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THE COED-PROCESS - A REVIEW

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ABSTRACT

The COED-process, a fluidized-bed pyrolysis coal conversion technique, is described in considerable detail. Using Illinois number 6 coal as feedstock for the process, the coal is taken through the pyrolysis stages to produce a raw pyrolysis oil. This oil is then filtered and hydrotreated to produce a synthetic crude oil - a syncrude. Further downstream processing of this syncrude is analysed to produce a final hydrotreated and hydrocracked product capable of being used as a synthetic jet or motor fuel.

This is the first of a series of reports intended to assess the worth of coal conversion processes currently under development. This example is chosen because it is the only coal pyrolysis process where sufficient data are available in the literature for any sort of realistic evaluation.

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THE COED-PROCESS - A REVIEW

1. INTRODUCTION

This technical memorandum is the first of a series in which various coal conversion processes will be reviewed. The COED-process is included in this general review because of its long historical development and because it is an example of a fluidized-bed pyrolysis approach. Although the current status for development of the COED-project is presently uncertain, it is considered to be worthwhile to analyse its potential as a producer of liquid fuels in view of the considerable quantity of available data. In addition, in spite of the fact that the overall liquid yields are low, the low severity of primary processing and the good quality of the syncrude produced still seem to offer attractions. In combination with the COGAS-process, COED is still receiving development attention.

2. DESCRIPTION OF THE COED-PROCESS

Project COED has been developed by the FMC Corporation since 1962. The process converts coal to a synthetic crude oil, gas and a byproduct char. The syncrude is low in sulphur and can be used as a feedstock to a refinery with certain possible modifications. The gas can be used as fuel or be converted to pipeline gas or hydrogen. The char can be burned as a fuel as long as sulphur regulations can be met or can be gasified to fuel gas and hydrogen.

Successful operations of bench scale units led to the construction of a 100 lbs/hour P.D.U. followed by the construction of a 36 ton/day pilot plant. The pilot plant was also designed to hydrotreat 30 bbls/day of pyrolysis liquids.

In summary, the COED-process heats crushed, dried coal in a series of fluidized-bed pyrolysis units to successively higher temperatures. In each pyrolyser a portion of the volatile matter is released from

the coal. The temperatures of the pyrolyzers are selected so that they are just below the agglomeration temperature of the coal. Agglomeration could result in rapid bed defluidization. The pilot plant uses four stages in the approximate temperature region of 600^o, 850^o, 1 000^o and 1 500^oF. Process heat is developed by the combustion of char in stage four and by using the hot combustion gases and char to heat the remaining stages.

The plant has been used to process American coals ranging in rank from lignite to HVA bituminous. Table 1 shows the product yields obtained from the coals processed in the COED pilot plant.

The COED pilot plant consists of two main sections, pyrolysis and hydrotreating. Also there is a coal preparation system for pulverizing and partially drying the coal and an oil filtration system for removing micron-range char particles from the pyrolysis oil³. The pyrolysis system consists of four pyrolysis vessels (4 to 6 feet in diameter) and char transport lines (3 and 4 inches in diameter).

A simple schematic of the process is shown in Figure 1.

The main consideration as far as the overall process stability was concerned was the continuous flow of solids. This was related to the char particle size distribution and to particle surface condition when agglomerating coals were processed. As the coal rank and Free Swelling Index increased, the difficulties in processing also increased. For coal considered in this detailed report, Utah King, the F.S.I. is 2 and required no oxidative pretreatment in the stage 1 pyrolyser.

When heated rapidly in the pyrolysis vessels, highly agglomerating coal particles form relatively large cenospheres or agglomerates of several char particles. Lower rank coals, on the other hand, form large quantities of very small particles. Thus proper adjustment of bed heights and fluidizing velocities are required when pyrolysing

TABLE 1

(Reference 2)

SYNCRUDE PRODUCT YIELDS OBTAINED FROM COALS PROCESSED IN THE PILOT PLANT

Coal - Source	Utah	Illinois	Western Kentucky	Colorado	Illinois	West Virginia	Wyoming	North Dakota
Seam	Hiawatha	No. 6	Nos. 9 &	Somerset C	No. 6	Pittsburgh No. 8	Monarch	-
Mine	King	Peabody No. 10	Colonial	Bear	Sahara No. 6	Ireland	Big Horn	Glenharold
Rank (ASTM D388-38)	hvBb	hvCb	hvBb	hvBb	hvBb	hvAb	Sub B	Lignite
Syncrude Product Yield - BBL/Ton of dry coal fed to pyrolysis vessel	1,29	1,11	1,00 ⁺	0,99	0,96 ⁺	0,93 ⁺	0,69	0,36

⁺ Feed coal preoxidized to overcome agglomerating characteristic.

lower rank coals to prevent overloading the internal cyclones and thus injecting excessive amounts of fines into the oil absorber recovery system.

Pyrolysis oil yield is the most important dependent variable of the process based on overall process economics. Pyrolysis liquid yield from coal is generally considered to be an inverse function of the oxygen content and a direct function of the volatile matter content. For the seven coals pyrolysed in the COED-process, a plot was made of the pyrolysis oil yield against the function VM/O (see Figure 2).

The vapours driven off the coal during pyrolysis are quenched directly with water to condense the oil in one of the collector modifications. Another procedure uses an oil absorption tower system described below. Occluded with this oil during condensation are tiny char particles. These have escaped collection by the cyclones. The size of particles are in the micrometre to sub-micrometre range and must be removed from the raw pyrolysis oil before the oil is passed to the hydrogenation reactors. A rotary pressure precoat filter is used to remove these particles. The filter operates at 350°F and 40 psig. A 20 psig pressure drop is taken across the filter drum as the driving force. The rotary filter operates on two cycles, first a precoating cycle that adds the filter aid as a coat on the rotary drum, and second a filtering cycle where the solids are collected on the cake and then continuously scraped off by an advancing knife blade. With solids in the feed ranging from 3 to 10 weight per cent, the solids in the filtrate are reduced to 0,01 to 0,09 weight per cent.

The method of direct aqueous quench to recover pyrolysis oil was successfully demonstrated both in the PDU and in the pilot plant. Aqueous quench is a simple and effective means of oil recovery, but may not be the best method for the overall process. Oil absorption or oil scrubbing is used in conventional petroleum refining for off-gas cleaning and oil product collection from fluidized-bed petroleum coking units. Figure 3 shows a schematic of the oil absorption tower used in the COED-process.

There are three distinct contracting zones in the absorption tower as can be seen in Figure 3. The bottom section collects the highest boiling constituents of the oil along with entrained char fines. Middle and top section oils are lower boiling and essentially solids free (0,1 wt per cent and less). Oil from these two upper sections is collected as product oil for hydrotreating while the oil in the bottom section containing the solids is pumped and injected by atomizing with steam into the third stage pyrolyser. This heavy oil is thermally cracked to lighter oils, gases and coke. The coke and char fines agglomerate and leave the reactor along with the rest of the char product.

This oil absorption has several advantages over the aqueous quench system. For example the tower oil product will be essentially solids free, thus obviating the need for an oil filtration system. Operating costs are expected to be less for oil absorption rather than aqueous quench and oil filtration. The oil product from the oil absorber should be easier to hydrocrack because the heavy bottom oil is thermally cracked, thus destroying a lot of the coke precursor compounds in the pyrolysis oil. This should therefore prolong hydrotreating catalyst life and reduce hydrogen consumption in hydrocracking.

The filtered pyrolysis oils contain the unwanted elements of nitrogen sulphur and oxygen. In addition the API gravity, pour point and viscosity all indicate a very heavy oil⁴. To upgrade this raw oil to a saleable syncrude it is hydrotreated. Hydrotreating studies were conducted by ARCO prior to the pilot plant design. The experimental data generated by these studies indicated that pressures of 2500 psig and above are required to achieve 95% nitrogen removal. Sulphur and oxygen are readily removed from the oils. The reaction temperature should be in the region of 750^oF but was increased to maintain catalyst activity. LHSV of from about 0,5 - 1,5 were used. These conditions are fairly severe from a conventional refining viewpoint. American cyanamid HDS-3A Ni-Mo catalyst on alumina was used in all process variable studies.

The COED hydrotreating pilot plant was designed to hydrotreat 30 bbls of oil per day. The fixed bed hydrotreating system was found to be adaptable to hydrotreating of pyrolysis oils from different coals. Coking of the heavy constituents in the pyrolysis oils onto the catalyst and metals deposition that caused irreversible catalyst deactivation were problems requiring attention. The original hydrotreating reactor configuration consisted of two reactors in series. This system, however, was susceptible to coke and demetallization deposits resulting in the need for frequent catalyst replacement. To help overcome this problem the first reactor was used as a guard chamber. The concept of the guard chamber is to allow the major coking and demetallization reactions to occur in it before the oil is hydrotreated in the subsequent catalyst beds. The use of high void materials in the guard chamber increased operating time between hydrotreating catalyst replacement.

Even with guard chamber installation the activity of the catalyst still declines quite rapidly. The estimated catalyst usage is 0.2 lbs/bbl oil processed.

3. EVALUATION OF THE PROCESS USING UTAH COAL

3.1 Operations

In the original product recovery system, the stage 2 reactor off-gases are scrubbed and cooled in venturi scrubbers using an aqueous liquor stream. The resulting scrub liquor and oil mixture is separated in a decanter. The raw pyrolysis oil is then dried in steam heated dehydrators while the scrub liquor is cooled and recycled to the scrubbers.

The overall process yields from the COED-process are different from the net yields because the pilot plant requires the input of oxygen and steam or nitrogen to fluidize the char in the 4th stage pyrolyser and to provide process heat by burning a portion of the char. However, net yields of oil are identical to the process yields.

Average net product yields obtained from four coals processed are given in Table 2.

TABLE 2

AVERAGE NET PRODUCT YIELD OBTAINED FROM FOUR COALS PROCESSED

Coal	N.D. Lignite	Utah	Illinois	W. Kentucky
Yields, dry coal basis, Wt. %				
Char	55,8	54,5	59,5	63,0
Oil	5,3	21,5	19,3	17,3
Gas	37,6	18,3	15,1	6,7
Liquor	1,3	5,7	6,1	13,0

For the purposes of this evaluation, coal from the Utah King mine was used because of its high oil yield. It is also found that product yields and product properties from operations with a particular coal are rather insensitive to operating conditions.

Although several coals were tested in the pyrolysis pilot plant, this report will concentrate on Utah King coal and on two successful operational runs.

The first of these runs, designated P-40⁵, uses the aqueous quench recovery system. The second run, designated P-43A, uses the oil tower recovery system.

