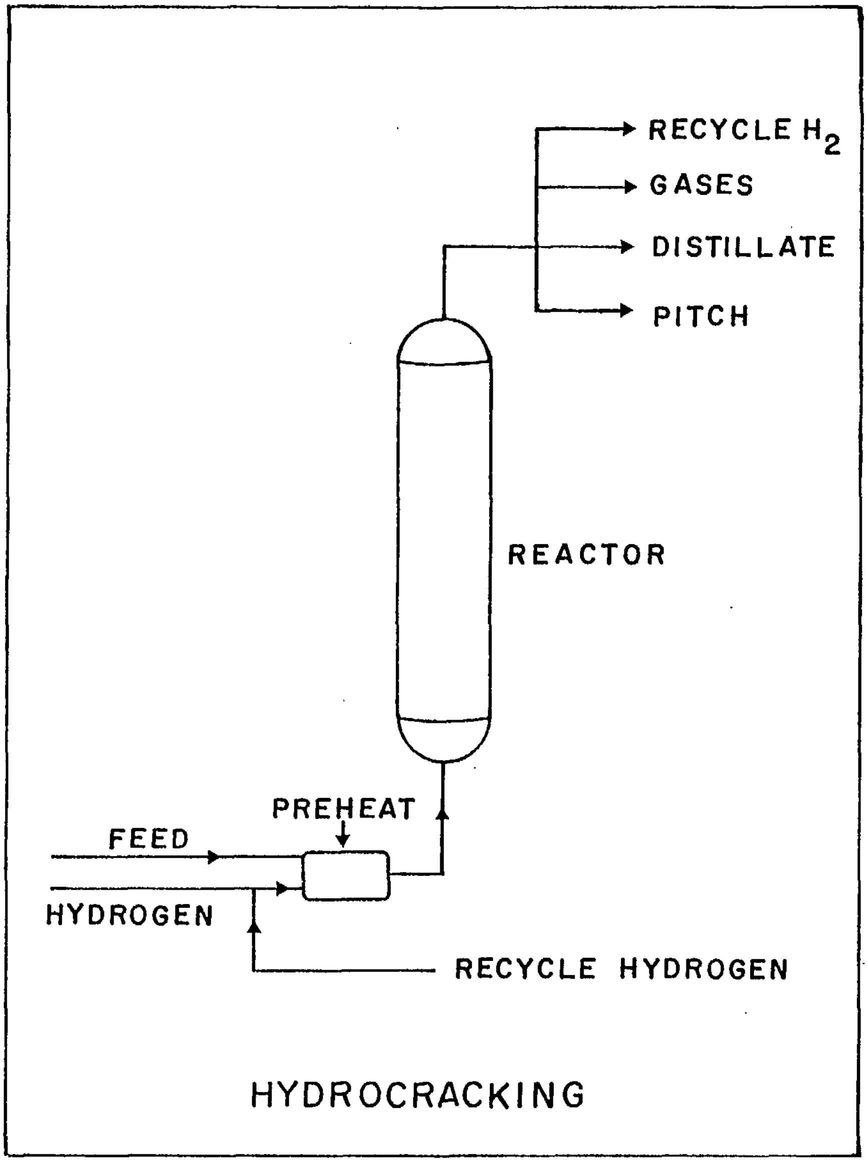
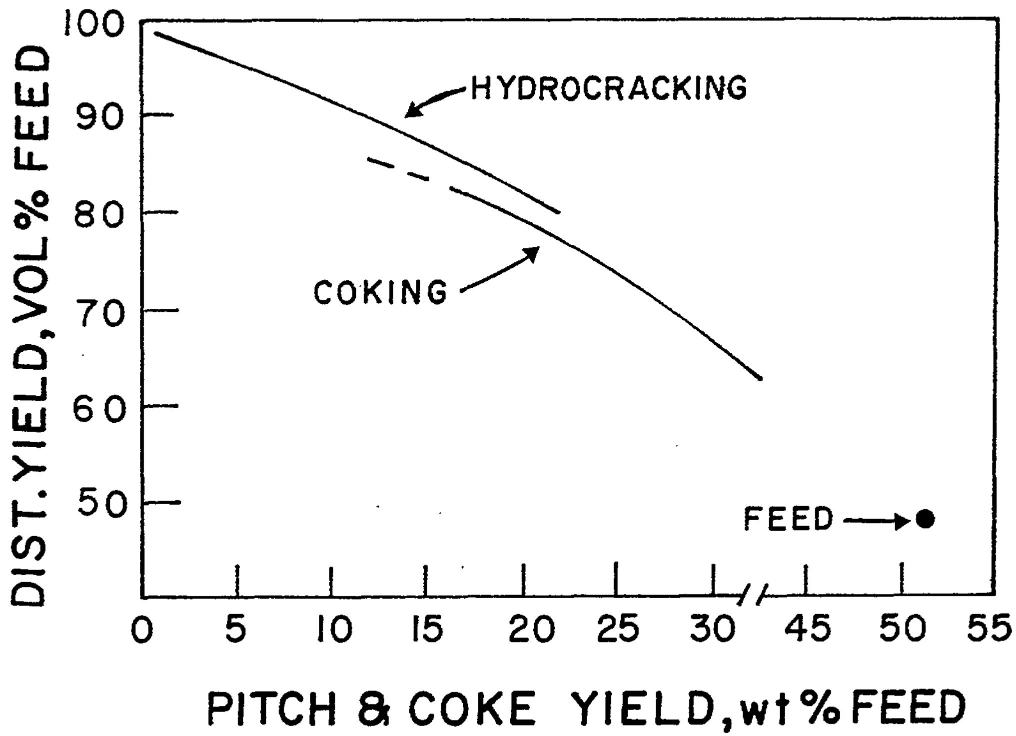
