COAL-OIL COPROCESSING

by Michio Ikura

August 1986

ERP/ERL 86-83(OP)

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERP/ERL 86-83(OP)

AUG. 26, 1986
MICHIO IKURA
ERL/CANMET/EMR
OTTAWA CANADA

COAL-OIL COPROCESSING

1) INTRODUCTION

Shortly after the petroleum crisis in the 70's, many nations began to develop various processes to economically liquefy coals which are abundant but restricted in their use due to technical and economical problems.

There are two routes to liquid products from coal - indirect and direct. In the indirect route all coal molecules are gasified once to carbon monoxide and hydrogen which are recombined catalytically to produce liquids (Fischer-Tropsch synthesis).

In the direct route, coal is slurried into its own oil and heated to between 400°C and 460°C under high hydrogen pressure (150 to 300 atm). Coal radicals formed by thermal decomposition are stabilized by hydrogen molecules. It is now well established that capital costs per barrel of oil for any existing coal liquefaction process is very high, and until the price of conventional crude oil becomes sufficiently high to offset the high capital costs it is unlikely that straight coal liquefaction provides a realistic solution to the production of oil from coal.

Another possibility for the replacement of conventional crude is the hydrocracking of heavy oil which is relatively abundant in North America and South America. In hydrocracking, heavy oil is thermally or catalytically cracked and resulting radicals are stabilized by hydrogen. A number of hydrocracking processes are now available or being demonstrated by various process developers.

Yet another possibility is a hybrid of coal liquefaction and hydrocracking, which is now known as "coal-oil coprocessing" or simply "coprocessing". In coprocessing, coal particles are mixed with heavy oil such as atmospheric or vacuum residues and hydrogenated under high temperature and pressure. Whereas coal liquefaction involves a large quantity of product oil recycle for slurrying coal feed, coprocessing eliminates or virtually eliminates the oil recycle which increases the efficiency of reactor volume utilization.

Figure 1 shows a simplified comparison of coal liquefaction with

coprocessing. The two processes are very similar except in coprocessing solvent recycle can be eliminated or virtually eliminated as stated earlier.

2) H/C RATIO OF VARIOUS HYDROCARBON SOURCES
The following shows the atomic H/C ratio of various hydrocarbon sources.

HYDROCARBON	H/C RATIO
Coke & anthracite	0.5
SRC (Solvent Refined Coal)	0.8
Coals	0.5-1.1
Peat	1.0-1.3
Asphalt & Tar sand	1.3-1.6
Shale oil	1.6
Petroleum	1.5-1.9
Petroleum residues	1.6-1.8
Petroleum distillate	1.8-2.0
Petroleum products	2

As shown above the objective of coprocessing is to produce liquid products having H/C in the range of 1.8-2 using coal and heavy oil such as petroleum residues.

3) CANMET COPROCESSING
Since the early 80's CANMET(Canada Centre for Energy and Mineral Technology) of the Federal Department of Energy, Mines and Resources has been involved in the development of coprocessing technology. CANMET coprocessing is an extension of CANMET hydrocracking technology which employs a disposable additive for the processing of heavy oils such as vacuum bottoms of various origins. The following section presents a brief summary of the work performed at CANMET.

3-1) DEFINITION OF TERMS
The definition of terms used in this presentation is discussed below.

$$\text{Coal conv.(wt\%)} = \left(1 - \frac{\text{THF insol. in product}}{\text{THF insol. in feed}}\right) \times 100$$

As seen in this definition if there is coke formation, coal conversion

calculated by this equation will be lower than the true value.

$$\text{Pitch conv.(wt\%)} = \left(1 - \frac{525°C+ \text{ fraction in product}}{525°C+ \text{ fraction in feed}}\right) \times 100$$

It should be noted that coal is included in the 525°C+ fraction.

$$\text{Severity} = 10**10 \int_{t=0}^{t=t} \exp(-E/RT) \, dt$$

,where E is activation energy (30 Kcal/mole, fixed), R gas constant, T temperature in Kelvin, and t is time in min.

3-2) CANMET CONTINUOUS HYDROGENATION UNIT
Figure 2 shows a simplified process flow diagram of CANMET's continuous bench-scale hydrogenation unit. Coal ground to less than 200 mesh is slurried with vacuum bottoms and charged into a feed tank whose temperature is kept above 100°C to keep the viscosity of slurry low. The slurry recirculation pump provides a certain head required by the high pressure slurry feed pump. Compressed and preheated reducing gas (either hydrogen or synthesis gas) and the coal-oil slurry enter the reactors which can be operated as single- or two-stage coprocessing.

Product mixtures leave the reactors and enter a hot vapour/liquid (V/L) separator via air-cooled product cooler. Heavy ends which contain solids such as unconverted coal, coke and ash are continuously flashed through a pressure let-down valve and collected into a heavy end sample pot. Gases generated by the pressure reduction are sent, through a heavy end off-gas condenser, to a caustic scrubber, gas flowmeter and then to the flare.

Light ends leave the hot V/L separator and enter a light end condenser where water, naphtha and light gas oil are condensed and collected into a light end sample vessel. A major portion of non-condensibles is returned to the entrance of the reactor system through a recycle gas compressor and a recycle gas furnace. Excess non-condensibles are sent to the flare through a pressure let-down valve, caustic scrubber and a gas flowmeter.

Table 1 compares the performance of coal liquefaction with coprocessing.

It is evident that coprocessing is a very attractive option. Coprocessing produces three to four times more liquid for a given reactor volume than coal liquefaction. (It should be noted that the liquid yields for coal liquefaction are given on slurry basis). Hydrogen efficiency defined as "g distillate produced/g hydrogen consumed" also shows coprocessing is better than coal liquefaction.

Table 2 compares coprocessing with hydrocracking. Liquid yields indicate coprocessing is slightly inferior to hydrocracking in terms of distillate production and hydrogen consumption efficiency. However, as discussed later, relatively expensive oil is substituted by inexpensive coal in coprocessing, which may overcome the slight inferiority of coprocessing to hydrocracking.


3-3) MECHANISM OF COAL-OIL COPROCESSING
Coal-oil coprocessing involves two major chemical reactions; coal dissolution into heavy oil and the hydrocracking of resulting very heavy oil (preasphaltenes and asphaltenes) and feed heavy oil (asphaltenes and residual oil).