3.2 Discussion of Run P-40

3.2.1 The analysis of the coal as received and as fed to the stage 1 pyrolyser is shown below in Table 3.

TABLE 3
ANALYSES OF UTAH KING COAL

Utah King	Coal as recd.	Fed to stage 1
Moisture wt %	4,5	4,0
Proximate analysis dry basis wt%		
V.M.	38,2	41,4
F.C.	50,1	50,1
Ash	11,7	8,5
Ultimate wt % (d.a.f.)		
C	75,6 (85,6)	75,3 (85,3)
H	5,5 (6,22)	5,7 (6,45)
N	1,5 (1,69)	1,2 (1,34)
S	0,6 (,68)	0,6 (0,68)
O	5,1 (5,77)	8,7 (9,85)
Ash	11,7	8,5
H/c atomic ratio	0,873	0,908
H.H.V. Btu/lb dry	14030	13860

3.2.2 Run P-40 Process conditions

The following process conditions were used in Run P-40.

Coal feed rate lb/hr dry 2112

Pyrolysis staging temperatures °F

Stage 1	410
Stage 2	850
Stage 3	995
Stage 4	1465

3.2.3 Material balances and yields

Inputs:	oxygen lbs/ton (coal)	262
	steam lbs/ton	360

Outputs: (intrinsic yields wt %)

Char	55,3
Oil	20,8
Gas	17,2
Liquor	10,1

Yields obtained:

Net dry oil out lbs	85940,4
Liquor lbs	30951,3
Gas lbs	58192,3
Char out lbs	229072,9
Net dry coal feed lbs	413959,8

3.2.4 Analysis of pyrolysis char from stage 4 pyrolysis reactorTABLE 4

Moisture wt %	1,1	
Proximate analysis dry basis wt %		
V.M.	5,2	
F.C.	77,5	
Ash	17,3	
Ultimate wt%		Ultimates (d.a.f.) %
C	79,5	96,1
H	1,4	1,69
N	1,3	1,57
S	0,5	0,60
O	-	
Ash	17,3	
H/c atomic ratio	0,211	
Calorific value (gross) BTU/lb dry	12180	

A comparison of this product char with the feed coal to the pyrolysis reactors shows that on a d.a.f. basis 86% of the volatile matter has been evolved in the process and the H/c ratio has dropped from 0,908 for the parent coal to 0,211 for the product char. Also the calorific value of the char is only 12% less than that of the parent coal. The sulphur content on a d.a.f. basis of the char is only slightly less than the parent coal whereas the ash content is almost doubled.

3.2.5 Properties of unfiltered pyrolysis oilTABLE 5

Moisture wt %	2,9
Quinoline insolubles (pre-asphaltenes) wt %	2,93
Ultimate C	85,5
H	10,2
N	0,7
S	0,4
O	3,1
Ash	0,1
H/c ratio	1,43
Flash point °F	325
Pour point °F	95

The ASTM D-1160 distillation curve of the Utah raw pyrolysis oils is shown in Figure 4. Note also that the H/c ratio of the oil is quite high, 1,43 compared to the feed coal of 0,908.

3.3 Operation with oil absorber recovery system (Run P-43)

For this detailed investigation data pertaining to Run P-43 were used. In this run the aqueous quench collection was replaced by the oil tower absorption system. Also the total bottoms were used as recycle to the Stage 3 pyrolyser.

Table 6 gives a comparison of oil quality using the oil absorber system and the aqueous quench system. These results show that the oil absorber system yields a lighter product oil, with a lower resin and asphaltene content, a lower metals content, a lower fouling tendency, a lower viscosity and a lower Conradson carbon figure.

TABLE 6
 COMPARISON OF PYROLYSIS OIL PROPERTIES FROM AQUEOUS
 QUENCH AND OIL ABSORBER RECOVERY SYSTEMS

Source: Utah King coal

Recovery system	Aqueous quench system	Oil absorber system
Run No.	P-37 through P-40 composite	P-43A
Properties		
ASTM Distillation		
IBP, °F	450	360
10% distilled	550	460
30% distilled	710	575
50% distilled	860	700
70% distilled	950 (EP)	840
80% distilled	-	880 (EP)
Type analysis, wt % ¹		
Oils	41,3	55,6
Resins	57,1	43,4
Asphaltenes	1,6	1,0
Metals, ppm ²		
Total	2620	437
Organometallic	75	51
Filter fouling No. ³	1,4	0,3
ESR, ⁴ spins/gmX10 ⁻¹⁷	1,1	1,0
Viscosity, cp @ 200°F	14,0	7,8
300°F	4,0	2,4
Con carbon, wt %	6,8	5,3
Pour Pt, °F	105	90
Flash Pt, PMCC, °F	260	235
QI, wt %	4,5	2,4
Ultimate, wt %		
C	84,2	83,9
H	9,6	9,3
N	0,7	1,0
S	0,4	0,4
O	5,1	5,1
Moisture, wt %	0,3	0,1

- ¹Type analysis determined by elution chromatography (AMOCO).
- ²Metals determined by Atomic Absorption Spectrophotometry (AMOCO). Total metals includes primarily particulate or finely divided metals whereas organometallics are those soluble metals found in the resin and asphaltene fractions. Most abundant metals are:
- | | |
|----------------------------|-----------------------|
| <u>PARTICULATE</u> | <u>ORGANOMETALLIC</u> |
| Al, Ca, Fe, Na, Si, Mg, Ti | Ca, Fe, Na, Si |
- ³Relative number that measures fouling resistance of feedstock as measured by relative pressure drop through porous metal filter (AMOCO).
- ⁴Electron spin resonance (ESR), which indicates the free radical content of an oil. This is a measure of the oil's tendency towards polymerizing and condensing to form coke (AMOCO).

3.3.1 Run P-43A Coal analyses

TABLE 7
ANALYSES OF COAL USED IN RUN P-43A

Coal analysis to Run P-43A		As fed to pyrolyser 1
Moisture wt %	6,3	2,7
V.M.	41,4	42,5
F.C.	51,5	49,2
Ash	7,1	8,3
Ultimate analysis (d.a.f. basis)		
C	75,6 (80,98)	74,2 (78,60)
H	5,8 (6,19)	5,8 (6,14)
N	1,7 (1,82)	1,6 (1,69)
S	0,6 (0,64)	0,7 (0,74)
O	9,7 (10,36)	12,1 (12,82)
Ash	6,4	5,6
Calorific value (gross) Btu/lb	13,330	13,530
H/c ratio	0,918	0,938

3.3.2 Process conditions for P-43A

Coal feed rate lbs/lb (dry)		1490
Staging temps. °F	1	310
	2	810
	3	975
	4	1400

3.3.3 Material balance and yields

Inputs O ₂ lbs/ton		287
Steam lbs/ton		503
Intrinsic yields wt %		
Char		57,8
Oil		17,1
Gas		23,5
Liquor		1,6
Net dry oil out (lbs)		24453,4
Liquor (lbs)		-1582,9
Gas (lbs)		41271,8
Char (lbs)		75429,2
Coal used (lbs) (dry)		143031,5

3.3.4 Properties of unfiltered pyrolysis oil from P-43A (TABLE 8)

Moisture wt %		0,15
Quinoline insolubles wt %		2,5 (Pre-asphaltenes)
C		84,0
H		9,5
N		0,9
S		0,4
O		4,9
Ash		0,3
Flash point °F		230
Pour point °F		70
H.H.V.		16 000
Con carbon		5,3
H/c ratio		1,357
API ° @ 60°F		-3,5

3.4 Oil filtration section

A Goslin-Birmingham rotary drum pressurized precoat filter is used for filtering the raw pyrolysis oils before they are sent to the hydrotreatment plant. The raw oil contains approximately from 2,5 to 10 wt per cent solids content (ash + Q.I. Quinoline insolubles). After the filtration procedure solids content is reduced to the range of 0,1 wt per cent Q.I. In the process approximately 2,5 wt % of the oil feed is captured on the filter cake.

The raw pyrolysis oil from the Utah coal runs were filtered using the "body feed" filtration technique.

"Body feed" is the addition of filter aid material to the oil. This provides additional filter aid material for the precoat. On/off doctor blade advance techniques were used. Filtration of the Utah oil was optimized by using doctor blade advance for 20% of the 30 minute cycle, a filter differential pressure of 20 psig and a drum speed of 1 r.p.m.

3.5 Hydrotreating section

There are two reactor vessels used in the hydrotreating plant. The first (R-420A) is used as a guard chamber for the purpose of removing metals and heavy quinoline insoluble hydrocarbons from the feed oil. The second is the main fixed bed catalytic reactor consisting of two separate catalyst beds (R-420B1 and R-420B2). The catalyst used was a mixture of HDS-3A (Ni/Mo) and HDS-3.

For this detailed analysis Run H-48 is followed. This run processed the filtered pyrolysis oil formed from Utah coal using the aqueous quench system.

The table below (Table 9) summarizes the hydrotreating conditions used together with heteroatom removal data and API gravity of the product.

TABLE 9

Run No. H-48	
Run duration, hrs.	48,0
Catalyst	
Catalyst age	
hours	640
l.b. oil/lb. cat.	192
Oil feed rate, pph	200,2
WHSV, hr.	0,44
Inlet pressure, psig	2450
System pressure drop, psig	400
Temperature, °F	
R-420A	805
R-420B1	755
R-420B2	775
Recycle gas purity, vol. %	96,3
Recycle rate, scf/bbl.	54249
Purge rate, scf/bbl.	4019
Make up rate, scf/bbl.	8430
API gravity, combined	20,1
Product oil	
Heteroatom removals, %	
S	97,4
N	81,0
O	82,2

TABLE 10

HYDROTREATING CONDITIONS RUN H-48

Reactor temperature °F (average)	770
Reactor pressure (psig)	2200
Oil feed rate (lb/hr) dry	200,2
Total hydrogen flow (scfh)	28640
Hydrogen consumption (scf/b)	3344
Overall space velocity (whsv)	0,44

TABLE 11

MATERIAL BALANCE AND YIELDS RUN H-48Material balance, lb.

<u>Input</u>	<u>Total</u>	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>H/c ratio</u>
Dry oil	9611,0	8054,0	855,4	549,7	105,7	40,4	1,27
Hydrogen	1135,1	0,0	1135,1	0,0	0,0	0,0	
Quench water	16,0	0,0	1,8	14,2	0,0	0,0	
Other water	0,0	0,0	0,0	0,0	0,0	0,0	
Misc.	0,0	0,0	0,0	0,0	0,0	0,0	
Total	10762,1	8054,0	1992,3	564,0	105,7	40,4	

Output

Dry syncrude	8987,0	7697,6	1170,1	98,1	20,1	1,1	1,82
Dry C4 - C6	191,7	162,5	29,2	0,0	0,0	0,0	
Dry C1 - C3	148,3	125,8	22,5	0,0	0,0	0,0	
Other gas	525,1	0,0	525,1	0,0	0,0	0,0	
Liquor	690,0	10,3	77,5	531,0	35,9	35,3	
Other water	0,0	0,0	0,0	0,0	0,0		
Misc.	61,9	53,0	8,2	0,7	0,1	0,0	
Total	10604,1	8049,3	1832,6	629,8	56,2	36,4	
Closure	98,5	99,9	92,0	111,7	53,1	90,1	

<u>Yields</u>	<u>Wt. per cent, based on dry oil input</u>	<u>Vol. per cent, based on dry oil input</u>
Syncrude	93,5	108,3
C4 - C6	2,0	
C1 - C3	1,5	
H2O	6,03	
NH3	0,454	
H2S	0,391	

Table 10 describes the detailed hydrotreating operating conditions used for Run H-48. Table 11 gives the detailed material balance and overall yields for Run H-48.

