LOGIC, TECHNOLOGY AND EFFECT OF COAL

LIQUEFACTION CONDITIONS ON FINAL

UP-GRADED PRODUCT SLATE

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ABSTRACT

Conditions chosen for the coal liquefaction reactor and for the de-ashing step determine the nature of the syncrude intermediate product. In the succeeding upgrading steps, this syncrude must be converted to salable products. A logical sequence is proposed to establish the overall process configuration, where hydrocracking, hydrotreatment and other refining steps are integrated with the initial conversion units and the hydrogen generation system.

Reactor parameters affecting coal conversion will be discussed with emphasis on the SRC-I process. Relation of hydrogen consumption to product distribution and product H/C ratio, sulfur, oxygen, and nitrogen content will be developed. Merits of two-stage vs. single-stage coal conversion and various ash removal methods will also be discussed.

A review of published data on upgrading of raw coal liquid will be made. Production of salable gasoline, jet fuel, diesel oil, and fuel oils from coal liquids will be compared to similar data starting with shale oil, petroleum, and tar sands. Processes employed are hydrocracking, hydrotreatment, catalytic reforming, and catalytic cracking. Delayed or Fluid Coking plus hydrotreating are also proposed for processing shale oils and tar sands.

INTRODUCTION

Direct coal liquefaction has rapidly approached the status of a commercial reality during the past few years. New processes, such as H-Coal, SRC, and Exxon Donor Solvent, offer advantages over indirect liquefaction routes where liquids were formed from synthesis gas generated by coal gasification. These advantages, primarily in improved carbon utilization, are gained by empployment of a more-complex processing scheme which in turn tends to increase the cost of a practically-sized facility. Preparation of designs for commercial-scale plants using direct coal liquefaction certainly involves a thorough understanding of the strengths and limitations of the several technologies involved. Beyond familiarity with individual process steps, however, planning of the overall design requires comparative studies of the options available and of the sequences in which they could be applied.

LOGICAL DEVELOPMENT OF PROCESS SEQUENCE

Experience and intuition strongly indicate that no single overall process scheme can be assembled to fully serve the needs of any and all who might contemplate direct coal liquefaction. Depending upon the nature of the selected coal feedstock, product requirements and preferences for byproduct sale or utilization, several process configurations are possible. For the discussion which follows, the product slate will be assumed to be restricted to transportation fuels, i.e., diesel and gasoline.

A complex processing scheme is necessary to apply direct coal liquefaction technology to ultimately yield transportation fuel. The coal conversion process itself, the downstream processing steps and the utility systems must be carefully integrated to achieve an optimum, yet practical, plant design. The task of greatest importance at the outset of design work is to establish the overall process configuration. This definition of basic plant architecture, in turn, allows the engineer to produce a well-defined scope of work for the process licensors, who then develop detailed process information from which the overall process design and then estimates of capital and operating costs are prepared.

Facilities for employing direct coal liquefaction (e.g., by the H-Coal process) to produce transportation fuels, can be visualized as a group of subsystems (see Figure 1):

- Coal liquefaction: coal preparation, slurrying and heating, hydroliquefaction, and reactor effluent separation.

- Liquid separation: ash removal, primary fractionation and residue stripping.

- Liquid upgrading: hydrotreatment, hydrocracking, catalytic reforming and final fractionation.

- Byproduct gas handling: acid gas removal and cryogenic separation.

- Hydrogen generation: partial oxidation of liquefaction residue (or steam reforming of light byproducts), gas purification and hydrogen distribution.

- Effluent treatment: recovery of sulfur, ammonia and phenols.

- Offsites: coal and oxygen supply systems and normal utilities.

Before design work can begin, key parameters which affect plant design and economics, for the particular facility being considered, must be clearly defined. Such parameters include:

- Feedstock definition: coal composition and characterization.

- Product requirements: gasoline and diesel fuel quantities and specifications.

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- Byproduct philosophy: preferences regarding sale and/or in-plant consumption of byproduct fuel gas, LPG, heavy oil, etc.

- Environmental standards and regulations.

- Specifications and transfer costs for any available utilities and credits allowed for net production of utilities (e.g., electric power).

- Site-specific conditions as necessary for capital cost estimation.