When coal dissolves in solvent under high temperature and hydrogen pressure, two reactions can occur; hydrogen deficient coal radicals produced by high temperature react with each other (polymerization) or receive active molecular hydrogen and become stable coal-derived molecules. Hydrogen is known to come from three sources; gaseous hydrogen via metal catalyst, hydroaromatics (hydrogen donor), and coal molecules (hydrogen redistribution).

Heavy oils consist of very large molecules, typically molecular weight larger than 500 to 1000, which contain a significant fraction of aromatic and hydroaromatics (hydrogenated aromatics). Hydroaromatics release chemically active hydrogen upon heating, which reacts with hydrogen deficient radicals (hydrogen donation). Thus it is logical to start with heavy oil feed rich in hydroaromatics.

Table 3 illustrates the hydrogen donor ability of typical hydroaromatics. When 1,1'-binaphthyl was mixed with one of the hydroaromatics and heated to 420°C, chemically active hydrogen was released and converted 1,1'-binaphthyl to perylene.
The numbers in this table show the molar ratios of perylene produced to 1,1'-binaphthyl charged. (The weight ratio of 1,1'-binaphthyl to hydroaromatics was kept at 1).

Gaseous hydrogen plays an important roll as well. Chemical equilibrium between aromatics and hydroaromatics is generally given as;

Aromatics + Hydrogen <-------> Hydroaromatics
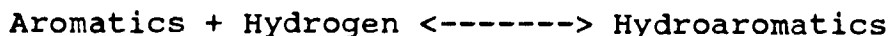
Thus it is imperative to maintain high hydrogen pressure to regenerate hydroaromatics which are consumed by hydrogen donation. Interestingly the above equilibrium tends to shift to hydroaromatics at relatively lower temperatures (360°C to 400°C) than hydrocracking temperatures (400°C to 460°C). Therefore there appears to be two optimum conditions for the two different mechanisms. In fact a number of process developers are attempting to optimize coal dissolution and hydrocracking separately.

Tables 4 and 5 compare the performance of single- with two-stage coprocessing. In single-stage operation the reaction temperature is kept essentially uniform whereas in two-stage operation temperatures of coal dissolution stage and hydrocracking stage are different. As shown in Tables 4 and 5 two-stage coprocessing improves the quality of distillate slightly. However, it should be borne in mind that two-stage coprocessing requires extra reactor volume.

3-4) EFFECT OF COAL RANK
As shown below when coal rank increases the oxygen content decreases ,which implies lower water production from coal or better hydrogen utilization when hydrogenated.

Rank: Peat --->Lignite --->Subbituminous --->Bituminous --->Anthracite

	Peat	Lignite	Subbituminous	Bituminous	Anthracite
%C	60	70	77	80	93
%O	35	25	18	15	3
Cal.value (Btu/lb daf)		6000-8000	8000-11500	11500-15500	15000-13500

However, hydrogen economy is only a part of total process economy. In North America, high rank coals are mainly found in the east coast and low rank coals in the west. The cost of coal plays an important role in the total economy as well. In Canada for instance, lignite and subbituminous coals are open-pit-mined and sold considerably cheaper than bituminous coal which is mined underground. Thus depending on the cost of coal, the use of low rank coal can be justified.

Figure 3 shows coal conversion as a function of coal type. Except Lingan and Highvale all behave similarly.

Figure 4 shows distillate yield as a function of coal type. Again there is no clear trend.

3-5) EFFECT OF COAL CONCENTRATION

Coprocessing can be viewed as hydrocracking where a part of oil feed is substituted with inexpensive coal. The performance and operability are affected by coal concentration in slurry feed. Experimental results indicate that the total distillate yield decreases by 2-3 % for every 10 % increase in coal content. However, the quality of distillate yield characterized by overall specific gravity, H/C ratio, and aromaticity remains approximately constant.

3-6) EFFECT OF OIL

In addition to the coal feed cost, the compatibility of coal and heavy oil is important. Certain oil and coal combinations give higher oil yields than others. Proper understanding of this phenomena is essential for the improvement of technology.

Heavy oils are available from conventional crude and synthetic crude. It is known that conventional crude is rich in aliphatic components whereas synthetic crude is rich in aromatic components. Figure 5 shows coal and pitch conversions as a function of solvent. Cold Lake and Athabasca are synthetic crudes and Ultramar and Blend 24 are conventional crudes.

Figure 6 shows the distillate yield as a function of solvent. Gross yield includes the 525°C- fraction in feed while net yield excludes the 525°C- fraction in feed.

Thus it can be generally stated that heavy ends obtained from synthetic crude are more suitable than conventional crude bottoms for coprocessing.

3-7) EFFECT OF REDUCING GAS

Figure 7 shows the effect of synthesis gas on distillate yields at various pitch conversions. The use of hydrogen results in slightly more naphtha and slightly less LGO yields but almost the same yield for HGO.

When synthesis gas was used in a continuous stirred tank reactor (CSTR) ,where gas residence time is nearly 5 to 10 times longer than that in a tubular reactor, the production of water was easily reduced to one half that from hydrogen runs. This is shown in Figure 8.

3-8) OPERABILITY OF PROCESS

Since coprocessing uses a significant amount of coal which has significantly heavier molecular weight than that of heavy oil, coking at high severity is always of concern. The upper limit of the operability of coprocessing is dictated by coking in the reactor. Figure 9 shows residue analyses as a function of reaction severity. The yield of coke and unconverted coal decreases as the severity is increased, indicating progressive coal conversion at higher severity. However, near a severity of 700, the yield of coke and unconverted coal begins to increase while other yields such as preasphaltenes and asphaltenes continued to decrease. At a severity of 1150, coking was so intensive that the coprocessing reactor needed extensive cleaning and polishing.

4) ECONOMICS
It is known that several process developers performed economic feasibility studies, but few are in the public domain. Recently HRI (New Jersey, USA) reported that the cost of product oil ranged US$ 22-25/BBL at US$ 15/BBL for Cold Lake residuum and US$ 30-35/Ton for Ohio No.5/6 coal.

5) CONCLUSION
Experimental work currently performed at CANMET was reviewed. Coal-oil coprocessing, a hybrid technology of coal liquefaction and hydrocracking, appears to offer a potentially attractive alternative to straight coal liquefaction.