Table 12 gives the feedstock oil analysis to Run H-48 and also the analysis of the heavy and light oil products after hydrotreating. This is from a single pass operation.

TABLE 12

Oil analysis	Oil feed	Product oil	
		Heavy	Light
Moisture, wt. per cent, dry	0,00	0,00	0,00
Solids, wt. per cent, dry	0,20	0,00	0,01
<u>Ultimate analysis, wt. per cent, dry</u>			
Carbon	83,80	85,48	87,53
Hydrogen	8,90	13,18	11,29
Oxygen	5,72	1,10	1,00
Nitrogen	1,10	0,23	0,16
Sulphur	0,42	0,01	0,03
Ash	0,06	0,00	0,00
API gravity, API	-1,0	17,6	46,5
Pour point, F	124,	65,0	<-112,
Viscosity, sus	350,	69,8	30,4
Viscosity, cp	78,	12,0	0,6
H/c ratio	1,27	1,85	1,55

Note that the nitrogen content is still high in the heavy product (i.e. 2300 ppm). The total syncrude yield is 93,5wt. % of the dry oil input so hydrocarbon gas make is quite small in the order of 4 wt. %.

The properties of the total syncrude are given in Table 13.

TABLE 13

SYNCRUDE PROPERTIES

Run No.	H-48
<u>Ultimate analysis</u>	
Weight per cent	
Carbon	85,68
Hydrogen	13,00
Nitrogen	0,22
Sulphur	0,01
Oxygen	1,09
Ash	0,00
API Gravity	20,1
Viscosity, cp at 100 ^o F	9,3
Weight fraction	
Heavy oil in the syncrude	0,92

From a single pass hydrotreatment the API gravity has increased from -1,0 to 20,1 and the H/c ratio has been upped from 1,27 to 1,82. The ASTM D-1160 distillation data for the heavy and light oil products are given in Table 14. Note that only 8 wt. % of the total syncrude is a light fraction.

TABLE 14

DISTILLATION DATA FOR THE HEAVY AND LIGHT OIL PRODUCTS

Vol. % distilled at ^o F ¹	Heavy	Light
IBP	330	112
5	450	170
10	515	190
20	580	210
30	630	228
40	680	244
50	750	270
60	800	298
70	870	330
80	920	378
90	990	442
95		
100		
EP	990	460
% Rec.	90,0	94,0
% Res.	10,0	6,0
% Loss	0,0	0,0

¹ASTM D1160 test corrected to atmospheric pressure.

This can be compared with the distillation data for the filtered pyrolysis oil feedstock shown in Table 15. Unfortunately no distillation data are given for the total syncrude but fairly good estimations of yield below 500^oF (i.e. up to kerosene boiling range) can be made.

TABLE 15

DISTILLATION DATA FOR THE FILTERED PYROLYSIS OIL FEEDSTOCK
HYDROTREATING FEED OIL DISTILLATION

Vol. % distilled at ^oF

IBP	450
5	500
10	535
20	645
30	770
40	830
50	875
60	930
70	
80	
90	
EP	930
% Rec.	60,0
% Res.	40,0
% Loss	0,0

Table 15 is represented graphically in Figure 4 for both filtered and unfiltered pyrolysis oil feed stocks.

A process variable study was undertaken by FMC to determine the effect of reactor pressure on various important parameters. Heteroatom removal efficiency, an important variable for downstream process considerations, was studied with reactor pressure. Figures 5, 6 and 7 graphically represent this data. S removal efficiency levels out at about 1800 psig hydrogen pressure while N and O removal efficiency is still pressure dependent up until 2400 psig and

presumably beyond. Hydrogen consumption data are important both economically and chemically (i.e. higher H/c ratios in product oil). The graph shows an almost step function dependence between 2000 and 2300 psig (Figure 8). The dependence of API gravity on hydrogen pressure is shown in Figure 9.

Reference 5 gives no data on component analysis of the feed or product oils, however, for a similar oil also derived from Utah King coal⁶ the information in Table 16 is available.

TABLE 16

<u>PDNA⁺ ANALYSIS (VOL %) OF AN</u>	
<u>OIL DERIVED FROM UTAH KING COAL</u>	
Paraffins	23,7
Olefins	0
Naphthenes	42,2
Aromatics	34,1
API ⁰	28,5

Note the API is 8⁰ higher than the oil considered in detail here, yet it is considered that the PDNA analysis will not be significantly different from that produced in Run P-43A.

3.5.1 Overall yields

Up to this point a sample of Utah coal was pyrolysed in the COED-process and yielded a raw pyrolysis oil. From the yield data available 20,76 wt % (dry coal basis) of pyrolysis oil was obtained from the coal. (22,7 wt % on a DAF basis). This raw oil was filtered (assure 2,4 wt % loss) and the filtered oil was fed to the hydrotreating reactors. (22,1 wt % D.A.F.) Hydrotreating produced a syncrude equivalent to 93,5% of the feed oil (20,6 wt % d.a.f.)

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⁺PDNA = paraffins, olefins, naphthenes and aromatics.

3.6 Further refining3.6.1 Introduction

The only data available at the time of writing on the further hydrotreatment and hydrocracking of COED syncrude is taken from reference 7. (Gallagher et al). ARCO received a sample of COED syncrude prepared from Utah coal having the characteristics given in Table 17.

TABLE 17
COED OIL COMPOSITE FEED AND FRACTIONS

	Feed	IBP-422 ^o K (IBP-300 ^o F)	422-561 (300-550)	561-616 (550-650)	616-700 (650-800)	700+ (800+)
Gravity, kg/m ³ (^o API)	945,2 (18,2)	789,2 (47,8)	903,0 (25,2)	946,5 (18,0)	956,0 (16,5)	1002,8 (9,6)
% hydrogen	10,94 ⁺	14,8	11,23	10,58	10,86	10,09
% carbon	87,48	85,2	86,45	87,9	88,10	87,54
% sulphur	,023 ⁺	,027	,021	,016	,032	<0,02
Nitrogen, ppm	3853	677	3696	3726	3399	4285
% oxygen	,98 ⁺	0,34	1,31	0,86	0,74	1,02
% ash	0,05	-	-	<0,001	<0,02	0,03
Pour point ^o K (^o F)	300(80)					
Kinematic viscosity, cs						
255 ^o K (0 ^o F)	-	1,449	12,42	-	-	
311 ^o K (100 ^o F)	11,81	-	2,228	9,128	41,06	
372 ^o K (210 ^o F)	-	-	-	2,092	4,860	
Saybolt viscosity 372 ^o K (210 ^o F), cs						17,7
% Resins		-	-	9,0	9,1	21,8
% Mono aromatics		16,2	51,0	34,4	20,0	14,1
% Polyaromatics		0,0	8,1	25,1	37,4	34,8
% of total	100	4,0	32,5	18,0	27,0	18,5

⁺ Back calculated from analyses of fractions

Although the ASTM distillation is a little different from the final product obtained from P-43A the source coal is the same and the API gravity is very similar (18,2^o compared to 20,1). It is assumed that this is a comparable syncrude to that obtained from P-43A and its subsequent hydroprocessing as followed in detail in the remainder of this report. The COED syncrude distillation curve is shown in Figure 10.

ARCO used the following refining scheme (Figure 11) to evaluate the COED syncrude feedstock.

The COED syncrude was fractionated into the following cuts (Table 18).

TABLE 18

API ^o	Boiling range ^o F	Vol % of total
47,8	IBP - 300	4
25,2	300 - 550	32,5
18,0	550 - 650	18,0
16,5	650 - 800	27,0
9,6	800+	18,5

3.6.2 IBP - 550^o cut

This cut was hydrogenated at high and low severities prior to blending with hydrocracked product to produce a high yield coal syncrude jet fuel sample. Hydrogen content is the limiting factor in meeting the required product quality levels.

The high severity production run was conducted in a two inch diameter isothermal reactor using 1,1 lbs of catalyst (HDS - 3A). For temperature control the catalyst was diluted with 3 parts tabular alumina to 1 part catalyst at the top of the bed ranging to a 1:8 ratio at the reactor outlet. Reaction conditions used were:

Temperature, $^{\circ}\text{K}$ ($^{\circ}\text{F}$)	641 (695)
Pressure, N/m^2 (PSIG)	$13,8 \times 10^6$ (2000)
WHSV ⁺ , hr^{-1}	0,5
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

Catalyst activity declined at an average rate of 11% per day (on a relative WHSV basis) during the high severity operation. To compensate, it was necessary to increase reactor temperature to 647°K (705°F) by the end of this portion of the programme. Low severity treating to produce the 12,75 per cent hydrogen product followed immediately on the same catalyst charge. Conditions were set at:

Temperature, $^{\circ}\text{K}$ ($^{\circ}\text{F}$)	616 (650)
Pressure, N/m^2 (psig)	$13,8 \times 10^6$ (2000)
WHSV, hr^{-1}	0,8
H_2 Rate, m^3/m^3 (SCF/B)	1348 (8000)

Due to the extent of catalyst deactivation, an increase in temperature to 622°K (600°F) and a reduction in WHSV to $0,7 \text{ hr}^{-1}$ was required before specification quality product was obtained. Catalyst activity decline continued during the low severity programme at a rate of 8% per day, requiring a further reduction in WHSV to $0,65 \text{ hr}^{-1}$ by the end of the run.

Approximately $0,042 \text{ m}^3$ (11 gallons) of feed were treated at each of the severity levels.

Results from the high and low severity hydrotreatment are given in Table 19.

24/.....

⁺WHSV = weight hourly space velocity.

TABLE 19

FEED AND PRODUCT INSPECTIONS
IBP-561^oK (550^oF) COED SYNCRUDE

	Feed	Low severity product	High severity product
Sample No.	33439	33487	33478
Density kg/M ³ (^o API)	887,7 (27,9)	851,4 (34,7)	832,8 (38,4)
Hydrogen, %	12,32	12,77	13,47
Sulphur, ppm	240	2,2	3,4
Nitrogen, ppm	3338	5	4

The rates of catalyst deactivation observed during the production runs were unusually high, for no immediately apparent reason. If they were to continue, operation would only be possible for a few weeks before the catalyst activity had declined to the point that regeneration or catalyst replacement would be required. It is possible, however, that activity might stabilize at some lower value and permit runs of practical duration. Longer term ageing studies would be required to resolve these questions. At present results from such studies are unfortunately unavailable, if indeed such studies have been attempted. Hydrogen consumption data available based on hydrogen content of product oil are given in Figure 12.

