



THE CANMET HYDROCRACKING PROCESS TO UPGRADE RESIDUAL OILS

T.J.W. de BRUIJN AND D.J. PATMORE
Canada Centre for Mineral and Energy Technology,
Energy, Mines and Resources Canada

G. FLAHERTY
Petro-Canada, Calgary, Alberta

L.W. CHAMBERS
Lavalin Inc., Toronto, Ontario

JUNE 1982

Presented at Synfuels' 2nd Worldwide Symposium, Oct. 11-13, 1982,
Brussels, Belgium.

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
Report 82-35(OP)

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.



•
•

•
•

•
•

THE CANMET HYDROCRACKING PROCESS TO UPGRADE RESIDUAL OILS

by

T.J.W. de Bruijn and D.J. Patmore
Department of Energy, Mines and Resources Canada
CANMET, Ottawa, Ontario CANADA

G. Flaherty
Petro-Canada Exploration Inc.
Calgary, Alberta CANADA

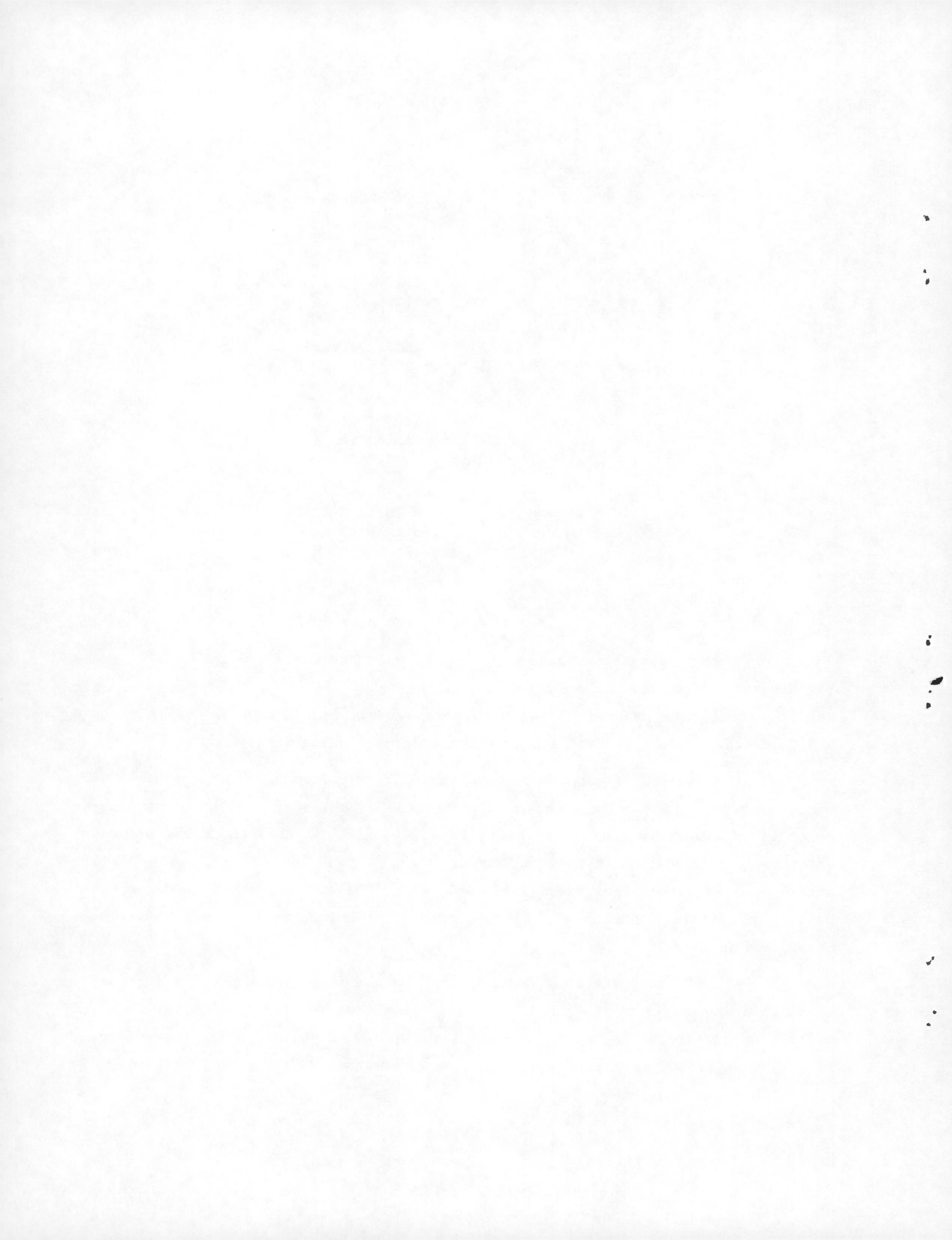
L.W. Chambers
Partec Lavalin Inc.
Toronto, Ontario CANADA

ABSTRACT

CANMET Hydrocracking Technology has been developed by the Canada Centre for Mineral and Energy Technology (CANMET) to upgrade bitumen, heavy oil and residuum. Use of this process allows very high conversion of material boiling above 524°C (pitch) to distillates with moderate hydrogen consumption.

The Process is capable of handling difficult feedstocks which have a wide range of pitch, sulphur, ash and metal contents. Results from pilot plant experiments using a variety of feedstocks will be presented to illustrate the behaviour of different feedstock types containing typically 50-100% pitch, 100-1300 ppm metals, 1.3-6% sulphur and up to 1.1% ash. The three main types of feedstock that have been investigated are tar sand bitumen, in situ heavy oil and conventional heavy residuum.

Although conventional residuum requires more severe hydrocracking conditions than bitumen or heavy oil, it will be shown that similar high conversions and distillate yields can be obtained for all three types. Data showing the effect of feed type on product properties will also be presented.



INTRODUCTION

The 1970's brought world-wide realization that a finite world has limits to its growth (1). One aspect was that one became aware of limits to the supply of several raw materials. For the refining industry it meant realization of an inevitable shortage of light crudes. This shortage must be made up by increased production of heavier crudes, heavy oils, bitumen and coal (2) which are still in relatively abundant supply. For example, western Canada and Venezuela have heavy oil reserves of close to 1 and 3 trillion barrels, respectively (3), and coal reserves are estimated to be at least four times the total proven oil reserves (4). The high viscosity and pour point of heavy crudes will necessitate primary upgrading to enable pipeline transportation of these materials from the production site to the refinery. In addition, the increased use of coal will lessen the demand for residual fuel oil products. Both circumstances increase the need for heavy oil upgrading. The refining industry, as revealed for example in the latest two annual refining reports in the Oil and Gas Journal (5,6) is adapting to this challenge.

This paper describes the CANMET Hydrocracking Process, which has a number of advantages over other upgrading schemes, and shows product yields and properties obtained by this process using a variety of heavy feedstocks, viz., reduced heavy oils, reduced bitumen and conventional vacuum bottoms resid.

THE CANMET HYDROCRACKING PROCESS

BACKGROUND

For more than 40 years now, CANMET (Canada Centre for Mineral and Energy Technology), a branch of the Department of Energy, Mines and Resources Canada, has been involved in bench-scale hydrocracking studies. These studies led to the development of the CANMET Hydrocracking Process and for the past 12 years extensive studies have been carried out in one, and since 1979, two 1 bbl/day continuous pilot plants.

In 1979 Petro-Canada was granted the exclusive right to commercialize and market the Process. A partnership was formed with Lavalin Inc., a major Canadian engineering company, to undertake further engineering and marketing of the technology. In 1981 a decision was made to build a 5000 bbl/day demonstration plant at the Petro-Canada refinery in Montreal. The preliminary design has been completed and start-up is scheduled for late 1984.

PROCESS DESCRIPTION

The CANMET Hydrocracking Process offers high liquid yield at very high pitch conversion. An inexpensive coal based additive is used which inhibits coke formation while also acting as a demetallization agent.

A simplified schematic of the CANMET Hydrocracking Process is shown in Fig. 1. The additive is prepared separately and slurried with the feedstock. Heated feed, mixed with a little additive, is combined with recycled hydrogen and fed into the bottom of an empty reactor. Residues from the additive and deposited feed metals contribute to the formation of a stable solids bed. Overhead liquid product is separated into different distillate fractions and pitch. Solids are continuously removed from the reactor; partly by entrainment of fines, and partly by a small withdrawal stream from the reactor bottom.

FEEDSTOCK FLEXIBILITY

An indication of the great flexibility of the CANMET Hydrocracking Process is shown by the variety of feedstocks processed to date. The properties of seven feedstocks, four of them processed only recently, are shown in Table 1. Results on some feedstocks were presented before (3,7-12).

All feedstocks, except the Boscan and Lloydminster, are exceptionally high in pitch content and some feedstocks contain extremely high concentrations of impurities. Due to high metals, sulphur, ash and C.C.R. concentrations, these feedstocks pose problems for catalytic upgrading processes. Coking units would have a low liquid yield since the coke yield would probably be between 20 to 40 wt %, when processing the listed feedstocks.

PRODUCT YIELDS AND PRODUCT QUALITY

Product data will be given for the following four feedstocks:

. Athabasca bitumen	vacuum resid	(+524°C)
. Cold Lake heavy oil	vacuum resid	(+454°C)
. Canadian blend of crudes	vacuum resid	-
. Arabian Light	vacuum resid	(+549°C)

All feedstocks were processed at identical conditions.

Fig. 2 shows the pitch conversions vs. reactor temperature. An almost linear relation is obtained up to about 80-90 wt % pitch conversion. Vacuum resids from conventional crudes require more severe operating conditions to obtain identical pitch conversions. The differences between the other feedstocks are very small.

Sulphur conversions are plotted against reactor temperature in Fig. 3 and correlated with pitch conversion in Fig. 4. At identical pitch conversions the sulphur conversions for the conventional vacuum resids are lower, although the difference is reduced at higher pitch conversions. Figure 4 shows that at high pitch conversions a sulphur conversion of 60 to 70 wt % is obtained even though no specific desulphurization catalyst is employed.

Total liquid yields, shown in Fig. 5, decrease gradually with increasing pitch conversion. At 90 wt % pitch conversion liquid yields amount to about 88 to 93 wt % of the feed; corresponding volume yields range from about 105 to 107%.

Distillate yields (liquids boiling below 524°C) for the conventional resids fall within the range of yields for the non-conventional resids (Fig. 6). This figure shows that high distillate yields of about 79 to 86 wt % of feed are obtained at 90 wt % pitch conversion.

Fig. 7 shows the naphtha yields which all fall within a small band. The process yields 20 to 24 wt % naphtha at about 90 wt % pitch conversion.