LIQUEFACTION VERSUS COPROCESSING			
(g/100g maf slurry feed)	COPROCESSING	RUHRKOHLE-VEBA	H-COAL
DESCRIPTION			
Process Type	Single Stage	Single Stage	Single Stage
Coal	Forestburg	Forestburg	Forestburg
Solids Concentration	30	40	50
GAS YIELDS			
C_1-C_4 Hydrocarbons	7.7	5.9	4.9
H_2S-NH_3-CO_X	4.0	2.2	2.6
HYDROCARBON LIQUID YIELDS			
Naphtha	16.4	3.3	8.9
Mid-distillate	28.1	11.2	11.0
Heavy Oil	28.3	4.9	5.6
Total Distillate	72.8	19.4	25.5
Residual Oil	8.3	2.3	6.1
TOTAL LIQUIDS	81.1	21.7	31.6
OTHER YIELDS			
Water	4.9	4.9	7.5
Residue	5.9	5.4	4.9
Recycle Solvent	----	61.7	51.3
TOTAL	103.6	101.8	102.8
HYDROGEN DATA			
Consumption	3.6	1.8	2.8
Consumption Efficiency	20.2	10.8	9.1
(g distillate/gH_2 consumed)			

Table 1

COPROCESSING VERSUS HYDROCRACKING		
(g/100g maf slurry feed)	COPROCESSING	HYDROCRACKING
DESCRIPTION		
Process	Canmet	Canmet
Coal	Forestburg	---
Solids Concentration	30	<1
Feed (Vacuum Bottoms)	Cold Lake	Cold Lake
GAS YIELDS		
C_1-C_4 Hydrocarbons	7.7	8.0
$H_2S-NH_3-CO_X$	4.0	4.3
HYDROCARBON LIQUID YIELDS		
Naphtha	16.4	18.3
Mid-distillate	28.1	30.1
Heavy Oil	28.3	32.7
Total Distillate	72.8	81.1
Residual Oil	8.3	1.0
TOTAL LIQUIDS	81.1	82.1
OTHER YIELDS		
Water	4.9	0.6
Residue	5.9	7.2
TOTAL	103.6	102.2
HYDROGEN DATA		
Consumption	3.6	2.2
Consumption Efficiency	20.2	36.9
(g distillate/gH_2 consumed)		

Table 2

H – DONOR ABILITY IN COPROCESSING			
SOLVENT	H-DONOR ABILITY x 10^2	AROMATICITY (^{13}C NMR)	COAL CONVERSION
1,1'BINAPHTHYL	0.19	100.	---
TETRALIN	0.51	60.	90.4
COLD LAKE VACUUM BOTTOMS	5.40	31.	71.2
9,10-DIHYDRO-ANTHRACENE	10.0	86.	---

Table 3

LFK/ERCO AWARD LECTURE, 1985

COPROCESSING LABORATORY COMPARISON		
(g/100g maf slurry feed)	Single Stage	Two Stage
DESCRIPTION		
Reactor(s)	Tubular	Tubular
Coal	Forestburg	Forestburg
Coal Concentration	30	30
Oil Feed (Vacuum Bottoms)	Cold Lake	Cold Lake
YIELDS		
C_1-C_3 Hydrocarbons	4.4	5.4
Residues	12.7	11.9
HYDROCARBON LIQUIDS		
Naphtha (+ C_4)	11.5	12.3
Light Gas Oil	11.5	16.5
Heavy Gas Oil	43.7	36.3
Total Distillate	66.7	65.1
Residual Oil	9.5	8.8
TOTAL	76.2	73.9
CONVERSIONS		
Coal	93.7	94.1
Pitch	77.7	76.6
HYDROGEN DATA		
Consumption	2.2	3.2
Consumption Efficiency	30.3	20.3
(g distillate/gH_2 consumed)		

Table 4

JFK/ERCO AWARD LECTURE, 1985

DISTILLATE CHARACTERISTICS		
FRACTION	SINGLE STAGE	TWO STAGE
Light Ends		
Specific Gravity	0.804	0.793
Aromaticity	15	14
H/C Ratio	1.84	1.88
Heavy Ends		
Specific Gravity	0.970	0.962
Aromaticity	34	33
H/C Ratio	1.49	1.50

Table 5

JFK/ERCO AWARD LECTURE, 1985

LIQUEFACTION

RECYCLE OIL

COPROCESSING

BITUMEN
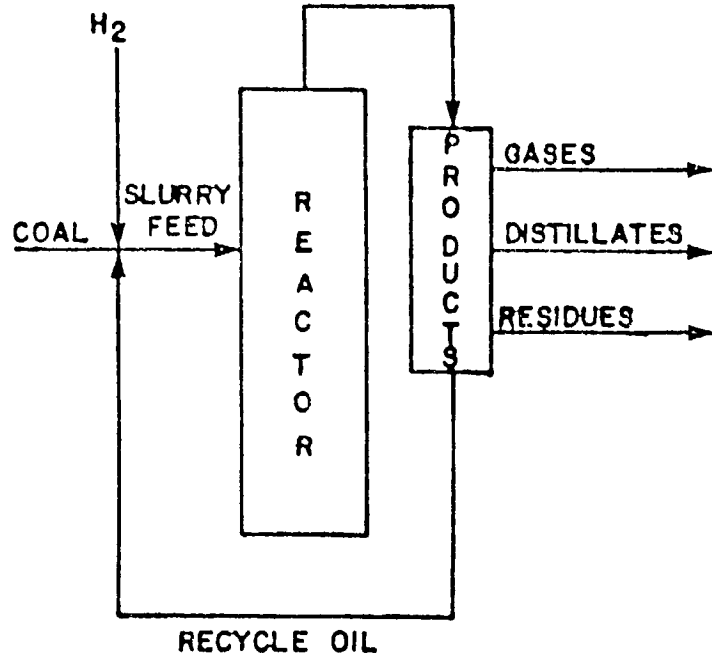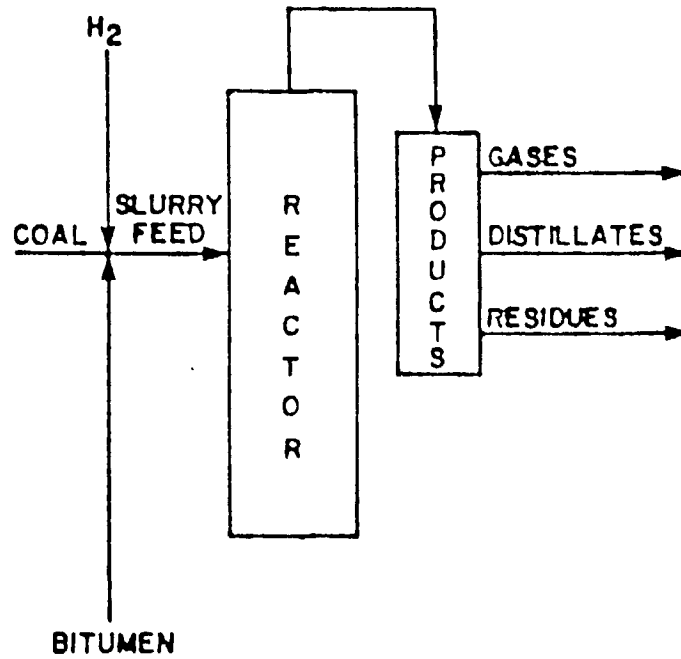
Process schematics