Notice the high denitrogenation efficiency obtained when using this lower boiling fraction. This fraction is 36,5% of the total syncrude.

Total liquid product yield is assumed to be essentially 100 per cent (no actual yields given).

3.6.3 Hydrotreating of the 550 - 800^oF COED syncrude

The nitrogen levels in the 550 - 800^oF feedstock were too high for direct hydrocracking, so an initial hydrotreatment stage was necessary to bring the nitrogen levels down to within the 200 - 400 p.p.m. range required for this step. The following relatively severe conditions were used:

1,54 lbs. HDS - 3A catalyst

Temperature 735^oF

WHSV 0,70 (1,16 lb/hr feed rate)

Pressure 2000 psig

Hydrogen rate 8000 SCF/B.

Feed and product analyses from this hydrotreatment run are shown in Table 20. Notice the nitrogen level has been reduced to the required 237 p.p.m. level.

TABLE 20
COED 561-700^oK (550-800^oF) HYDROTREATING
PRODUCTION RUN

	FEEDSTOCK		COMPOSITE PRODUCT	
Sample No.	33358		33386	
Gravity kg/M ³ (° API)	951,6 (17,2)		916,4 (22,9)	
% Sulphur	0,025		0,002	
% Hydrogen	10,63		11,91	
PPM Nitrogen	3578		237	
% Chlorine	0,039		0,011	
Distillation (G.C.)	°K	°F	°K	°F
IBP	560	548	379	222
5%	571	569	507	453
10	576	578	537	507
20	589	601	564	556
30	602	625	581	586
40	616	650	597	616
50	630	675	615	647
60	644	699	632	678
70	658	725	650	710
80	673	752	669	744
90	694	789	691	785
95	708	815	705	809
EP	739	871	733	860

Gallagher et al⁽⁷⁾ estimate that this COED syncrude fraction is about 1,3 times more difficult to denitrogenate than a corresponding shale oil. Consumption of hydrogen was approximately 1900 SCF/B. Noticeable loss of catalyst activity occurred during the run. The G.C. simulated distillation shows that in addition to HDN, cracking occurred, resulting in about 20% conversion to 550^oF⁻. Total liquid product yield was, however, essentially 100 per cent.

3.6.4 Hydrocracking the 550 - 800^oF COED syncrude fraction

For hydrocracking this fraction two reactors in series were used. The first reactor denitrogenates the feed to an acceptable level for the second hydrocracking reactor. The total effluent from the HDN reactor is passed into the second.

The reactor conditions used for the hydrotreating reactor were as follows:

1,05 WHSV
700^oF
10 000 SCF H₂/B
2000 psig H₂ pressure.

These conditions produced an organic nitrogen content in the product of 22 p.p.m.

The process conditions for the hydrocracking production run were:

1,0 WHSV
634^oF
10 000 SCF/B
2000 psig H₂ pressure.

This was to yield 97% conversion to 650^oF⁻ product. In practice during the run the conversion level dropped to 79% and was maintained at that value. Over the 330 hour run the bed temperature was raised 42^oF to maintain a constant conversion value.

From the data obtained during the run Gallafer et al⁷ calculated the catalyst activity for conversion to 390^oF⁻ as a function of time on stream. This activity correlation is shown in Figure 13.

The activity, α , is defined as the relative WHSV required to obtain constant conversion. After 350 hours on stream, the catalyst activity was down to 0,13. This is a seriously rapid rate of deactivation. This means an activity decline of 74% in 350 hours. Whether this deactivation would continue at this rate beyond 350 hours operation or would stabilize is not possible to predict. Such a decline in catalyst activity would present a serious commercial processing problem.

The catalyst activity decline also affected product distribution. As the temperature is increased to maintain constant conversion of about 80% to below 650^oF, the production of lighter products and gases becomes more significant.

At this constant conversion of 80% to 650^oF⁻ H₂ consumption was approximately 1400 SCF/B. The overall yield on feed of the hydrocrackate was assumed to be 95%.

The total product from this hydrocracking run was composited and the boiling point distribution of the 100^oF+ liquid is shown in Figure 14.

The yields of 100 - 650^oF product was produced in approximately 70 weight % yield on the hydrocracker feed as shown in Figure 14. Since the 550 - 800^oF cut represents 45% of the total syncrude, the yield of the 100 - 650^oF product is about 30% of the total syncrude.

3.6.5 Summary

From a refinery viewpoint it is worth while to briefly summarize the hydrotreating scheme and to look closely at the feedstock and product characteristics of the syncrude.

Initially the feedstock syncrude contained 3853 p.p.m. nitrogen and 230 p.p.m. sulphur. It had 54,5% boiling in the IBP-650^oF boiling range. This comprises light and heavy naphtha, kerosene and light gas oil. After the refining scheme the oil contained less than 20 p.p.m. nitrogen and had 66,5 wt. % boiling in the IBP-650^oF boiling range.

3.7 Overall yields and conclusions

Using approximations the final yield of IBP-650^oF oil product may be estimated on a d.a.f. basis on the original coal after the above processing steps.

On a d.a.f. basis, the coal yielded approximately 23 weight % of pyrolysis oil. Assume 2,5 wt. % loss due to filtration and that 93,5 wt. % yield of syncrude is obtained from the filtered pyrolysis oil. Then if it is assumed that a 5 wt. % loss due to gas make occurs in the hydrofining and hydrocracking stages this gives 19 wt. % product oil. Of this 66,5 wt. % distils below 650^oF, thus 12,9 weight % on a d.a.f. basis of original coal ends up as liquid oil product boiling below 650^oF.

It should be emphasized that reference 7 did not attempt to optimize the processing systems to maximize yields of valuable products. Their programme was initiated to assess the feedstock as a potential precursor for jet fuels. In this respect the products generally proved to be undesirable, primarily because of high aromatic content which causes radiative combustion problems and high smoke emissions. The maximum specification for aromatics in jet fuels⁸ is 20 volume %. The aromatic content of the product using high severity complied with this value but for low severity processing did not (see Table 21).

TABLE 21
COED PRODUCT ANALYSIS (IBP-650°F)

	High severity	Low severity
°API gravity	39,9	37,8
Heat of combustion cal/gm	10,484	10,328
Aromatics %	9,3	22,4
Olefins %	0,7	0,6
Naphthalenes %	0,49	0,68
Hydrogen %	13,6	13,07
Nitrogen %	,0002	,0003

The technology for processing coal syncrudes is still in its infancy and additional research and development needs to be undertaken particularly in the areas of catalyst activity and stability and also in using new refinery schemes. For example delayed coking, black oil cracking technology, LC-fining, etc.

3.8 References

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SENIOR RESEARCH OFFICER

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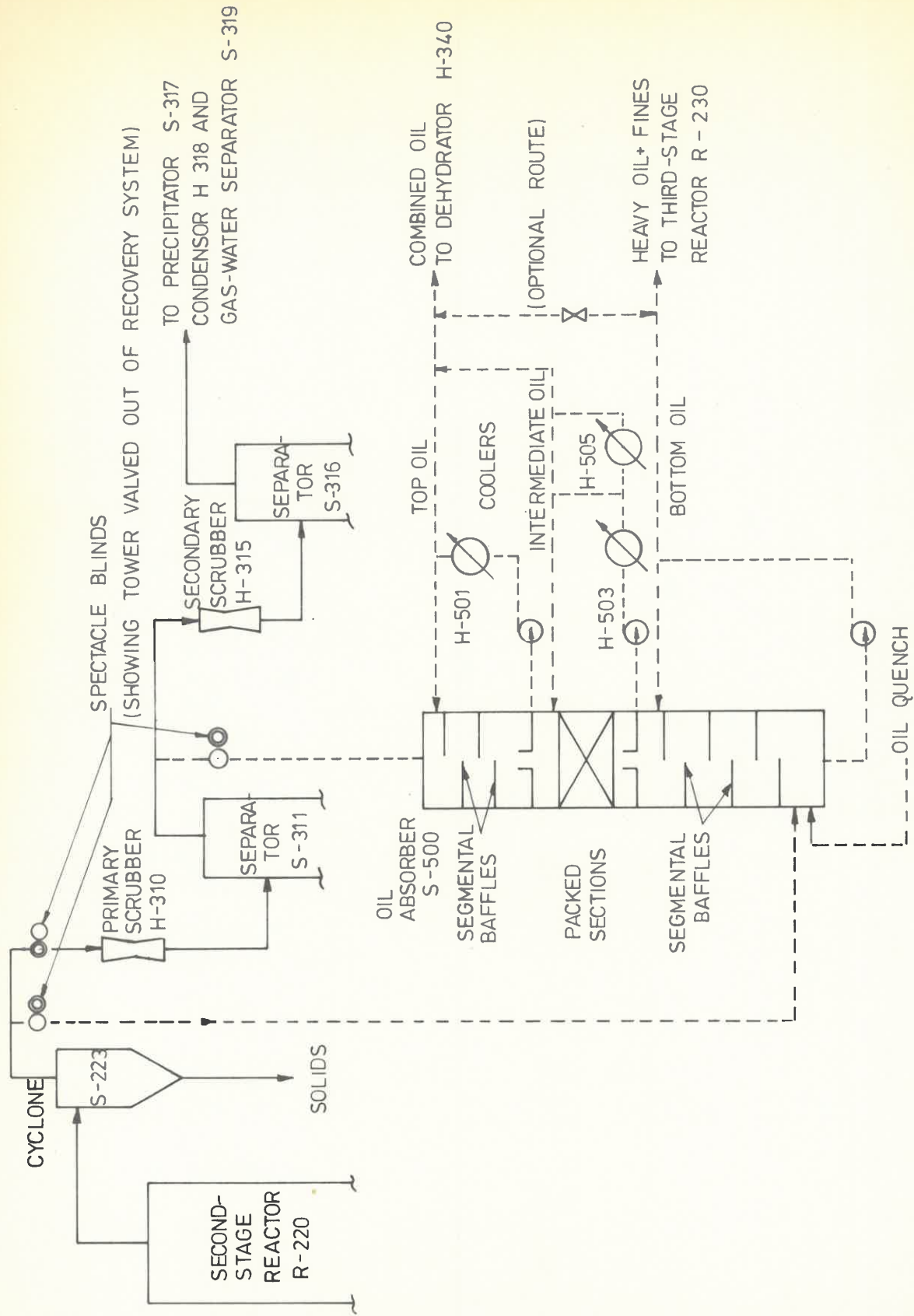