The light gas oil yields for all feedstocks are almost identical, especially at lower pitch conversions (Fig. 8). The yields of both naphtha and light gas oil increase rapidly at higher pitch conversions.

Differences in yield for the various feedstocks are most pronounced for the heavy gas oil (Fig. 9). However, the shape of the curves is similar for all feeds. Heavy gas oil yields reach a maximum around 70 to 80 wt % pitch conversion. Apparently more and more of the heavy gas oil is further converted to light gas oil, naphtha and gases at higher pitch conversions.

Gas yields as a weight percentage of feed are shown in Fig. 10. Yields increase rapidly above 80-85 wt % pitch conversion corresponding to the rapid decrease in heavy gas oil yield.

Hydrogen consumption is shown in Fig. 11. Above about 50 wt % pitch conversion, the conventional resids appear to consume slightly less hydrogen than the non-conventional resids. All feeds show an increased rise in consumption above about 70 to 80 wt % pitch conversion. This is caused by the conversion of primary products to lighter compounds.

The API gravity of the three distillate fractions is shown in Figs. 12 to 14. The naphtha and light gas oil fractions show only small changes with increasing pitch conversion. The largest differences are the result of differences in feedstock properties.

The sulphur concentrations in the naphtha, light gas oil and heavy gas oil are shown in Figs. 15 to 17. The sulphur concentrations in the fractions from Arabian Light and Canadian Blend are low as a result of the relatively low sulphur concentration in the feed. As expected, at more severe hydrocracking conditions, the sulphur concentration in all fractions decreases.

Table 2 lists the hydrogen and carbon contents of the pitches obtained at the given pitch conversions. The hydrogen/carbon ratios are low indicating that little hydrogen is wasted by upgrading the pitch fraction (compare with H/C ratios in the feeds, Table 1). The hydrogen consumed is added to the more valuable fractions.

ECONOMICS

A number of case studies were made to evaluate the economic performance of the CANMET Hydrocracking Process. The results of those studies were presented before (3,8,9) and are summarized in Table 3. All case studies showed attractive rates of return.

CONCLUSIONS

The results recorded in this paper indicate that the CANMET Hydrocracking Process is an excellent heavy crude or residuum upgrading process.

The main three types of heavy feedstocks, i.e. bitumen, heavy oil and resids from conventional crudes, can be upgraded by the CANMET Hydrocracking Process to very high pitch conversions even when containing very high concentrations of pitch, metals or other impurities. Vacuum resids from conventional crudes require more severe hydrocracking conditions to obtain the same pitch conversion than the other feedstocks. However, this does not appear to influence the total liquid yield or distillate yield which are in the same range as the yields of the other feedstocks. At pitch conversions of about 90 wt % the CANMET Hydrocracking Process produces 79 to 86 wt % or 96 to 100 vol % distillate depending on the feedstock.

The liquid distributions of all feedstocks are different though major differences only occur in the heavy gas oil yield; differences in naphtha and light gas oil yield are small. The yields can easily be varied by changing the operating conditions.

Above 70 to 80 wt % pitch conversion increased cracking occurs of primary products (mainly heavy gas oil) resulting in increased production of lighter products (gases, naphtha and light gas oil) at the expense of increased hydrogen consumption.

Other features of the CANMET Hydrocracking Process are:

- a good thermal reactor stability because the process does not employ an active catalyst;
- a relatively low operating pressure due to the suppressive effect of the additive on coke formation;
- efficient hydrogen utilization. Little hydrogen is added to the pitch fraction; almost all hydrogen goes to distillate product;
- attractive economics as indicated by several case studies.

REFERENCES

1. Meadows, D.H., Meadows, D.L., Randers, J. and Behrens, W.W. "The Limits to Growth", New York, Universe Books; 1972.
2. Johnson, A.R. Hydrocarbon Processing, Sept. 1979, 109-113.
3. Menzies, M.A., Scott, T.F. and Denis, J.M. Proceedings of the 15th Inter-society Energy Conversion Engineering Conference; August 18-22, 1980, Seattle, Washington.
4. Walters, P.I. Hydrocarbon Processing, May 1981, 50F-50JJ.
5. Aalund, L.R. Oil & Gas Journal, March 30, 1981, 63-65.
6. Aalund, L.R. Oil & Gas Journal, March 22, 1982, 79-81.
7. Menzies, M.A., Silva, A.E. and Denis, J.M. "Hydrocracking without catalysis upgrades heavy oil"; Chem. Eng., February 23, 1981, 46-47.
8. Lunin, G., Silva, A.E. and Denis, J.M. "The CANMET Hydrocracking Process, Upgrading of Cold Lake Heavy Oil"; Chemistry in Canada, March 1981, 17-21.
9. Menzies, M.A., Silva, A.E., Hepton, J. and Logie, R. "High conversion residuum hydrocracking with the CANMET Process"; 1981 NPRA Annual Meeting, March 29-31, 1981; San Antonio, Texas.
10. Patmore, D.J., Khulbe, C.P. and Belinko, K. "Residuum and heavy oil upgrading with the CANMET Hydrocracking Process"; 181st ACS National Meeting, March 29 - April 13, 1981; Atlanta, Georgia.
11. Ranganathan, R. and Pruden, B.B. "High conversion with the CANMET Hydrocracking Process"; Proceedings of the 2nd World Congress of Chemical Engineering; Oct. 4-9, 1981; Montreal, Quebec.
12. Chambers, L.W., Waugh, R.J., Silva, A.E. and Denis, J.M. "The CANMET Residuum Hydrocracking Process: An Update"; The 2nd International Conference on Heavy Crude and Tar Sands, February 1982; Caracas, Venezuela.

TABLE 1 - Characteristic Properties of Some Processed Feedstocks

		Athabasca (+524°C)	Cold Lake (+454°C)	Boscan (+343°C)	Canadian Blend	Arabian Light (+549°C)	Lloydminster (+343°C)	Laguna (+454°C)
Specific Gravity,	15/15°C	1.073	1.038	1.016	0.989	1.023	1.006	1.024
Gravity,	°API	0.37	4.8	7.77	11.57	6.82	9.16	6.7
Sulphur,	wt %	6.20	5.82	5.73	1.37	4.30	4.49	3.43
Carbon,	wt %	83.25	82.90	82.44	86.98	84.91	83.80	85.01
Hydrogen,	wt %	9.45	9.96	10.36	11.37	9.87	10.29	11.03
Nitrogen,	wt %	0.82	0.68	0.80	0.45	0.21	0.67	0.61
Ash,	wt %	1.08	0.05	0.24	0.034	0.035	0.035	0.12
C.C.R.,	wt %	27.5	19.8	16.7	15.9	21.3	14.0	18.4
Metals ¹ ,	ppm	1251 ²	357	1311	90	212	225	655
Viscosity at 99°C,	P1	- ³	3.63	0.585	0.303	1.24	0.342	-
Pentane Insolubles,	wt %	31.4	22.7	22.3	11.8	17.8	17.6	19.6
Toluene Insolubles,	wt %	0.86	0.07	0.09	1.74	0.04	0.06	trace
Pitch (+524°C),	wt %	98.5	85.10	66.7	90.0	98.7	58.2	81.6
H/C at. ratio		1.36	1.44	1.51	1.57	1.39	1.47	1.56

¹ V, Ni, Fe

² In addition this feed contained: Al - 0.16%, Si - 0.22%, other metals - 682 ppm

³ Did not flow into viscometer at 149°C

TABLE 2 - Hydrogen and Carbon Contents of Pitches

Feedstock	Pitch Conversion wt %	Pitch		
		Carbon	Hydrogen	H/C ratio
Athabasca	91.6	76.90	4.66	0.73
Cold Lake	87.5	86.53	6.30	0.87
Canadian Blend	91.0	89.69	6.99	0.94
Arabian Light	88.5	88.43	6.59	0.89

TABLE 3 - Summary of Case Studies

Feedstock	Type	Capacity bbl/day	Cut °C	DCF %
Lloydminster	"stand-alone" upgrader	50,000 (total) 35,600 (CANMET)	- +343	19.3 ¹
Cold Lake	"stand-alone" upgrader	100,000 (total) 72,500 (CANMET)	- +404	21.8 ¹
Laguna	upgrader within refinery	100,000 (total) ² 25,000 (CANMET) ³	- +454	25.5 ⁴