Fig. 1

Fig. 2

14

Fig. 3

JFK/ERCO AWARD LECTURE, 1985
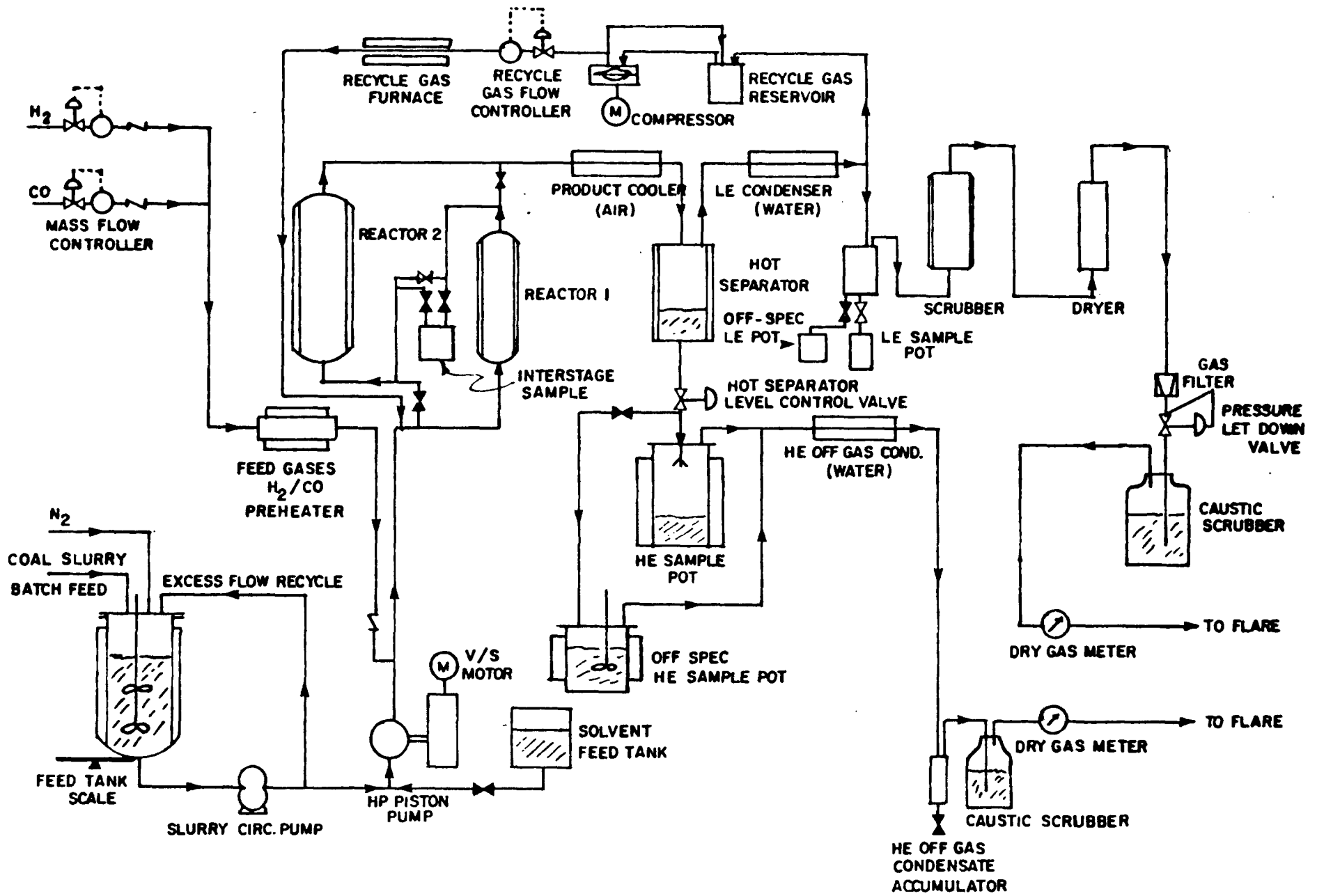
DISTILLATE YIELD AS A FUNCTION OF COAL TYPE

Fig. 4

16