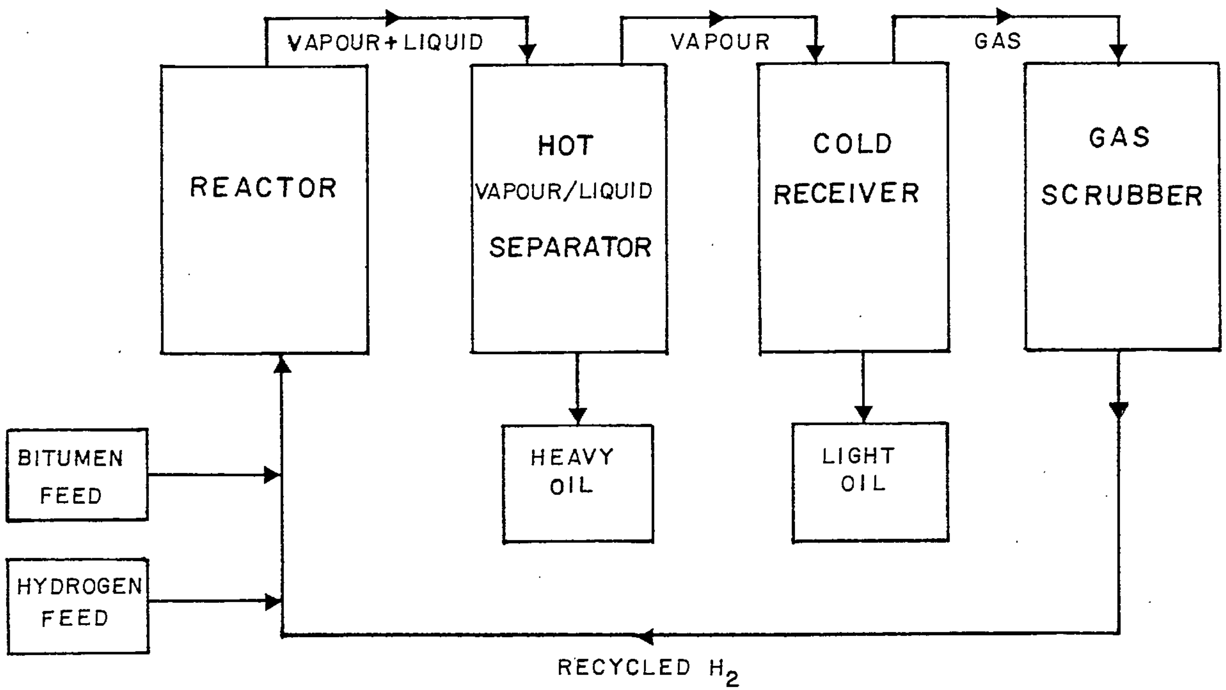