¹ Basis: \$ Canadian, first quarter 1980, Alberta location

² 50/50 Arabian Light and Laguna

³ Laguna vacuum resid

⁴ Basis: \$ U.S., fourth quarter 1980, Gulf Coast location

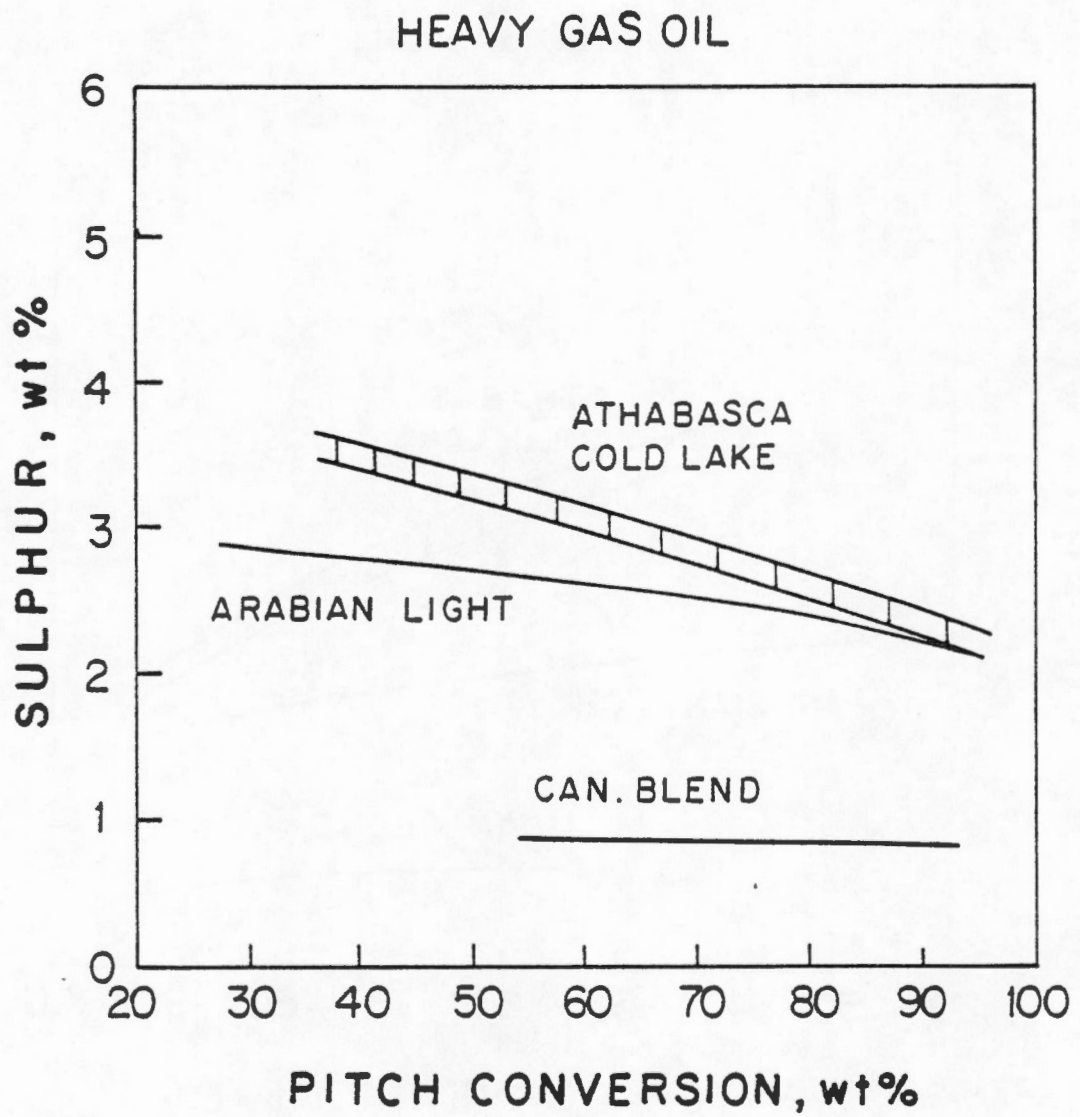


FIGURE 17: Sulphur Concentration in Heavy Gas Oil Fraction vs. Pitch Conversion

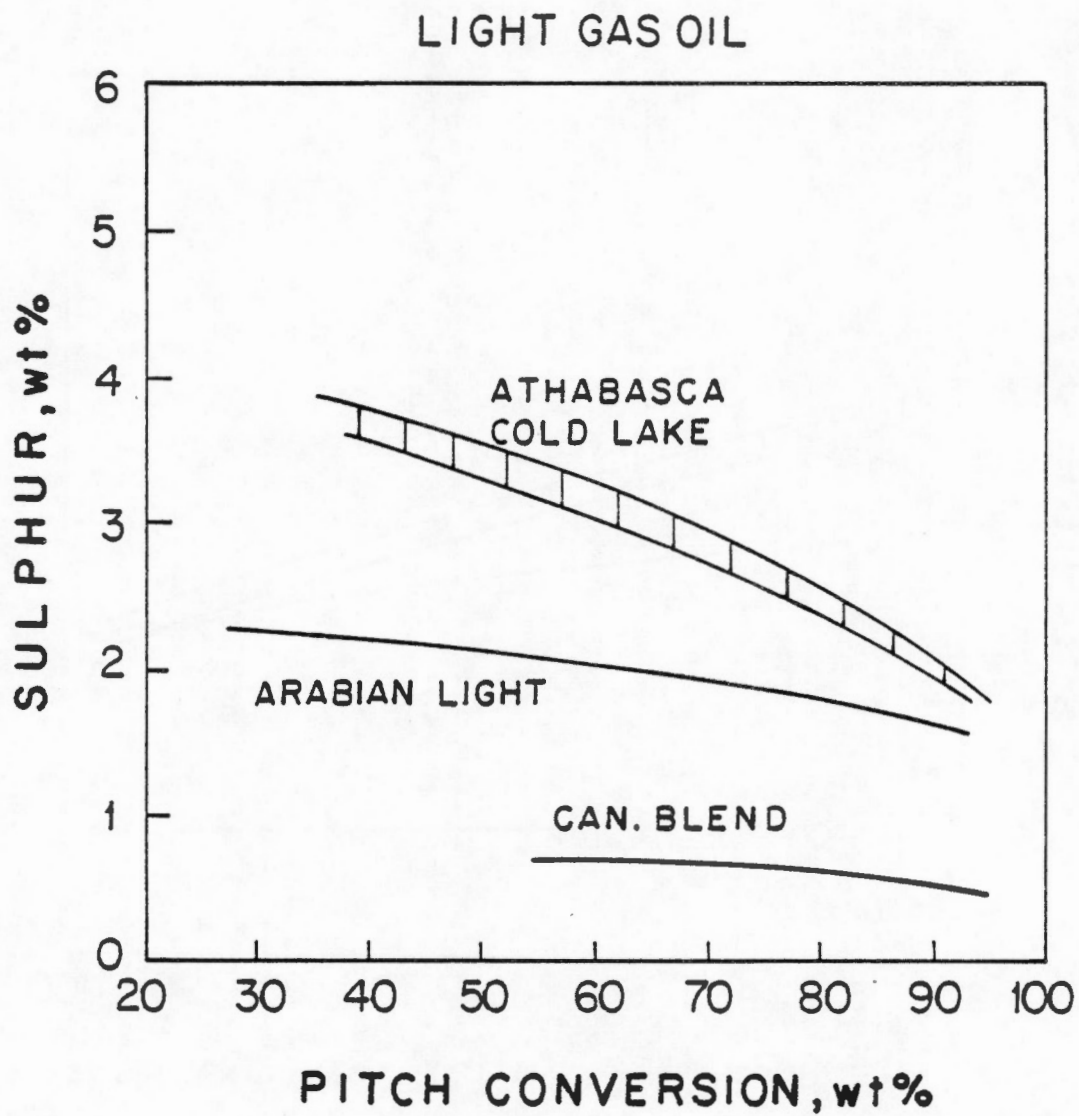


FIGURE 16: Sulphur Concentration in Light Gas Oil Fraction vs. Pitch Conversion

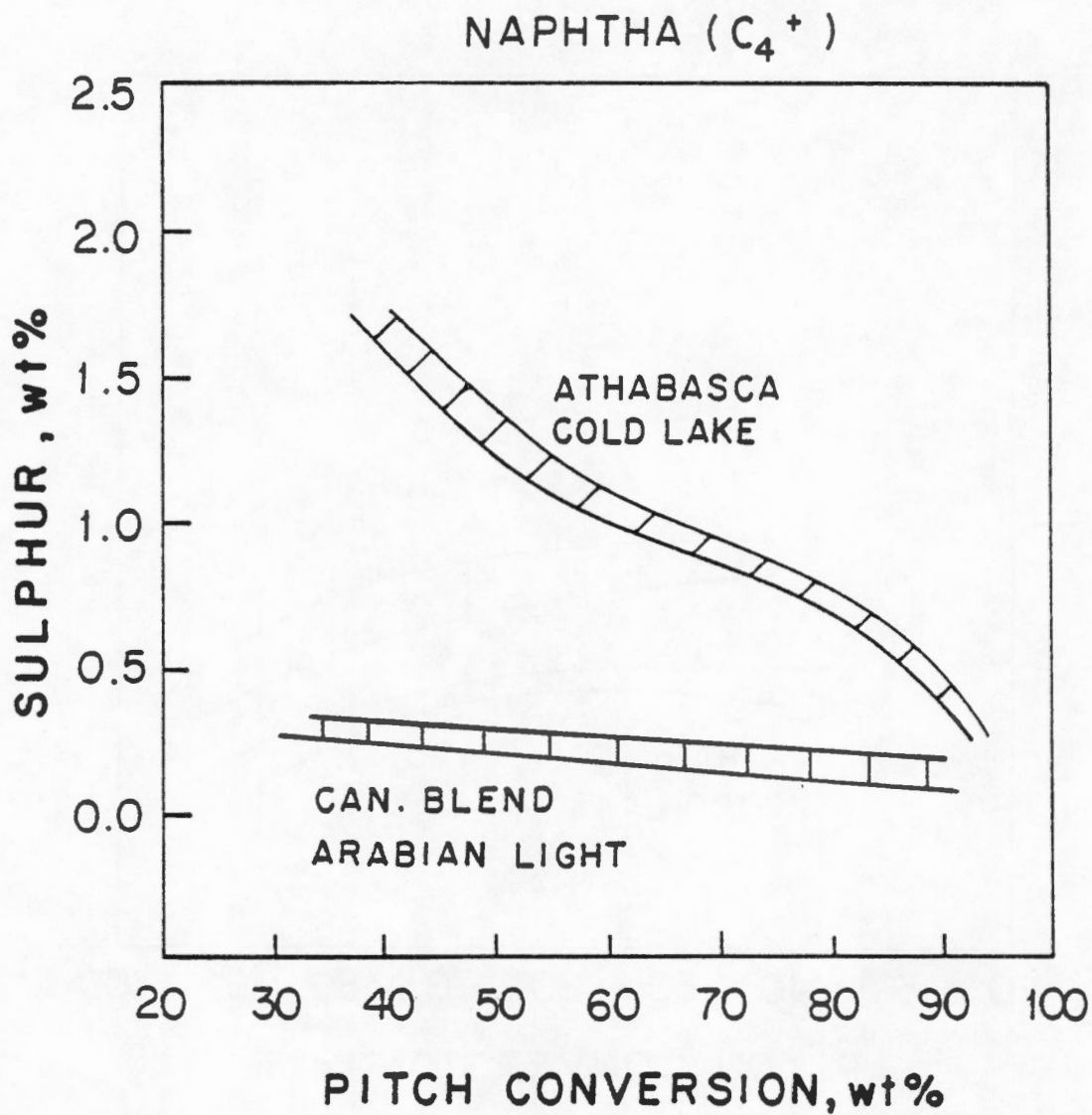


FIGURE 15: Sulphur Concentration in Naphtha (C_4^+) Fraction vs. Pitch Conversion