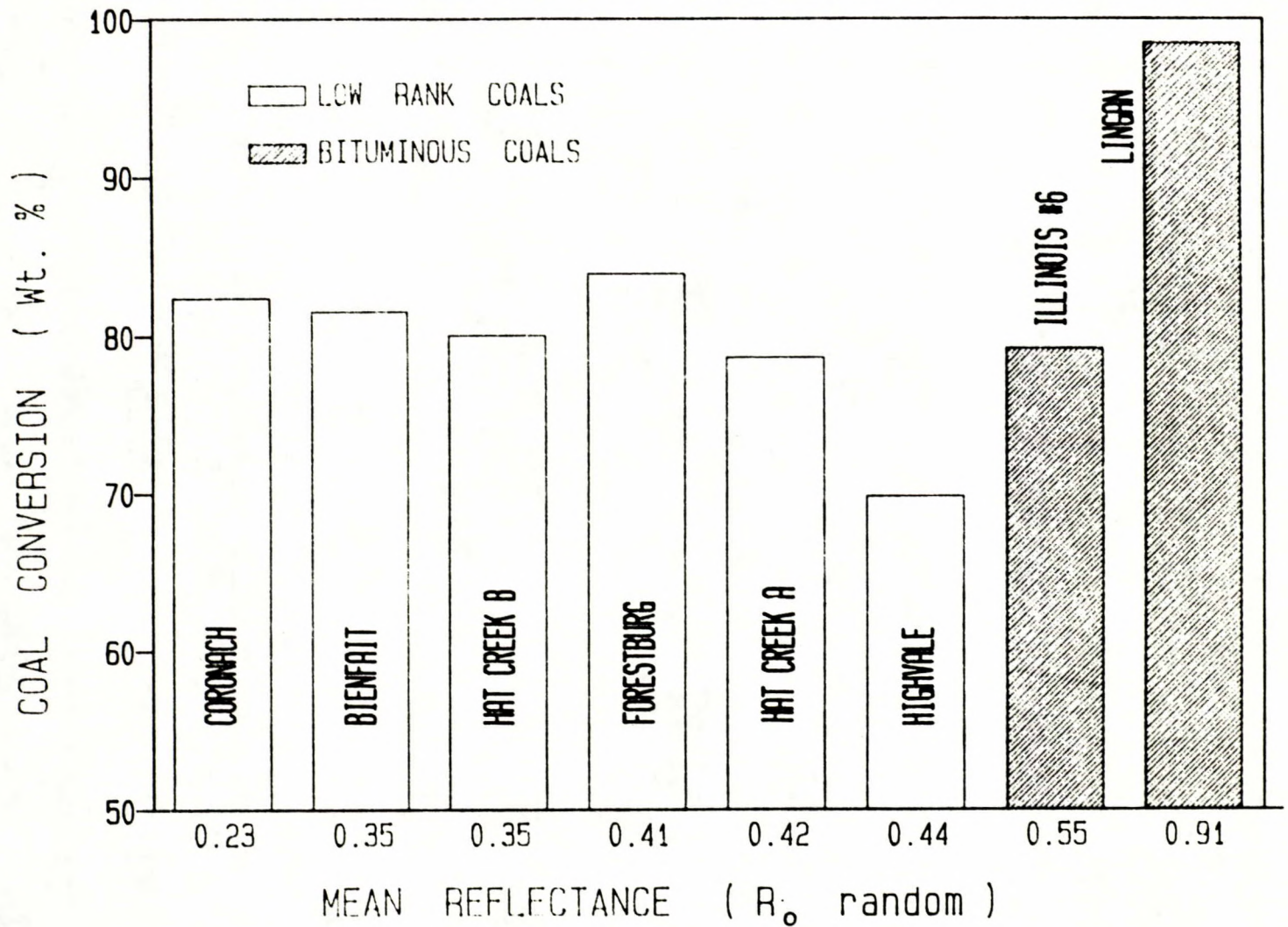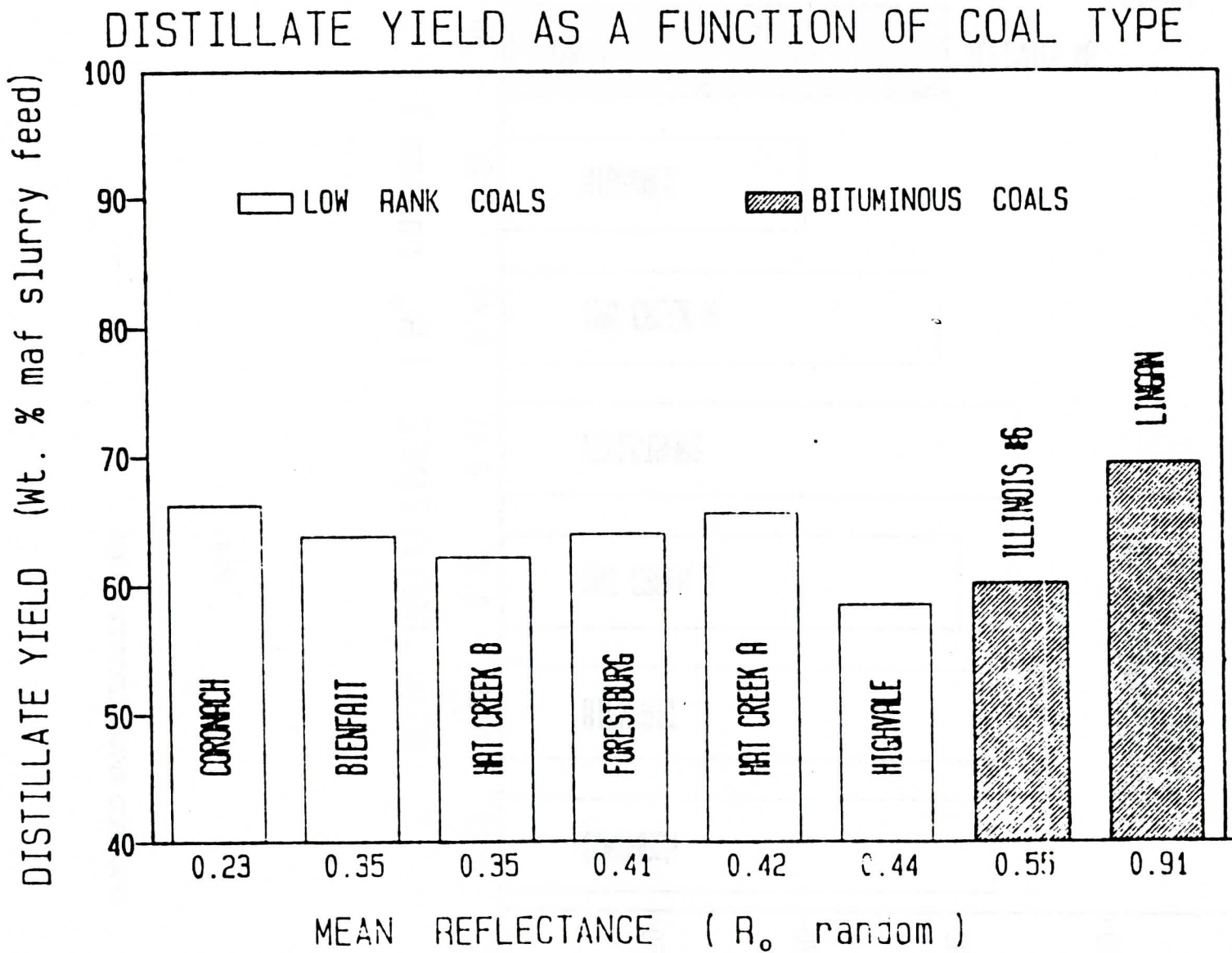
COAL AND PITCH CONVERSION AS A FUNCTION OF SOLVENT
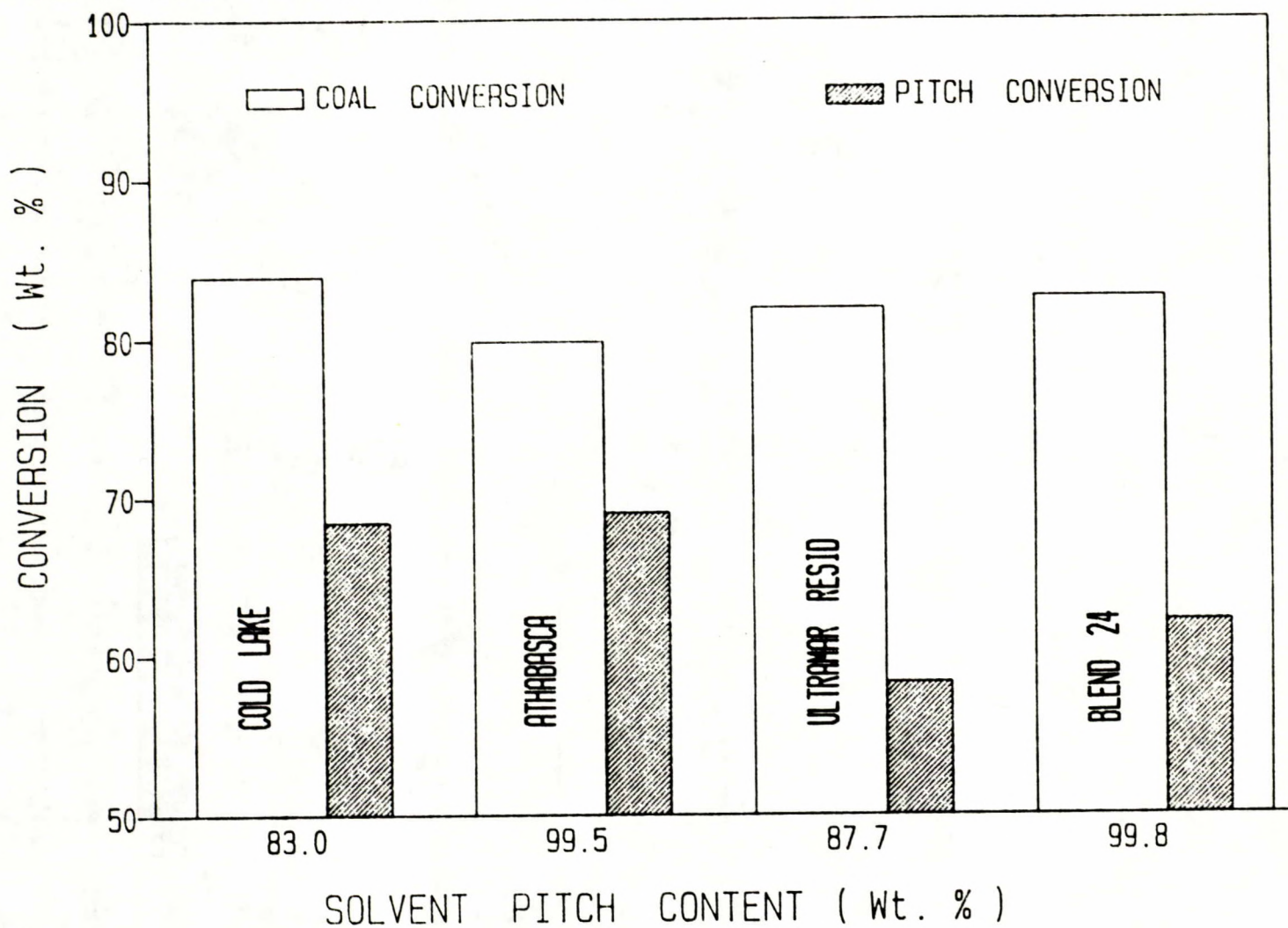
Fig. 5