- Economic criteria: values of coal, products and byproducts.

- Particular philosophies regarding tradeoffs and acceptance of developmental equipment and processes.

Development of the overall processing scheme to incorporate the several elements mentioned above requires a very careful and logical approach, if the final result is to be the optimum integration of the many process sections. Toward this end, KRSI has developed a system of logic "pathways" to define the sequence in which decisions must be made and to indicate where reiteration of process design calculations may be necessary.

The logic pathways are illustrated in Figures 2, 3 and 4. Activities, identified as A-1, A-2, ... are indicated by rectangles, while decisions (all of which are yes/no choices), identified as D-1, D-2, ... are indicated by diamonds.

The steps shown in Figure 2 concern the basic definition of products from the plant.

- After a coal liquefaction process has been chosen and preliminary raw liquid yields have been defined, the initial decision (D-1) is whether a solvent deashing method, such as Kerr-McGee Critical Solvent Deashing or Lummus Antisolvent Deashing, is to be used. A positive response calls for revision (A-1) of the raw liquid quantity and composition, since the solvent deashing processes recover significantly more heavy oil than do other separation techniques.

- Next, the raw liquid products (naphtha and middle distillates) are defined (A-2) as to quantity and characterization, as they would be produced by fractionation of the wide-range liquid from the liquefaction reactor system.

- The amounts and characterization of the gasoline and diesel fuel products are then defined (A-3), assuming classical refinery operations such as hydrotreatment and catalytic reforming in the upgrading steps. (Sources of data to aid in predicting finished product yields and properties are discussed later in this paper.)

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Following definition of the liquid products, steps to evaluate product acceptability and to define the hydrogen demand are necessary, as shown in Figure 3.

- The predicted quantities and characterizations of the liquid products must be compared (D-2) with the objectives of the design. If the relative production rates of gasoline and diesel fuel are acceptable and the required specifications are met, the upgrading scheme probably can be regarded as fixed. If not, revision (A-4) of the scheme, such as by adding a heavy oil hydrocracking step, is necessary. In such an instance, the design should be studied (A-5) and prudent revisions of the liquefaction section definition may be in order.

- Two or more iterations of the raw liquid/finished liquid definition "loop" (A-2, A-3, D-2, A-4 and A-5) may be necessary to establish an upgrading scheme which best satisfies the requirements of production rates and product properties. It is important to note that further definition of other plant areas is futile before the upgrading scheme is established.

- With the hydrotreatment and catalytic reforming (and possibly hydrocracking) steps defined, the total hydrogen balance can be established (A-6) from the demand/recycle side, allowing straight-forward calculation of the makeup hydrogen rate.

- Probably the most likely source of hydrogen is gasification of the unconverted coal (perhaps enriched with heavy oil) from the liquefaction reactor. The next step (A-7) is to estimate the amount of hydrogen which could thus be produced.

The balance of the effort in process sequence organization is primarily concerned with satisfying the hydrogen demand; see Figure 4.

- The next logical step is comparison (D-3) of the hydrogen demand with the supply available from gasification of unconverted coal/heavy oil. Further, the supply vs. demand situation must be assessed (D-4) as to whether a significant excess of hydrogen (e.g., supply exceeding demand by more than 5%) exists. In the event that supply and demand are just to the excess side of balance, the hydrogen system can be finalized and design work can proceed.

- If the hydrogen which could be generated from unconverted coal/ash is greatly in excess of the hydrogen makeup requirement, the upgrading scheme should be revised to promote additional production of liquids by utilization of the hydrogen in a hydrocracker. This iterative procedure is crucial in balancing the relative amounts of carbon which are consumed in the liquefaction and gasification steps.

- A discovery that the hydrogen supply is insufficient (at D-3) leads to consideration of other sources for hydrogen. The initial study (D-5) involves steam-reforming of the LPG byproduct; this decision may be dictated by initial guidelines, as discussed previously. Presuming that reforming is permissible, the potential hydrogen supply is estimated (A-9) and the total hydrogen supply is

compared (D-7) with the total demand. If the supply and demand are essentially in balance, design work can be undertaken.