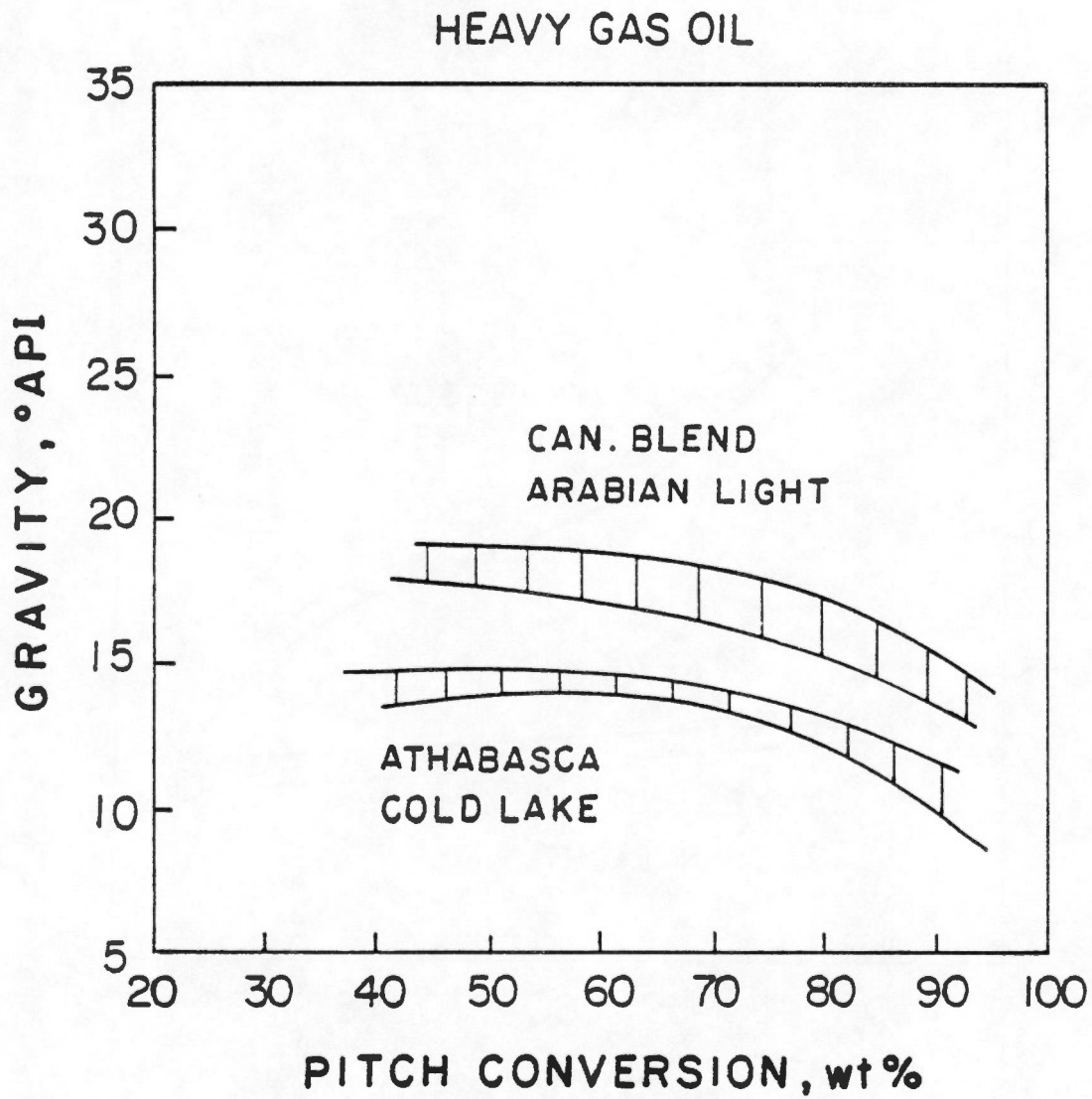


FIGURE 14: Gravity of Heavy Gas Oil Fraction vs. Pitch Conversion

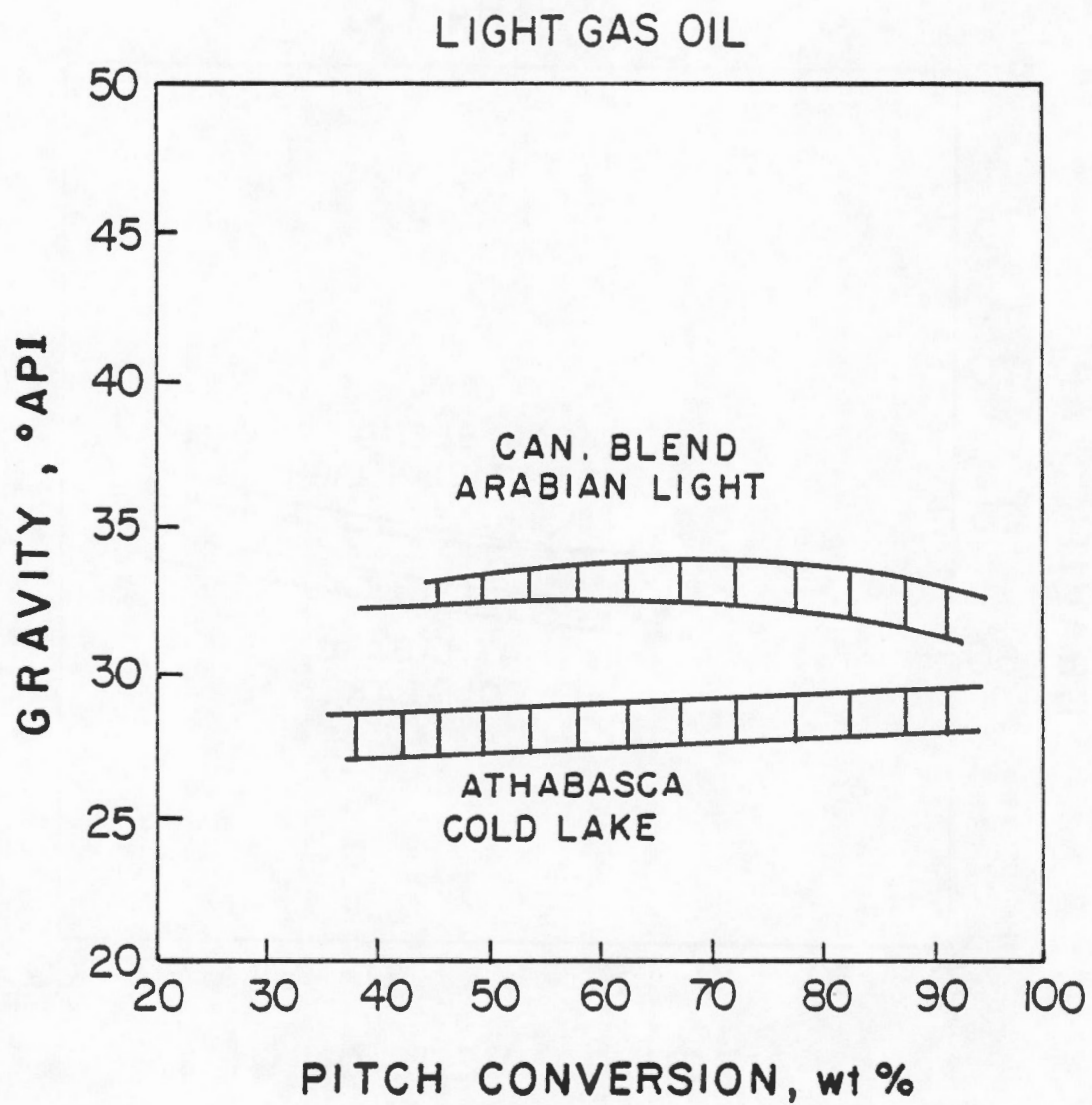


FIGURE 13: Gravity of Light Gas Oil Fraction vs. Pitch Conversion

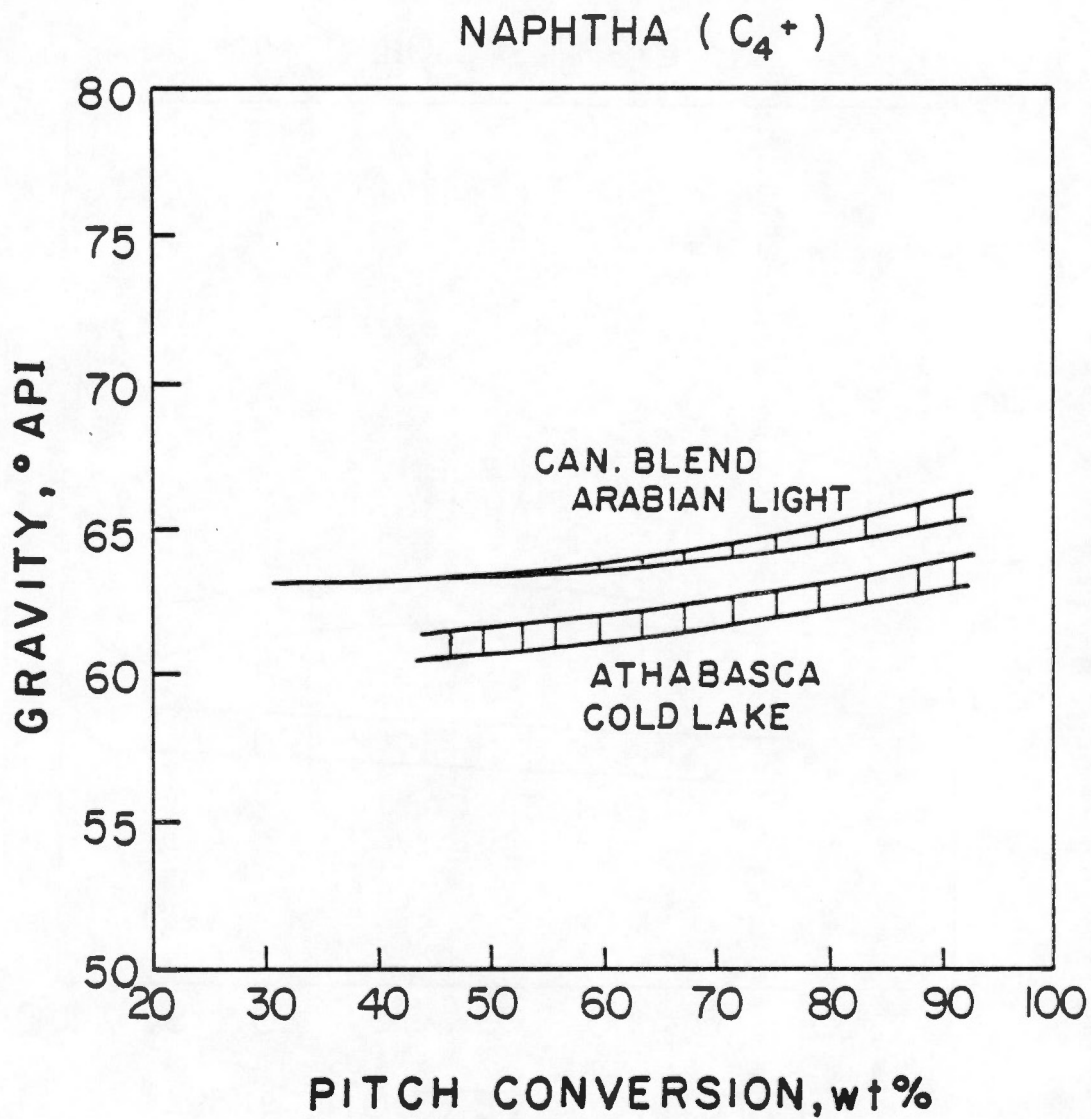


FIGURE 12: Gravity of Naphtha (C₄+) Fraction vs. Pitch Conversion

HYDROGEN CONSUMPTION

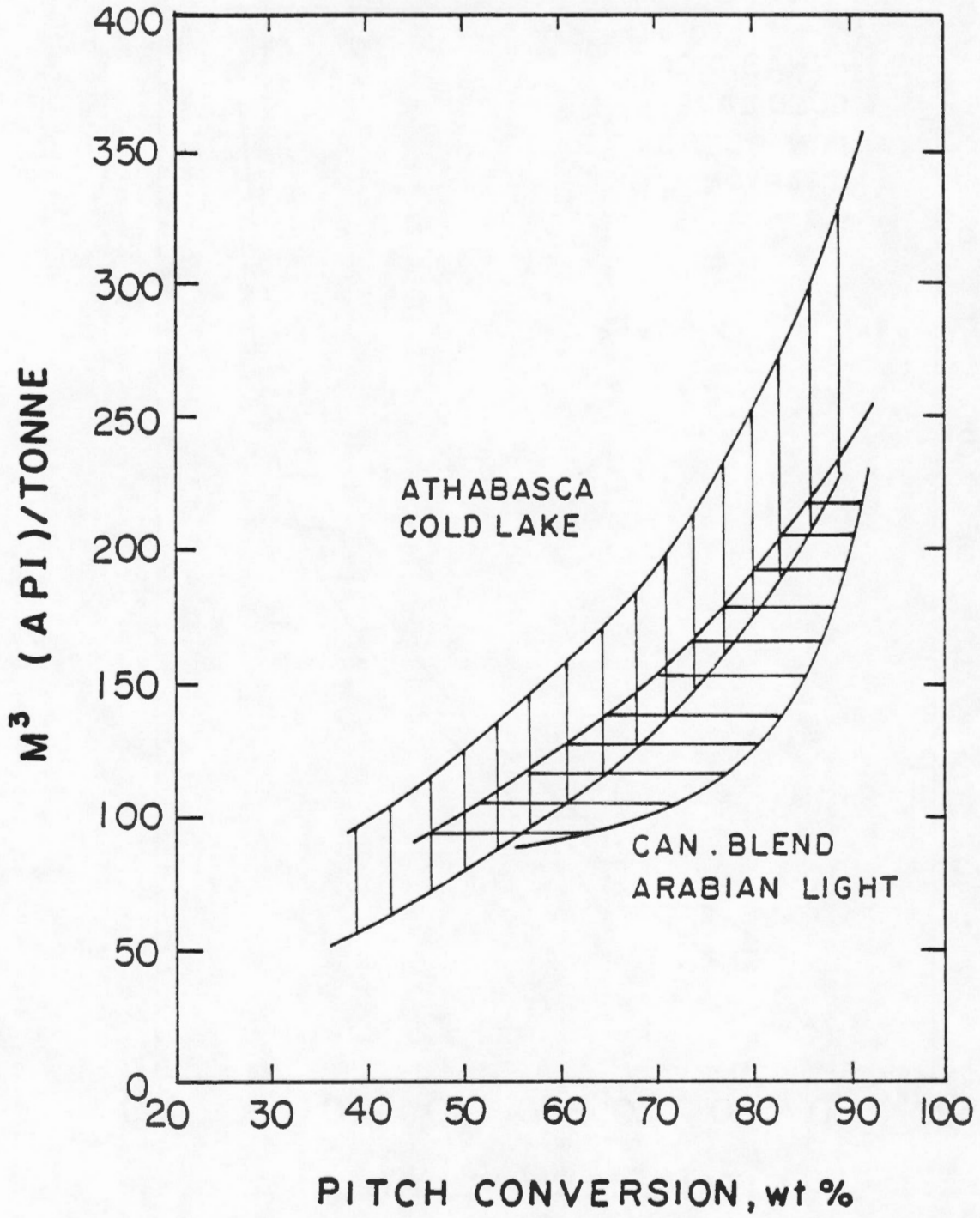