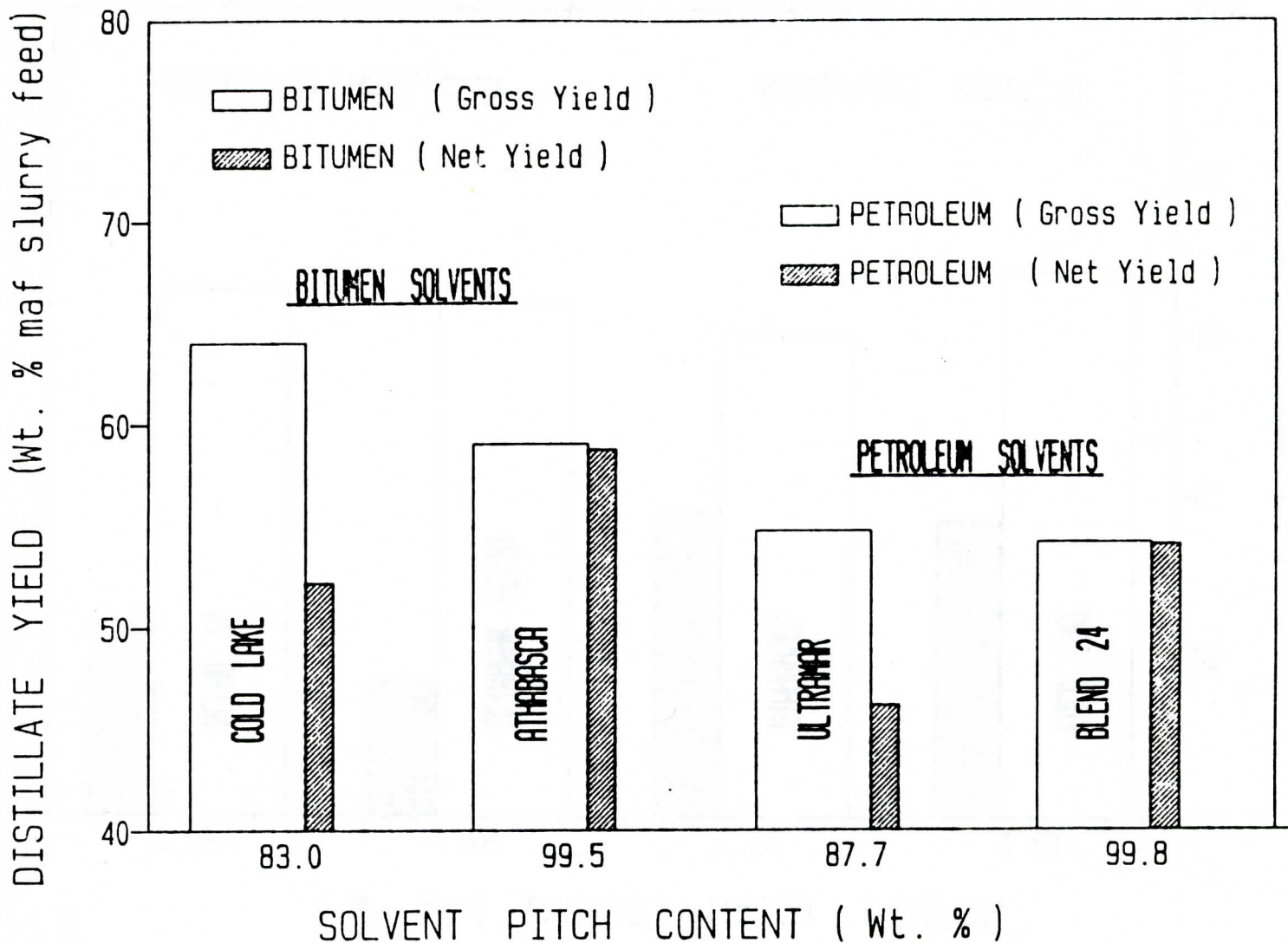# DISTILLATE YIELD AS A FUNCTION OF SOLVENT TYPE

Fig. 6

JFK/ERCO AWARD LECTURE, 1985