RECYCLE H_2
GASES
DISTILLATE
PITCH
REACTOR
PREHEAT
FEED
HYDROGEN
RECYCLE HYDROGEN
HYDROCRACKING

FIGURE-3



100
90
80
70
60
50
DIST. YIELD, VOL % FEED
HYDROCRACKING
COKING
FEED
0
5
10
15
20
25
30
45
50
55
PITCH & COKE YIELD, wt % FEED

FIGURE-4



SCHEMATIC DIAGRAM OF CANMET PILOT PLANT

FIGURE-5

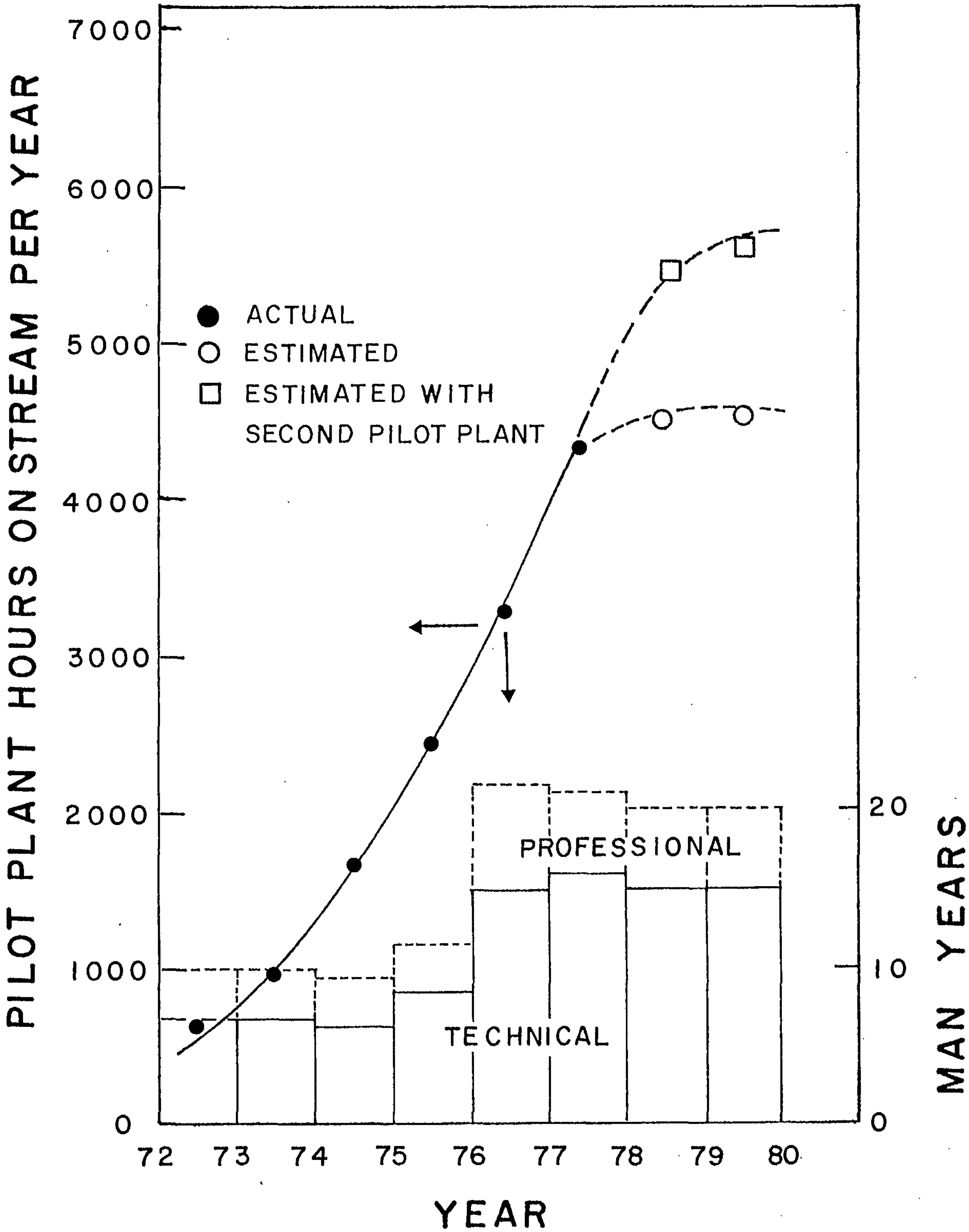

PILOT PLANT HOURS ON STREAM PER YEAR
7000
6000
5000
4000
3000
2000
1000
0
ACTUAL
ESTIMATED
ESTIMATED WITH
SECOND PILOT PLANT
PROFESSIONAL
TECHNICAL
20
10
0
MAN YEARS
72
73
74
75
76
77
78
79
80
YEAR

FIGURE-6