FIGURE 11: Hydrogen Consumption vs. Pitch Conversion

C₁ To C₃ GASES

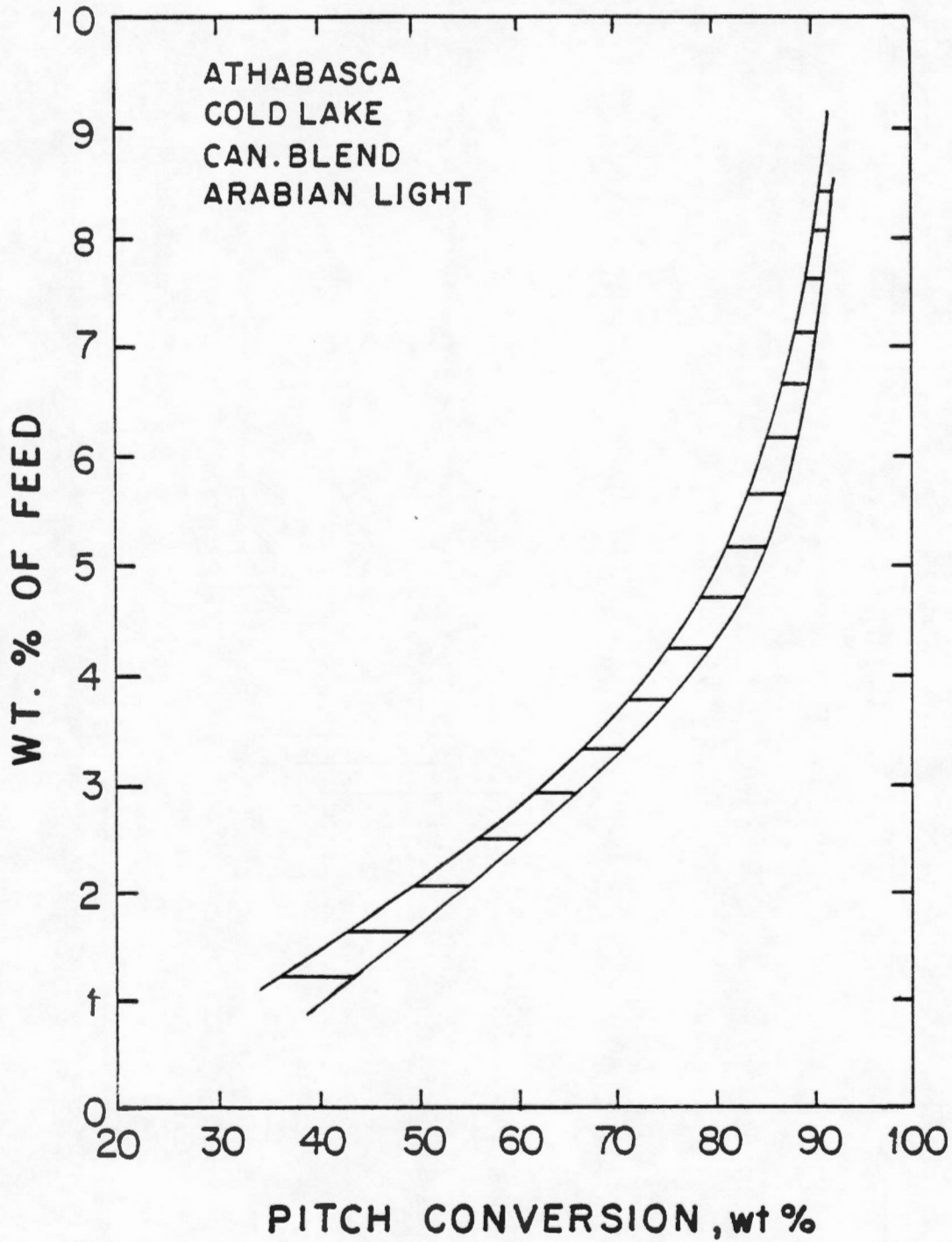


FIGURE 10: C₁ to C₃ Gas Yield vs. Pitch Conversion

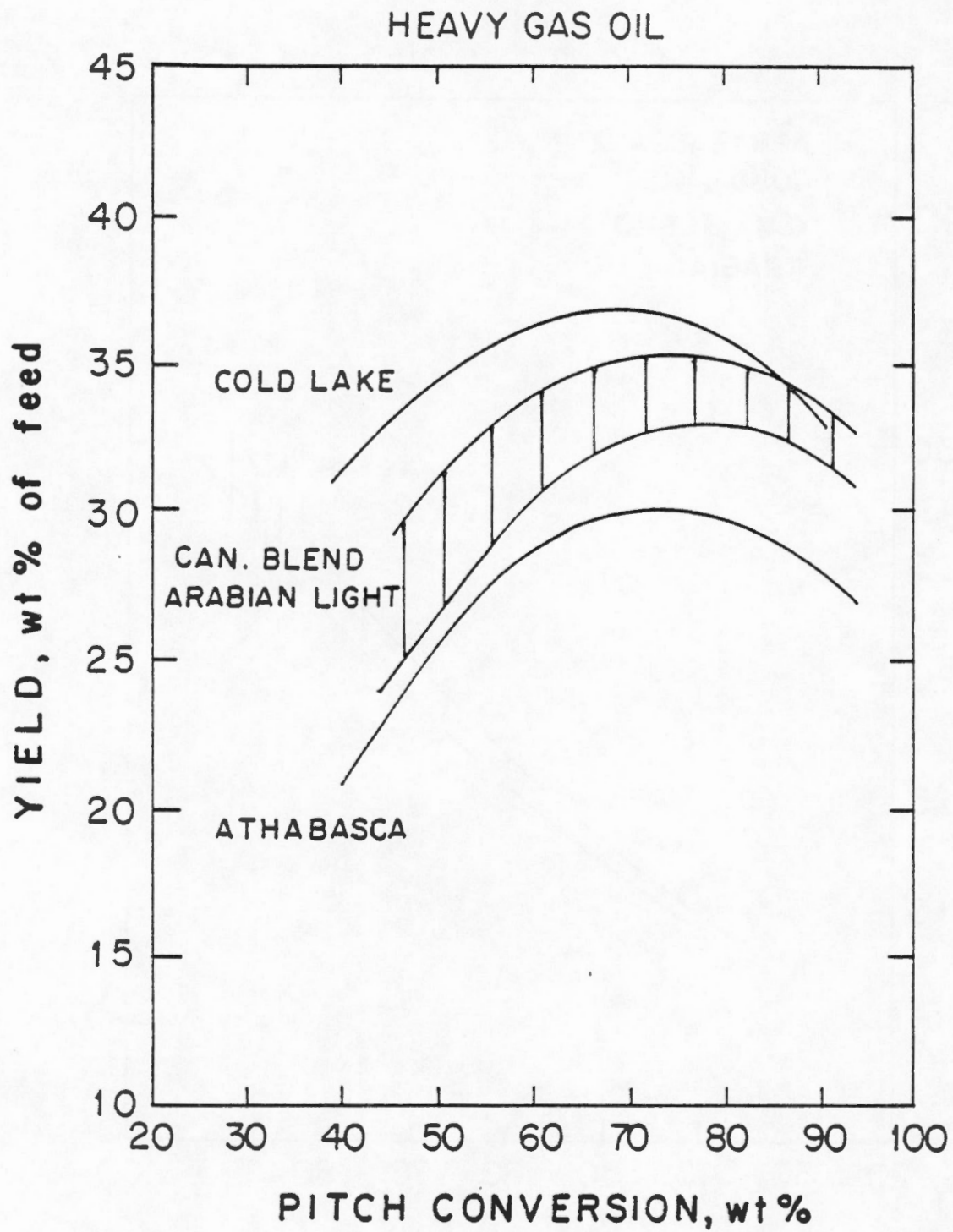


FIGURE 9: Heavy Gas Oil Yield vs. Pitch Conversion

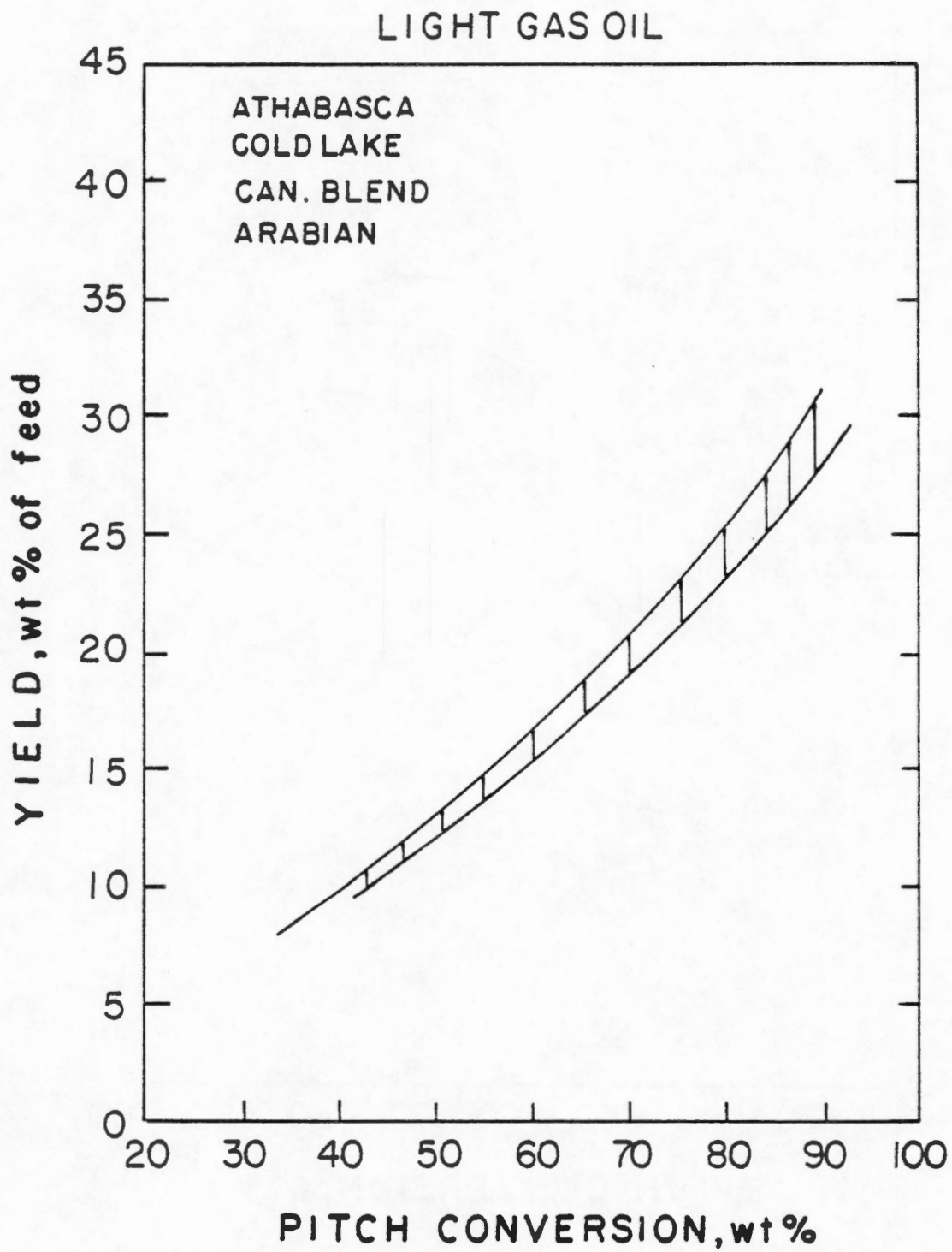


FIGURE 8: Light Gas Oil Yield vs. Pitch Conversion

NAPHTHA (C₄⁺)