EFFECT OF SYNTHESIS GAS ON DISTILLATE YIELDS
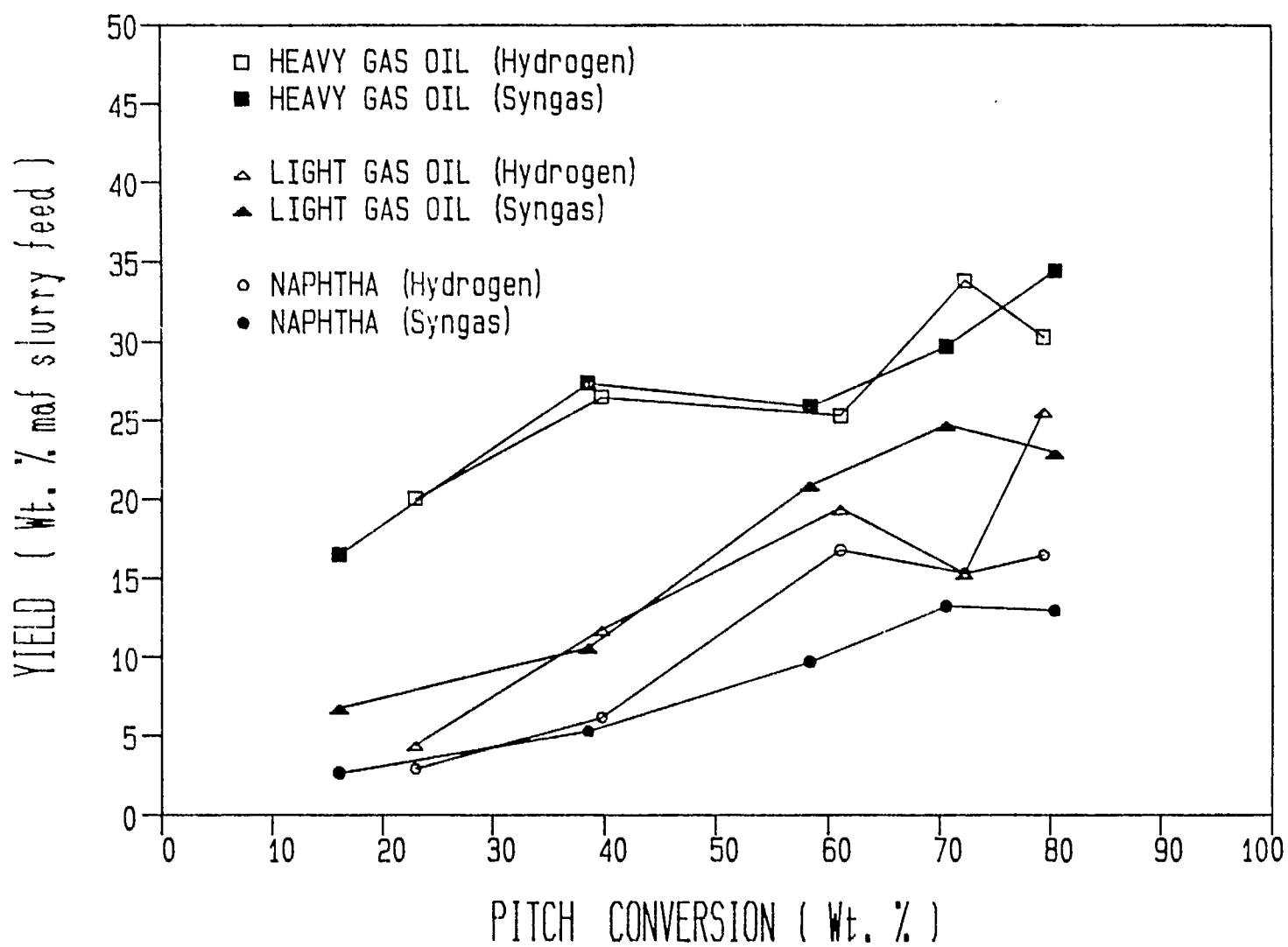
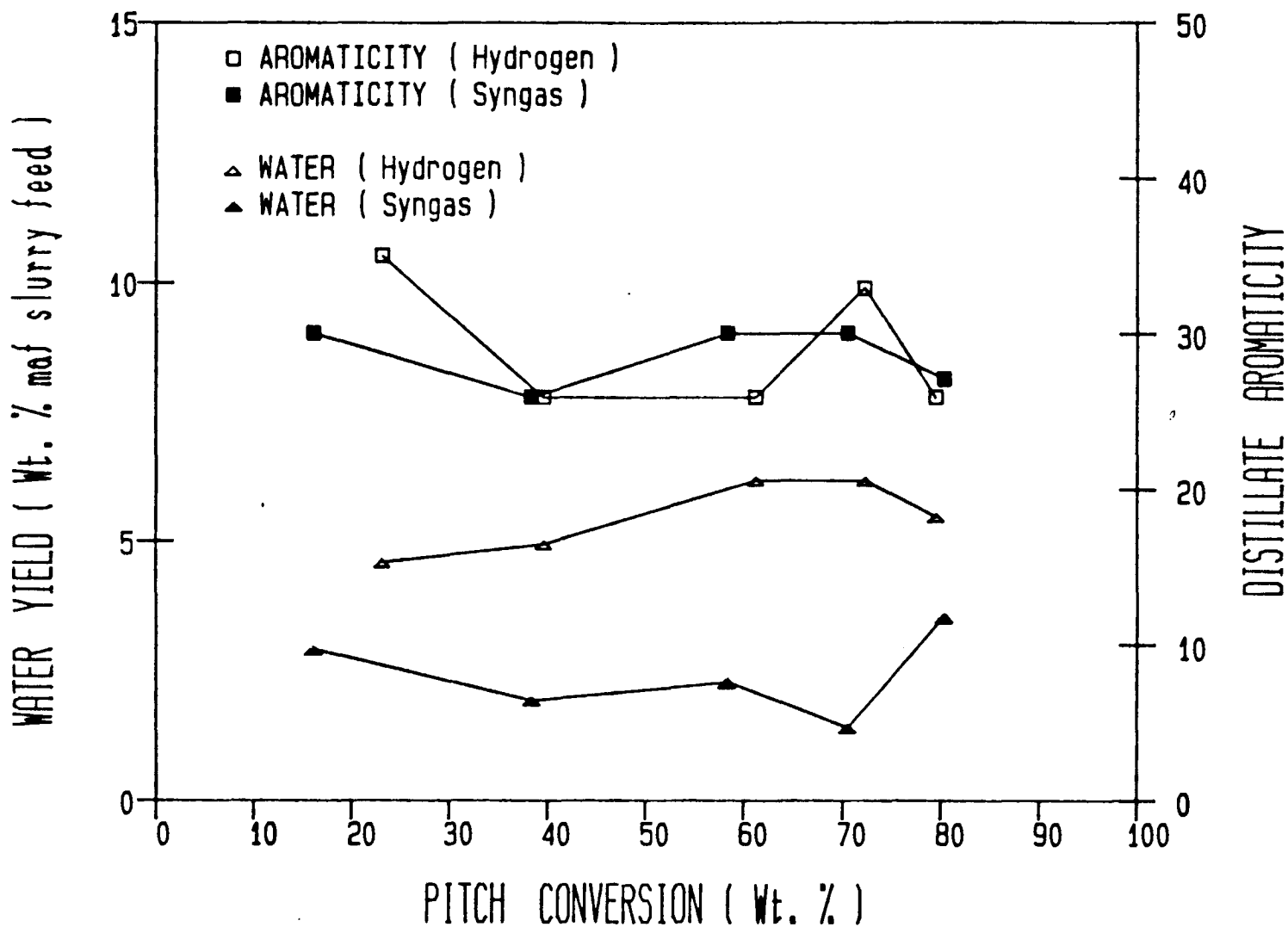Fig. 7