- If steam-reforming is not permissible, or if reforming does not provide sufficient additional hydrogen to satisfy the demands, a decision (D-6) must be made as to whether direct gasification of raw coal can be used. If so, an additional degree of freedom is at hand and design work can proceed.

- If direct coal gasification is not an acceptable option, for whatever reason, no choice exists except to again adjust the liquids balances (A-8) to allow additional flow of heavy oil to the hydrogen generation section.

COAL CONVERSION REACTOR PARAMETERS

The actual mechanism of coal conversion is very complex, and as yet, not fully understood. It is generally believed that coal liquefaction follows the following route [1] by breaking C-C, C-O, C-S and C-N bonds and stabilizing the free radicals by hydrogen transferred from a hydrogen donor solvent.
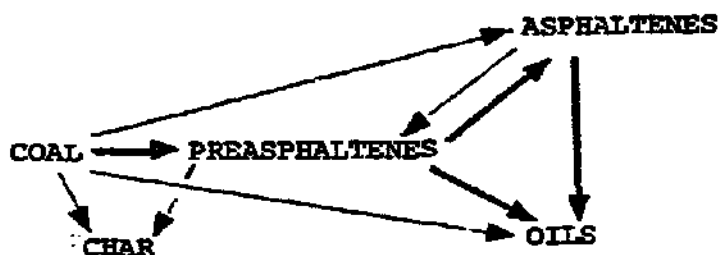
The major role of catalyst in liquefaction appears to be the replenishment of the hydrogen donor solvent and enhancement reactions of hydrogenation and hydrocracking.

Oil, asphaltene, preasphaltene and unconverted coal are characterized as follows, as to their solubilities:

Material	N-Pentane	Benzene Or Toluene	Pyridine/ Cresol/ Quinoline
Oil	Soluble	Soluble	Soluble
Asphaltene	Insoluble	Soluble	Soluble
Preasphaltene	Insoluble	Insoluble	Soluble
Char, undissolved or unconverted coal	Insoluble		

For a given type of coal, product slate (ratio of preasphaltene, asphaltene, process oil, medium and light oil cuts and gas) can be adjusted by changing the following variables:

- Dissolver operating temperature

- Residence time (dissolver volume) and recycle of higher boiling cut.

- Hydrogen partial pressure.

- Solvent quality and quantity-heavier cut, catalytic hydrogenation or recycle light solvent refined coal

- Catalytic variables-catalyst addition, mineral ash recycle or mineral ash accumulation.

Choosing proper operating conditions to maximize desired yields, while maintaining the process solvent quantity and quality, have to rely on the plant data. The coal conversion process is somewhat forgiving and lighter cuts can be increased at the cost of additional hydrogen consumption when operating conditions are more severe.

Since a major loss in efficiency results from hydrogen manufacture, it is desirable to use a minimum amount of hydrogen to achieve the desired end products.

A typical coal conversion yield structure and degree of desulfurization for SRC-I can be correlated with the hydrogen consumption reported from SRC-I Pilot Plant as shown in Figures 5 and 6.[2]

Oxygen and sulfur removal tend to be parallel as reported by TRW in Figure 7.[3] For Kentucky coal containing 11 wt% of oxygen, approximately five times as much hydrogen is consumed to remove oxygen from coal than is used to remove sulfur from coal.

Data obtained from the Wilsonville and the Tacoma SRC pilot plants indicate that the fuel-bound nitrogen content in the solid SRC fuel produced at both pilot plants is about the same (close to 2 wt%).[2,4,5] In the SRC II process, the fuel-bound nitrogen content in the naphtha, middle distillate and heavy distillate liquids produced is 0.6, 1.0 and 1.3 percent respectively.

SRC PROCESS COMPARISON

The four major coal liquefaction processes are SRC-1, SRC-II, Exxon donor solvent (EDS) and H-Coal processes.

The original SRC-I process differs from the other three processes by maximizing the solid SRC production during the conversion. Solid SRC can be subsequently catalytically hydrocracked to make various oil cuts if desired, as in the ICRC demonstration plant design.

SRC-II, FDS, and H-Coal processes are designed to maximize direct production of liquid products.

SRC-II process differs from other processes by recycling vacuum column bottoms containing mineral ash to add the mineral ash's catalytic effect and to increase the residence time for vacuum column bottom heavies.