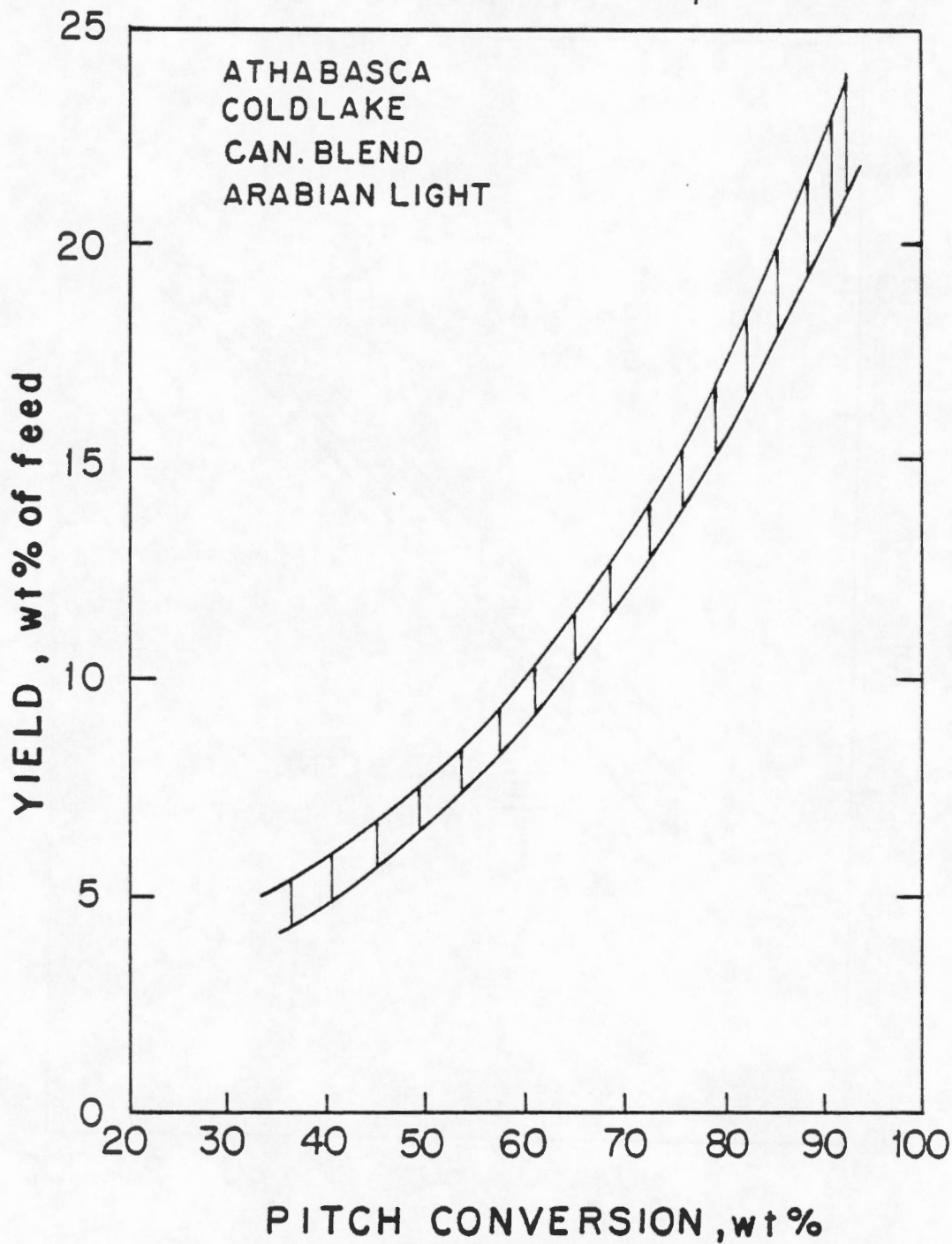


FIGURE 7: Naphtha Yield (C₄⁺) vs. Pitch Conversion

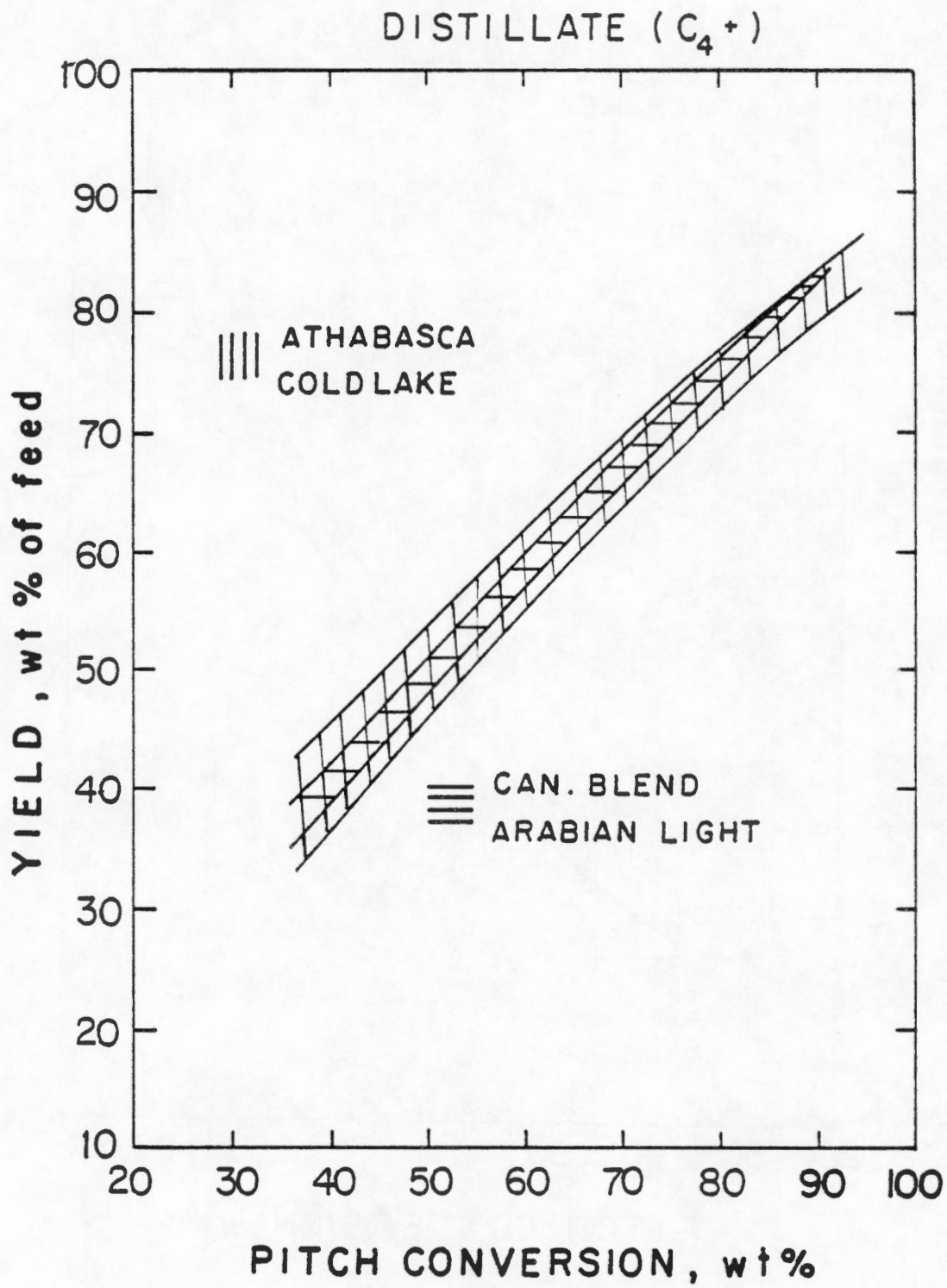


FIGURE 6: Distillate Yield (C₄+) vs. Pitch Conversion

TOTAL LIQUID (C₄⁺)