FIGURE 3 OIL ABSORBER SYSTEM

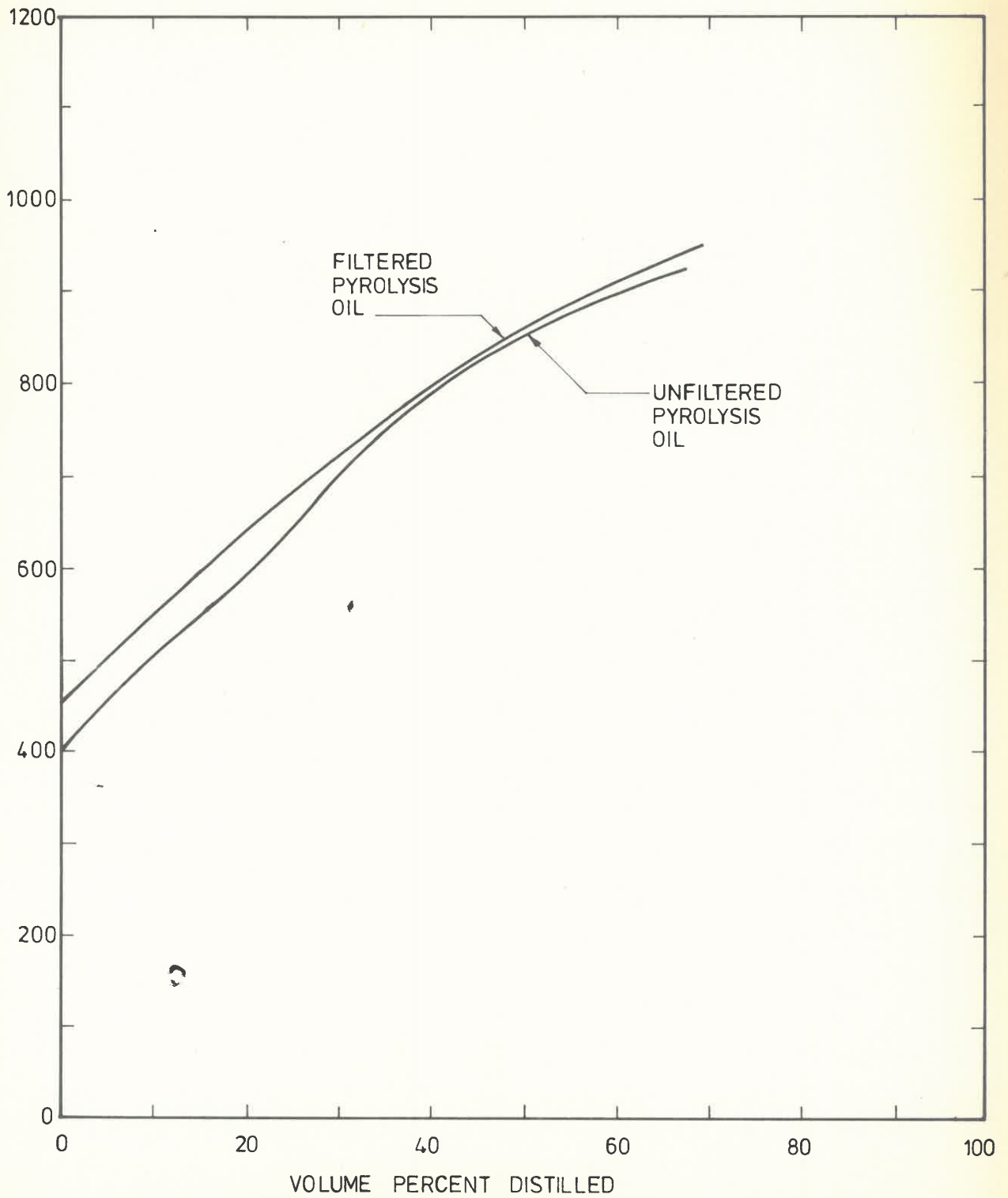


FIGURE 4 DISTILLATIONS OF UTAH KING COAL OILS
(ASTM D 1160)