The H-Coal process is characterized by feeding coal slurry in an ebullating liquid bed reactor containing catalyst in addition to the mineral matter originally present in the coal. Therefore, hydrocracking reactions for coal liquid and rehydrogenation for hydrogen donor solvent are enhanced inside the reactor.

The EDS process is unique in that it catalytically hydrotreats recycle process solvent in a separate reactor at an elevated temperature and pressure to enrich the donor solvent.

SOLID-LIQUID SEPARATION PROCESS
IN COAL LIQUEFACTION PROCESS

In the solvent refined coal liquefaction processes, heavy residues containing mineral ash, unconverted coal and unrecovered coal liquids are often fed to a gasifier to produce hydrogen for the coal conversion plant (the EDS process feeds the heavy residues to a flexicoking unit to produce light oil and fuel gas). Valuable coal liquid contained in the residue should be minimized or recovered as much as possible, or at least should not be in excess of the quantity required for producing plant hydrogen.

For coal conversions maximizing liquid products, it is required to have severe hydrogenation, hydrocracking and thermal cracking reactions to minimize the heavies which cannot be separated from the ash fraction in the vacuum column.

When solid SRC is the process product or an intermediate product, solid-liquid separation is required.

To date, two types of solid-liquid separation processes, which result in SRC containing less than 0.16 wt% mineral ash, have been demonstrated for coal liquefaction processes.

- **Filters**

  - Vertical filters (Funda filter) used at Wilsonville SRC-I Pilot plant are batch precoat-type pressure filters with horizontal filter leaves on a vertical shaft.

- **Solvent Deashing Processes**

  - Critical solvent deashing process (CSD)

  - Antisolvent deashing process

A vertical filter has demonstrated that a 95 percent SRC recovery can be achieved. Filterability is greatly affected by the coal liquid viscosity. Composition of the filtrate is identical to the filter feed while ash is removed.

The Kerr-McGee CSD process uses a deashing solvent to extract soluble coal liquids and separate the mineral matter near the critical point of the deashing solvent.[8] Deashing solvent extracts approximately 90 percent of the oils and asphaltenes, but only 35-60 percent of the preasphaltenes. The Wilsonville data indicates that if the ratio of benzene solubles to preasphaltene in the feed to CSD unit drops from 3.0 to 2.0, the SRC recovery drops from 85 to 72 percent.[9] Mineral ash and unconverted coal is discharged in the heavy phase which is different in composition from the light phase.

The Lummus antisolvent process employs a promoter liquid which causes the precipitation of preasphaltenes on ash particles. Coal liquid with a greater concentration of preasphaltenes will require less antisolvent to cause agglomeration and precipitation. However, a high concentration of preasphaltenes tends to decrease the underflow fluidity. Overflow and underflow streams from the deashing settler are similar in composition, except the underflow contains the solids present in the feed to the unit.[10]

SRC recovery from the CSD process and antisolvent process is affected by the ratio of the benzene soluble fraction to pre-asphaltene, while this ratio is affected by dissolver operating conditions, as mentioned earlier. Also, reversion of asphaltene to pre-asphaltene occurs during hold-up at an elevated temperature in the absence of hydrogen and will consequently affect the performance of solid-liquid separation in the coal liquefaction process.

TWO-STAGE COAL LIQUEFACTION

The two-stage liquefaction (TSL) process accomplishes the production of liquid fuels from coal by means of SRC-I technology in two stages.

- First Stage: conversion of raw coal to SRC, liquid and gas (known as SRC-I process).

- Second Stage: catalytic hydrogenation of the SRC to obtain high-quality liquids and solids.

During the second stage, the production of middle distillate liquid fuels can be enhanced. The formation of light hydrocarbon gases can be minimized, and hydrogen is utilized more efficiently.