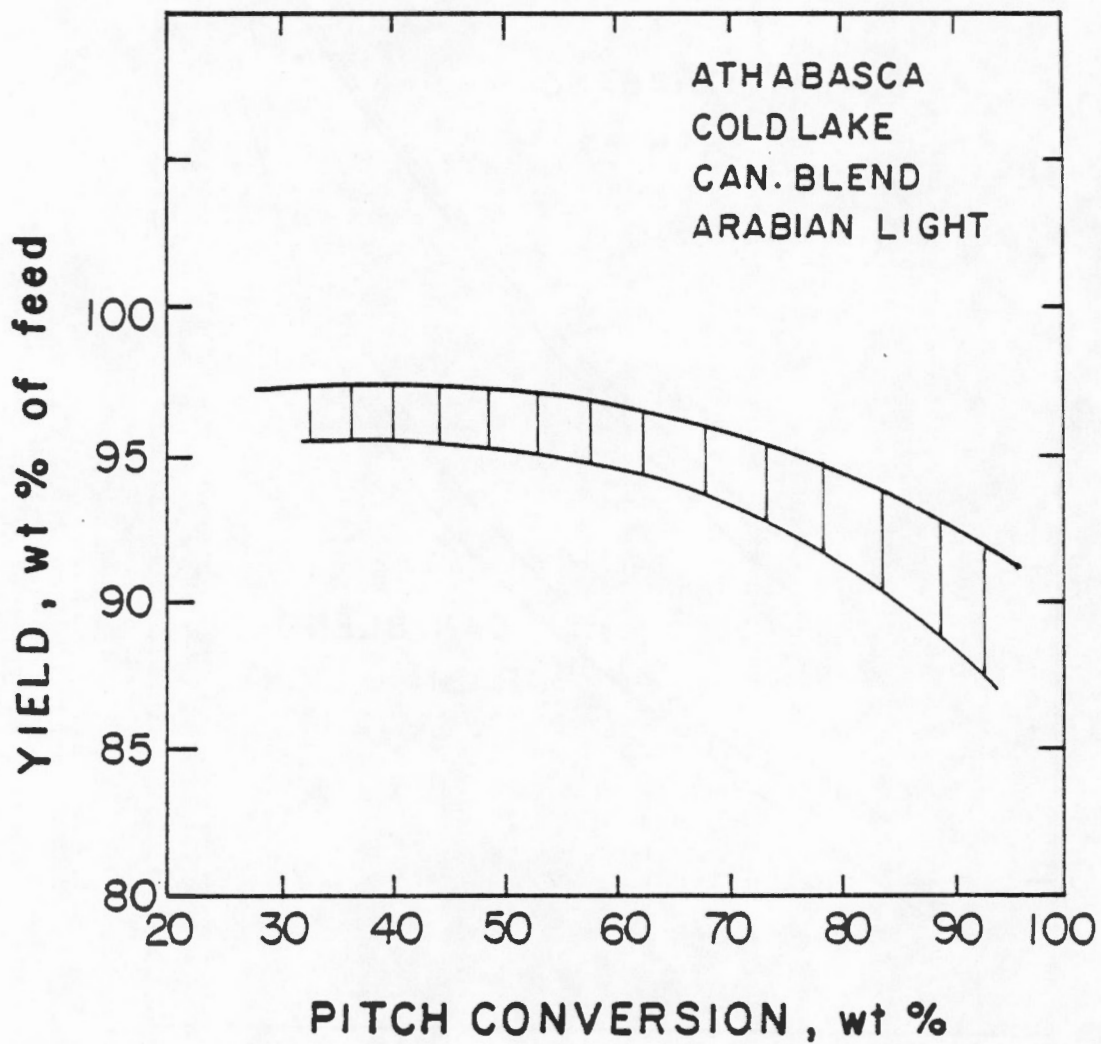


FIGURE 5: Total Liquid Yield (C₄⁺) vs. Pitch Conversion

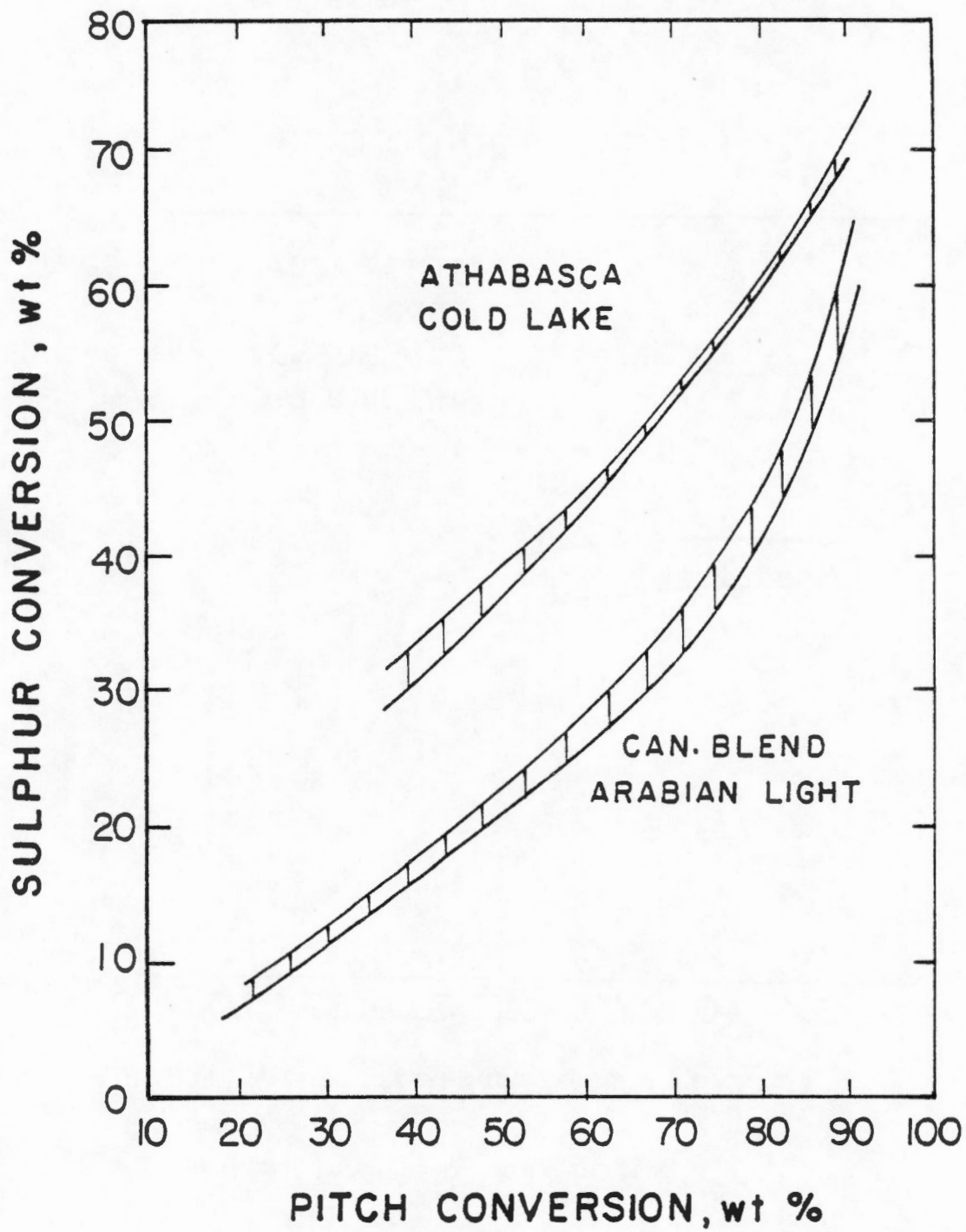


FIGURE 4: Sulphur Conversion vs. Pitch Conversion

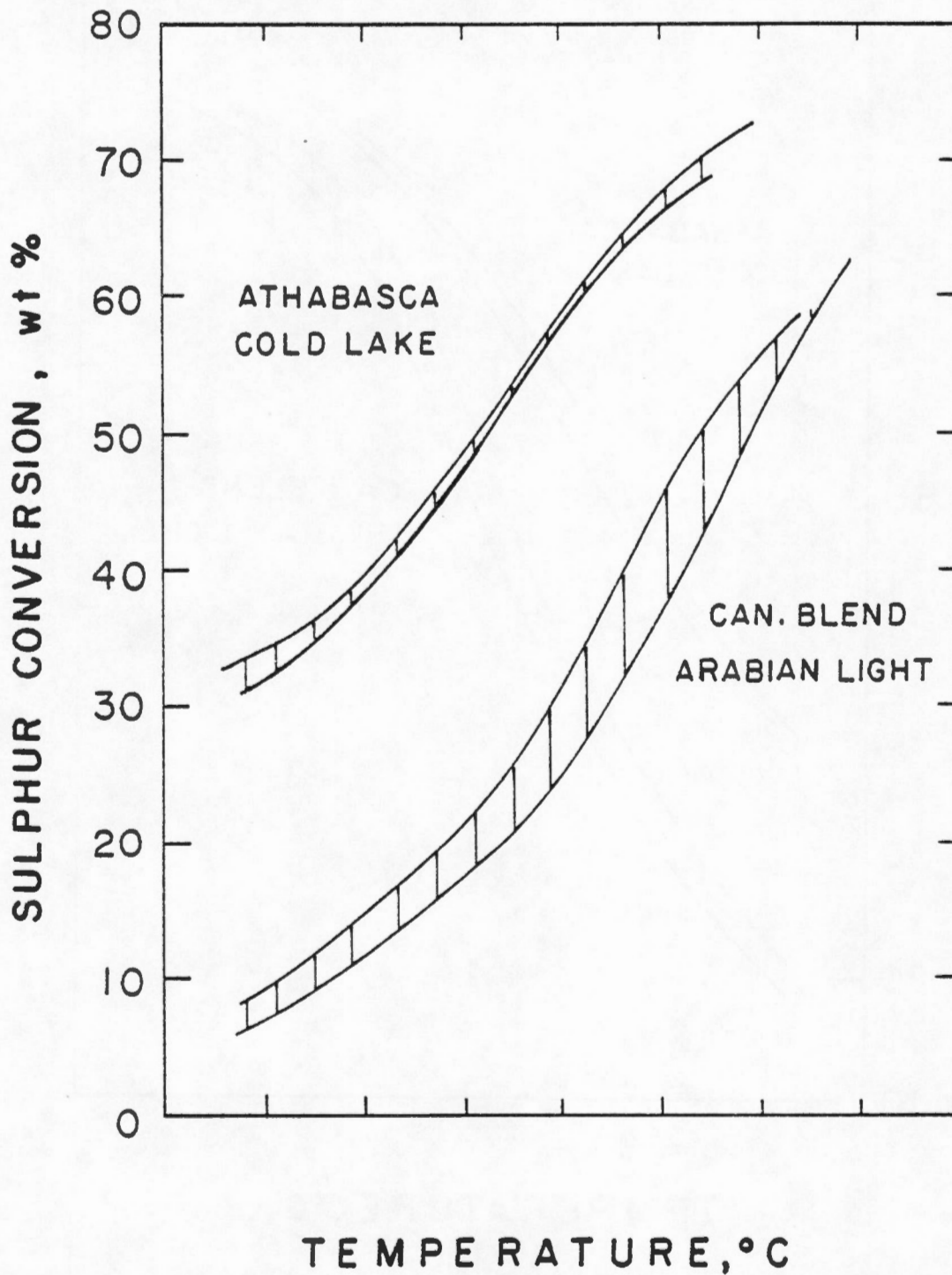