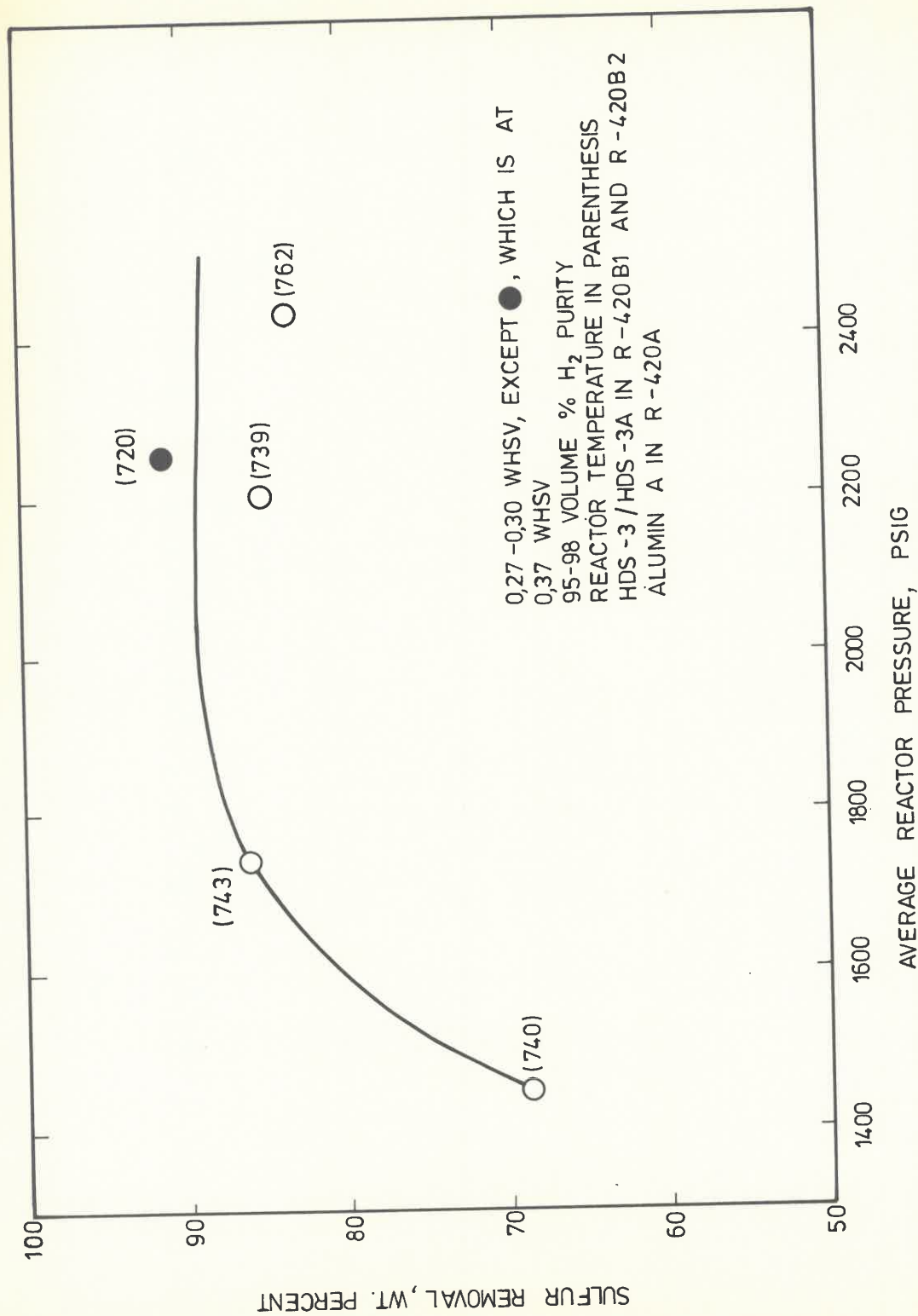


FIGURE 5 EFFECT OF REACTOR PRESSURE ON SULFUR REMOVAL EFFICIENCY
 UTAH COED OIL

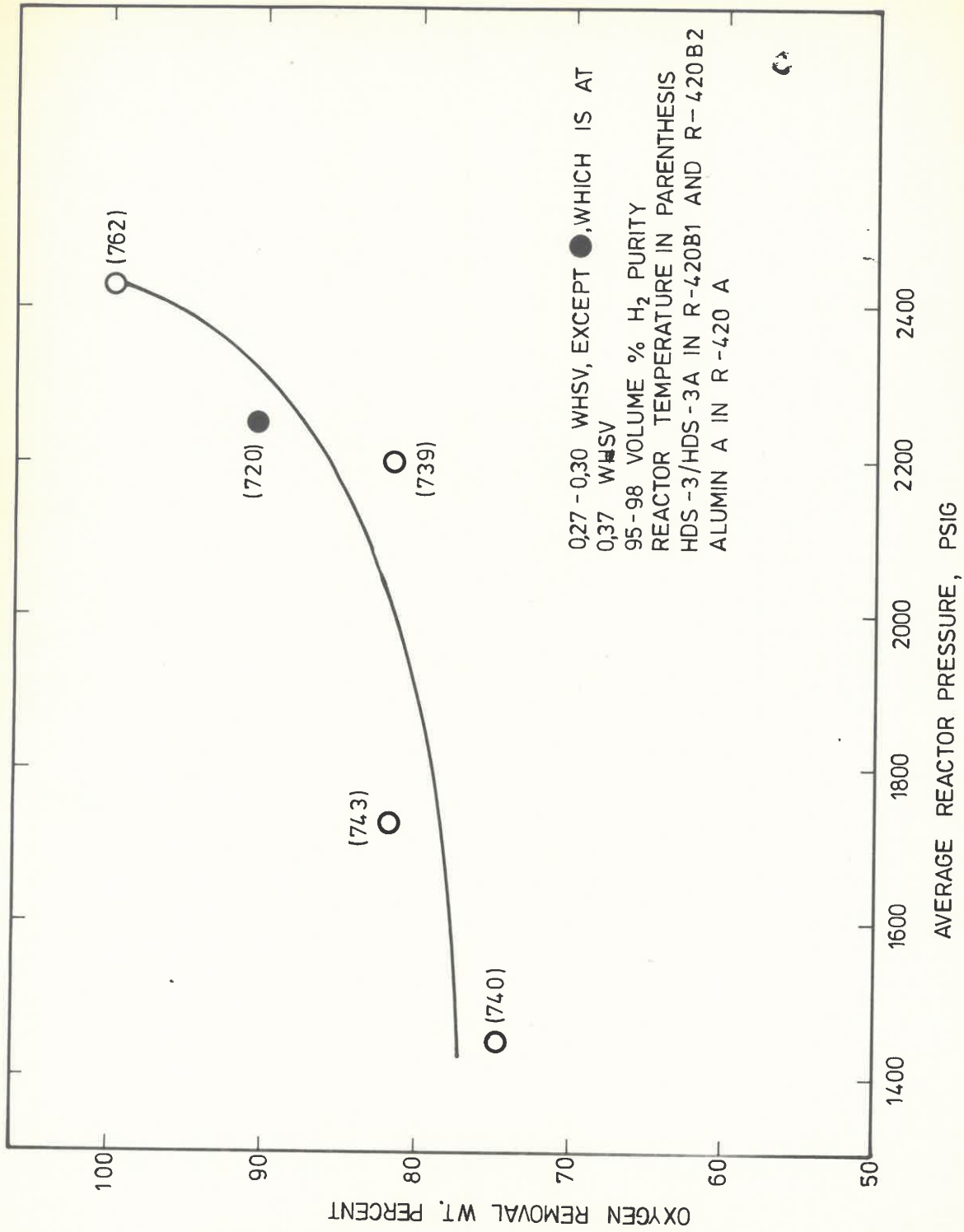


FIGURE 6 EFFECT OF REACTOR PRESSURE ON OXYGEN REMOVAL EFFICIENCY
 UTAH COED OIL

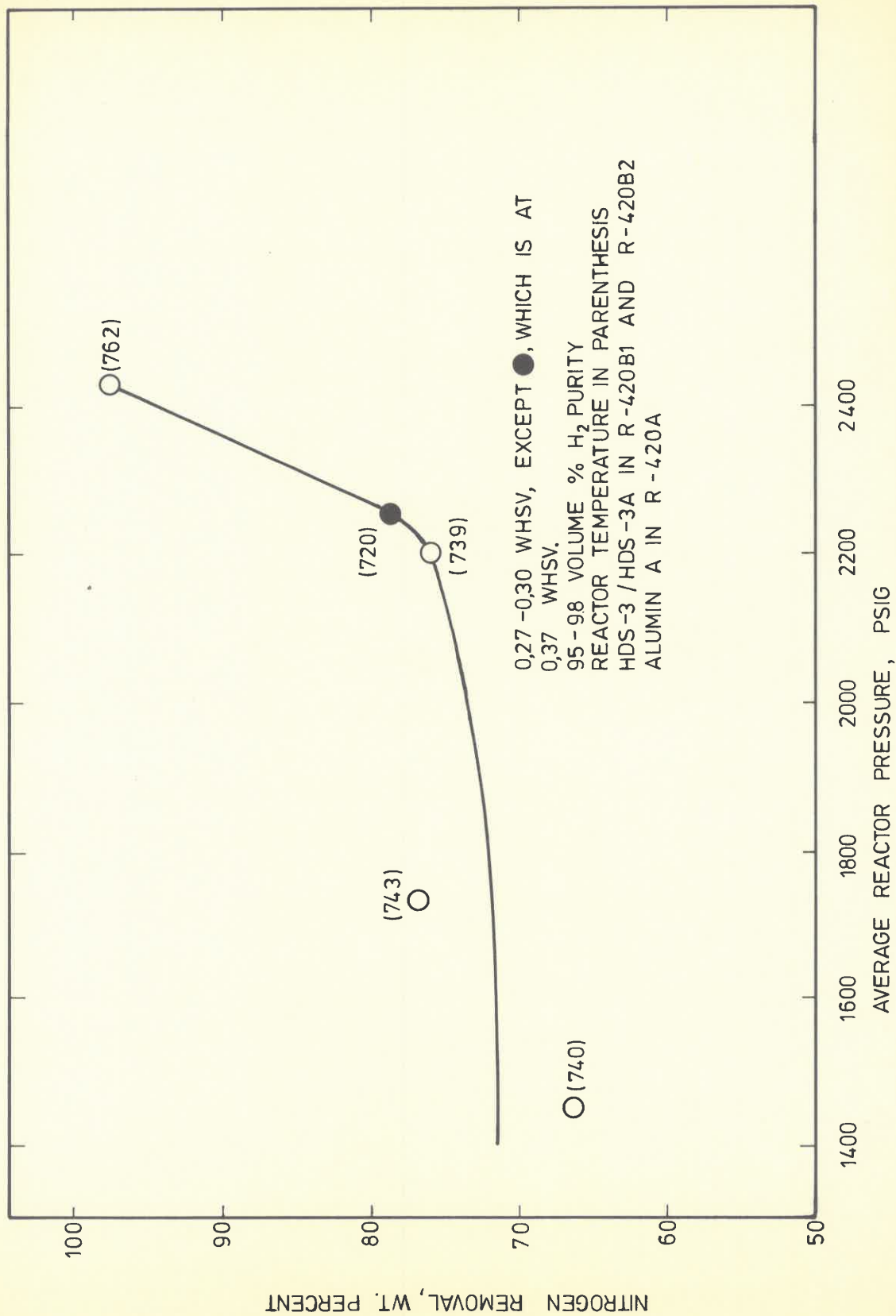


FIGURE 7 EFFECT OF REACTOR PRESSURE ON NITROGEN REMOVAL EFFICIENCY