EFFECT OF SYNTHESIS GAS ON DISTILLATE AROMATICITY AND WATER YIELD
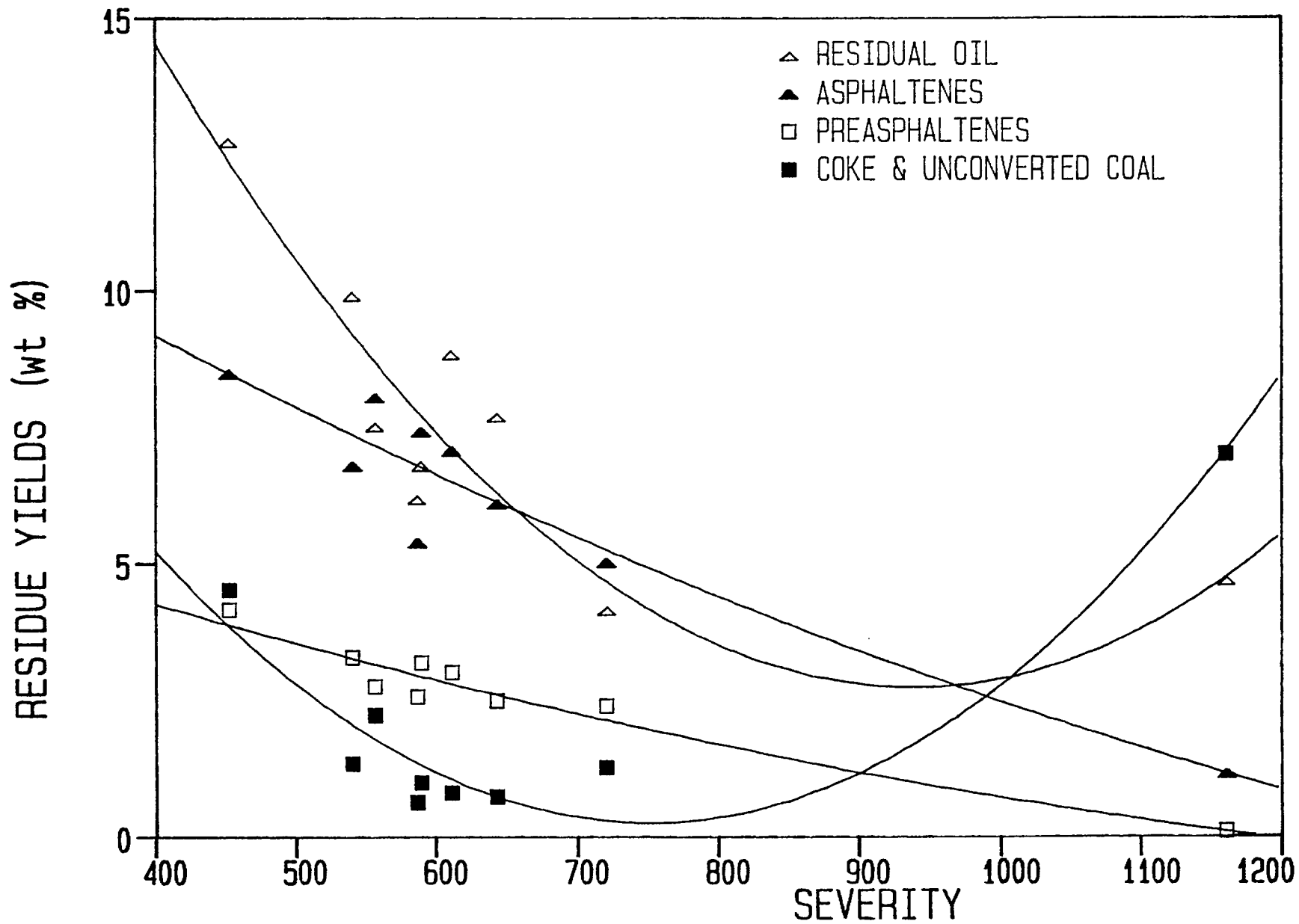

Fig. 8

RESIDUES VS. SEVERITY

Fig. 9