FIGURE 3: Sulphur Conversion as a Function of Reactor Temperature

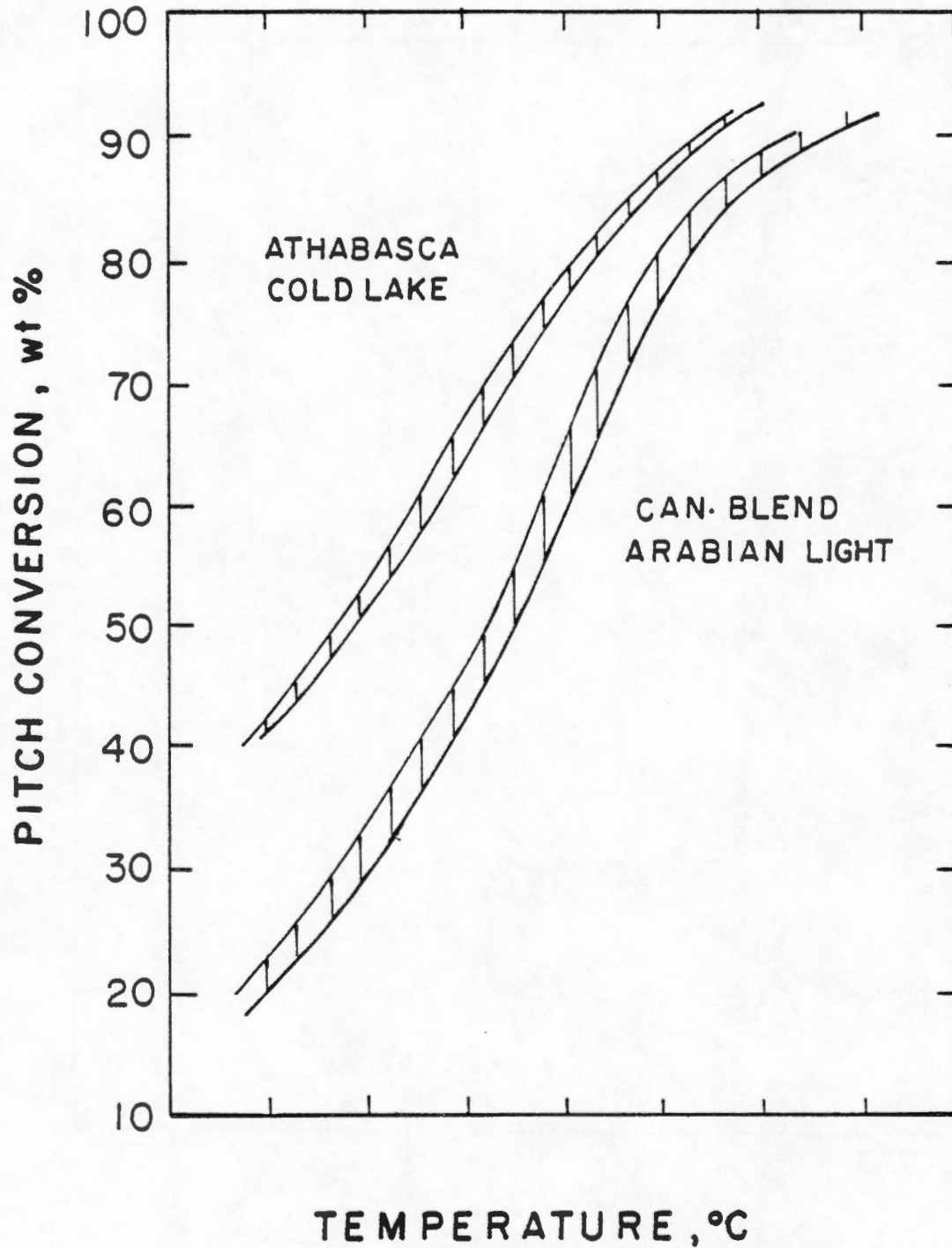


FIGURE 2: Pitch Conversion as a Function of Reactor Temperature

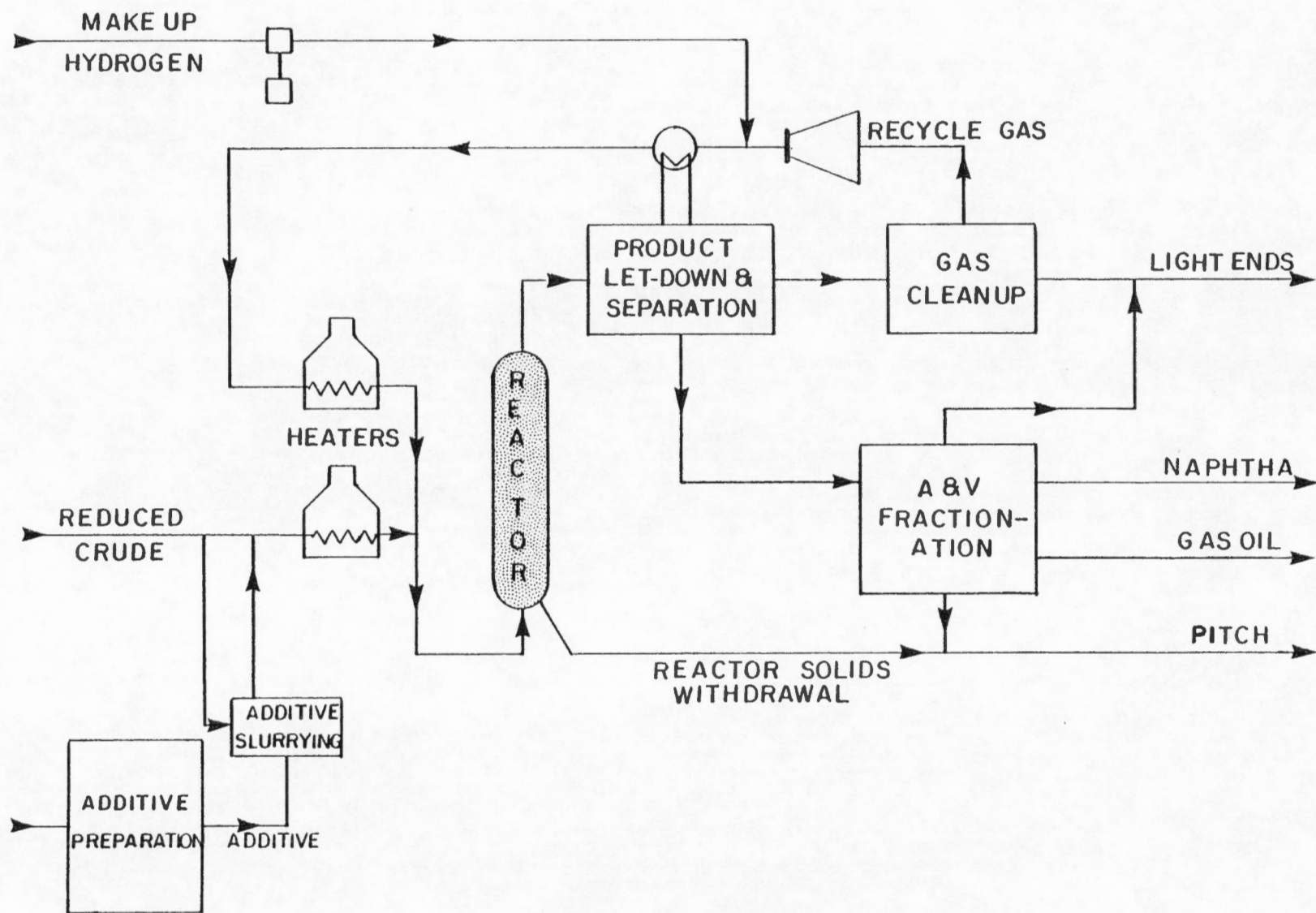


FIGURE 1: CANMET UNIT - SIMPLIFIED SCHEMATIC