UTAH COED OIL

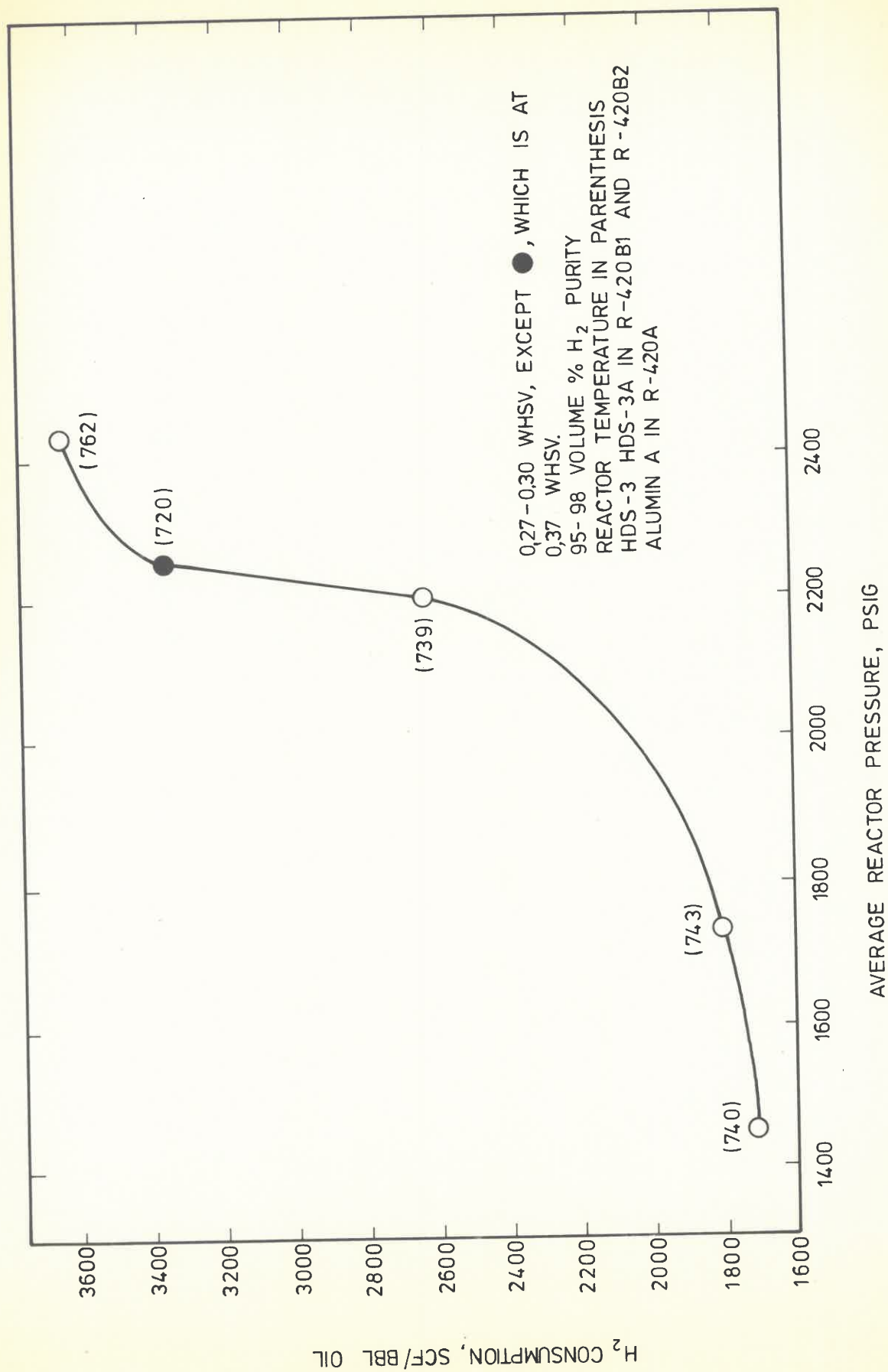


FIGURE 8 EFFECT OF REACTOR PRESSURE ON HYDROGEN CONSUMPTION UTAH COED OIL

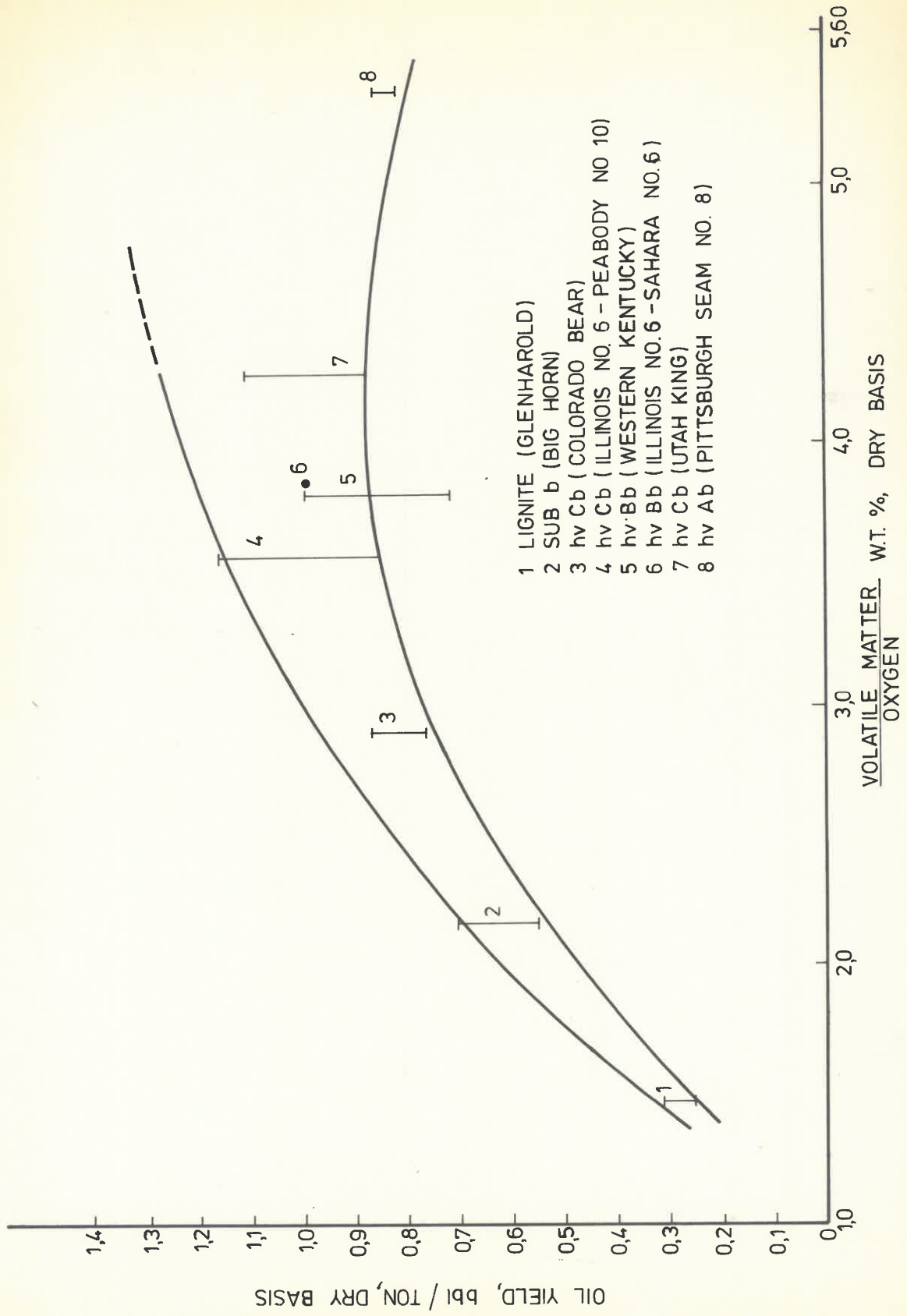


FIGURE 2 COED PILOT PLANT PYROLYSIS OIL YIELDS AS A FUNCTION OF COAL VOLATILE MATTER AND OXYGEN CONTENT.

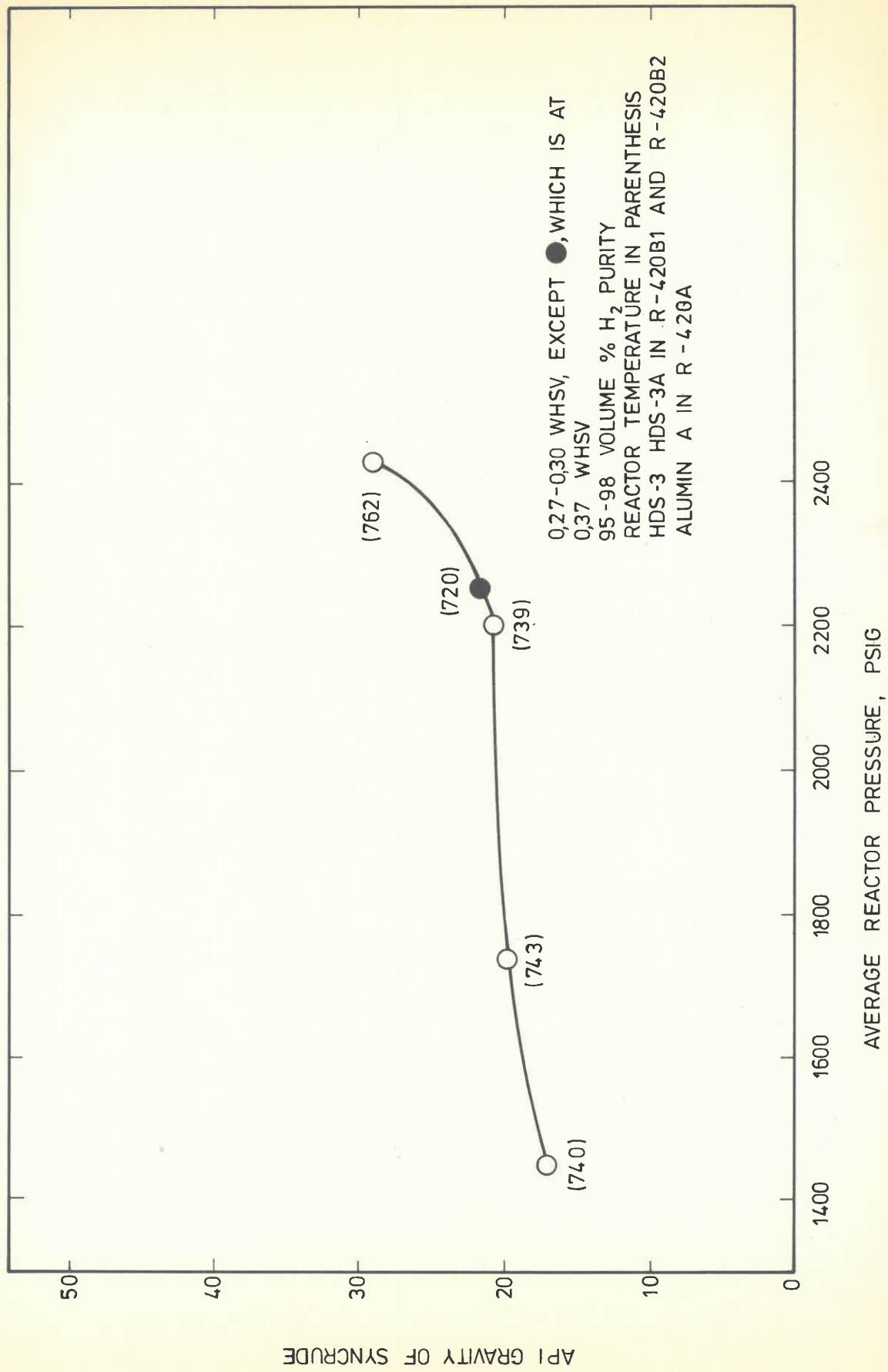
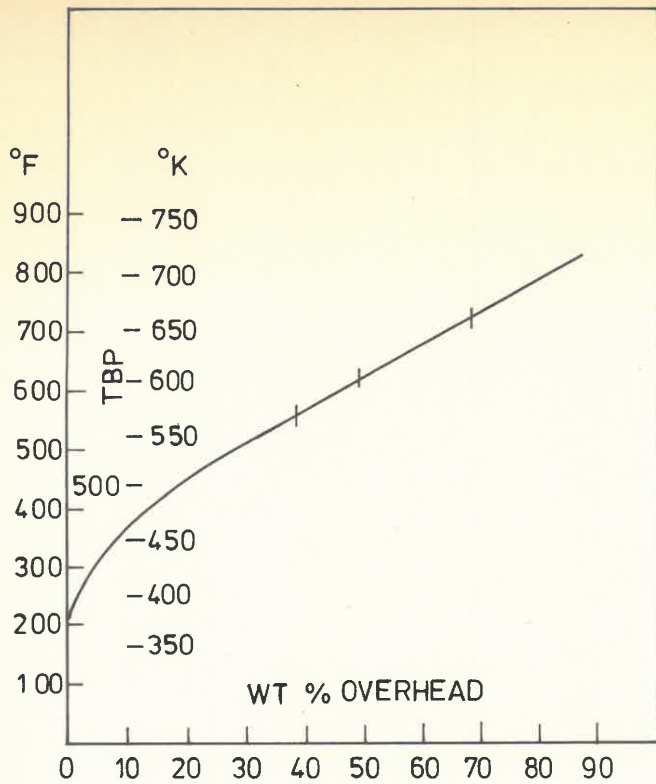


FIGURE 9 EFFECT OF REACTOR PRESSURE ON SYNCRUDE API GRAVITY UTAH COED OIL



NOTE.
COMPARE THE SYNCRUDE
BOILING RANGE WITH
FIGURE 4

FIGURE 10 COED SYNCRUDE DISTILLATION CURVE

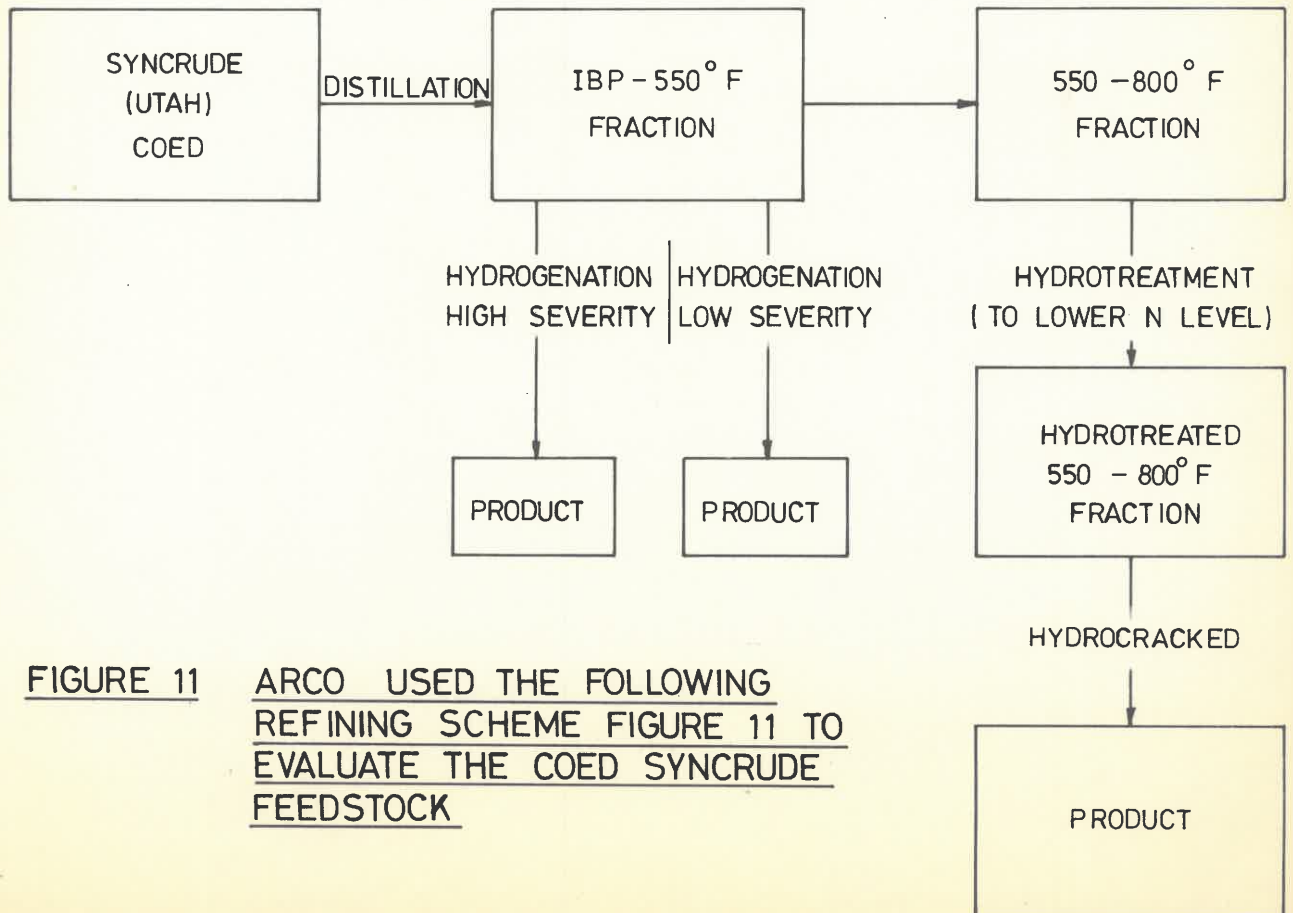


FIGURE 11 ARCO USED THE FOLLOWING
REFINING SCHEME FIGURE 11 TO
EVALUATE THE COED SYNCRUDE
FEEDSTOCK

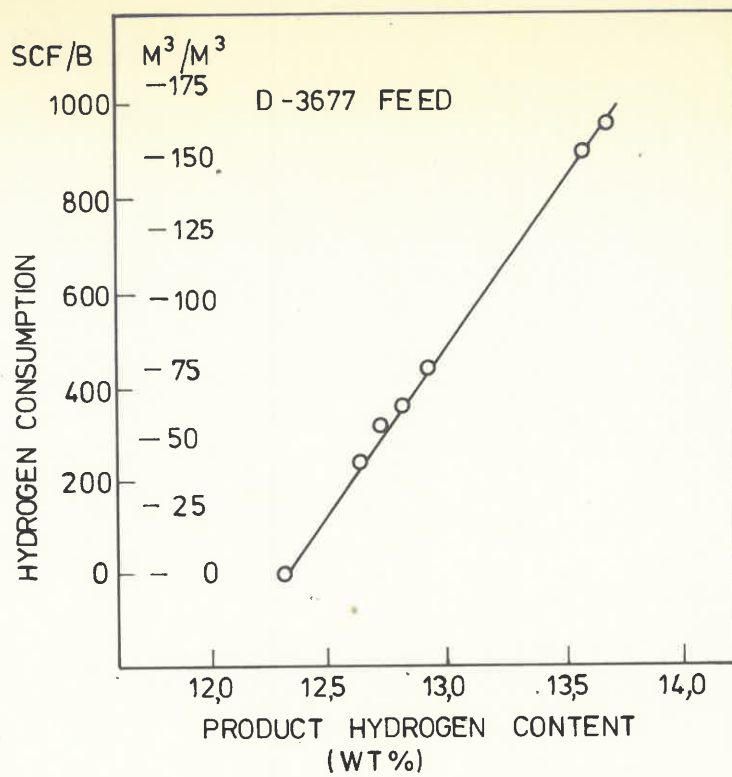


FIGURE 12 IBP-561° K (550° F) COED OIL HYDROTREATING
HYDROGEN CONSUMPTION RATE

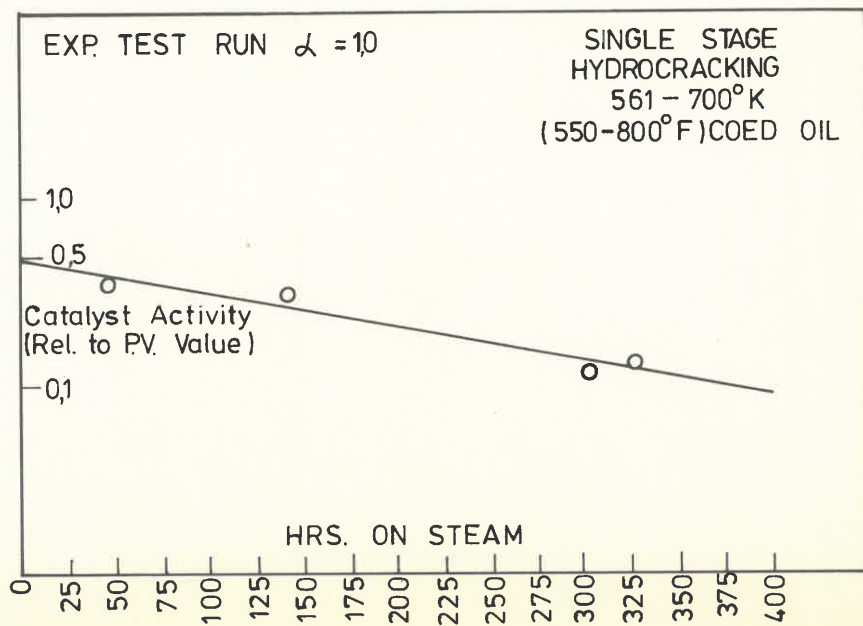


FIGURE 13 HYDROCRACKING CATALYST ACTIVITY

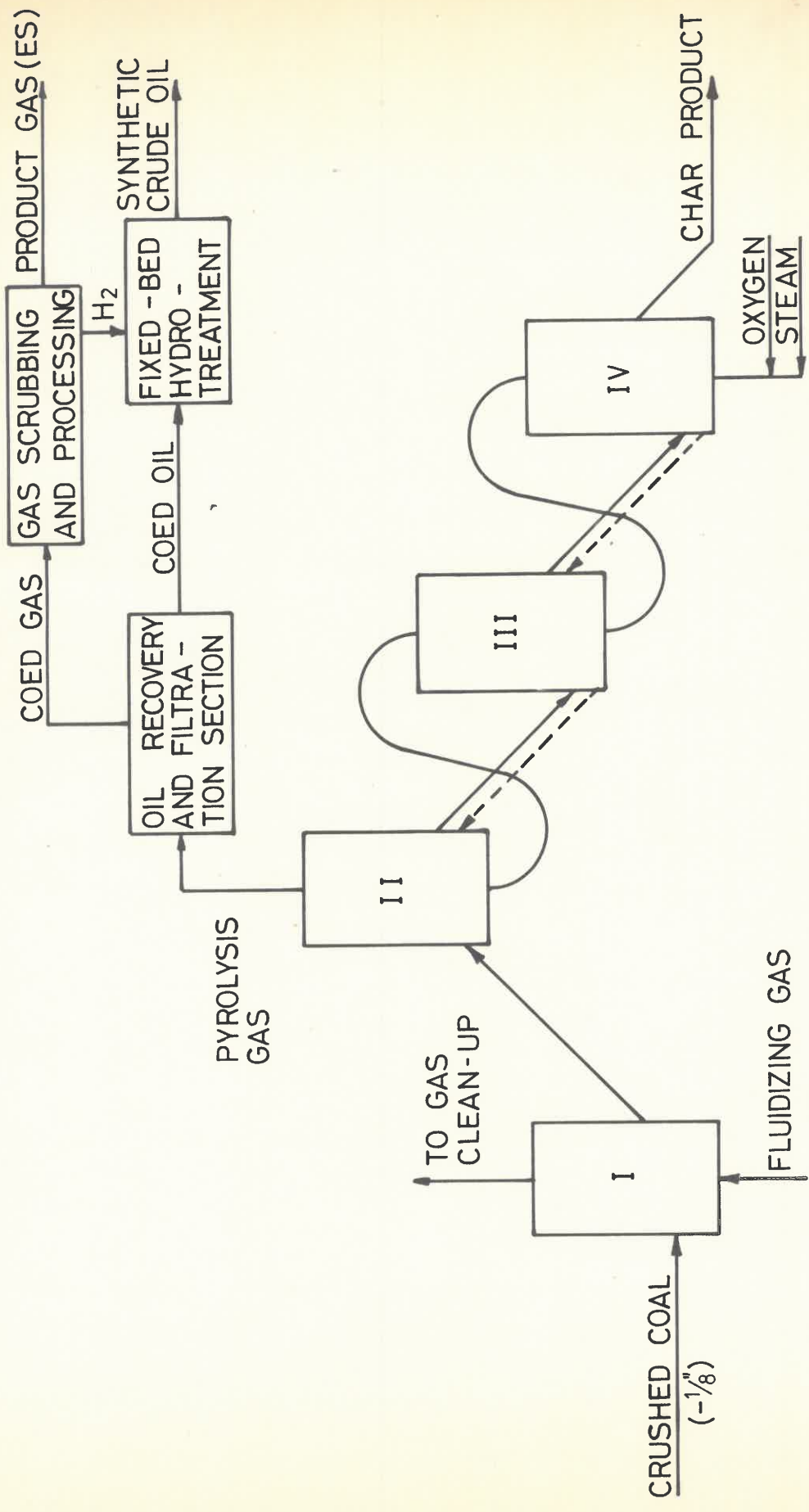


FIGURE 1 COED COAL PYROLYSIS

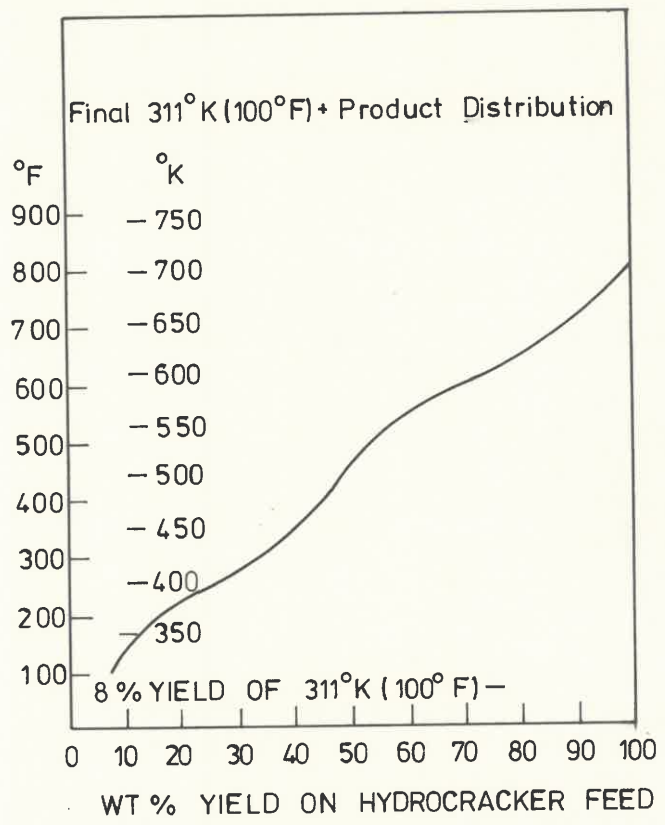


FIGURE 14 HYDROCRACKING OF 561-700°K (550-800°F)
COED SYNCRUDE