The two-stage liquefaction process designed for the 6,000 tons per day (coal feed) SRC-I demonstration plant by ICRC (a joint venture of Air Products and Wheelabrator-Frye) can be described schematically as follows:
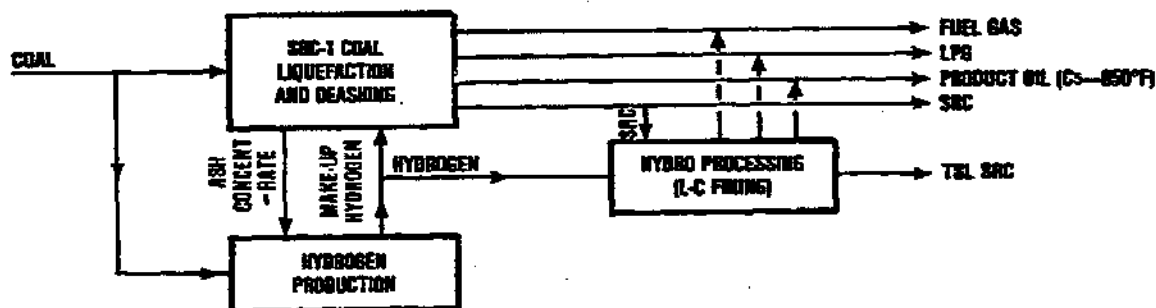
The hydrogen consumption for the TSL is approximately 3.8 wt%, compared to a hydrogen consumption of 4.8 wt% for a single-stage conversion at a comparable 40.1 wt% (MAF) distillate product,[11] as shown below.

Yields in Wt%	TSL	Single-Stage Conversion
C_1/C_4 Gas	13.0	18.4
Distillate	40.1	40.7
SRC	29.7	27.8
H_2 Consumption	3.8	4.8

Also, nitrogen and sulfur contents of the TSL yields are half of those of the single-stage process.

A key advantage of the separate stage of catalytic hydroprocessing is that it provides additional product flexibility while it also broadens the variety of coals that can be processed. The TSL process is less sensitive to coal quality than other SRC-based technology.

SOURCES OF DATA FOR LIQUID UPGRADING

Kellogg Rust Synfuels has reviewed the published literature regarding upgrading of coal liquids as well as the literature for upgrading shale oil, tar sands, and similar petroleum derived fractions. Most of the experimental data was produced by oil companies and at least partially supported by the Department of Energy, the Department of Defense (Air Force), or EPRI.

The primary upgrading process employed was hydrotreating, but coking plus hydrotreating was also found to be viable, especially for tar sands. Thrust of the investigations was to produce an upgraded synthetic which could be further processed in refineries to produce specification gasoline, jet fuels, diesel oils, and fuel oils.

Properties of syncrudes from a number of coal liquefaction processes are compared with Arabian light crude in Table 1. It can be seen that there is considerable variation among the different processes, due partly to coal source but primarily to the extent of hydrogen imparted to the coal in the process itself. For example, H-Coal, Exxon Donor Solvent (EDS), and SRC-II impart more hydrogen to the product and produce much lighter boiling range syncrudes than SRC-I, COED, or Synthoil. A further illustration of the boiling ranges is on Figure 8, which compares TBP distillations of Arabian Light Crude with SRC-II and H-Coal. Obviously, these processes produce liquids mainly in the gasoline and, jet fuel/diesel range. Exxon Donor Solvent boiling range data from Table 1, if plotted, would track the H-Coal data closely.

Coal liquid properties are compared with Arabian Light Crude, Paraho shale oil, Athbasca tar sand bitumen, a petroleum atmospheric residuum, and a total coker distillate from Athabasca bitumen on Table 2.

From this table the wide variation in properties from alternate source syncrudes can be appreciated. Shale oil is a thermally-cracked material with a wider and heavier boiling range than coal liquid. Tar sand bitumen is a much heavier material comparing closer with a petroleum atmospheric residuum in properties. The coker distillate from Athabasca bitumen, however, has a full boiling range somewhat between coal liquid and shale oil.

Table 3 compares the hydrogen contents of raw shale oil, coal liquid, and tar sand bitumen with crude oil. It can be seen that shale oil falls within the crude oil range, but coal liquid is very low in hydrogen content (due to high aromaticity) and tar sand bitumen is intermediate to coal and shale raw liquids.

Table 4 compares the sulfur and nitrogen contents of coal syncrude and shale oil to a typical petroleum for the same fractions. This table illustrates that coal liquids and shale oil are likely to be lower in sulfur than most crude oils, but higher in nitrogen. This higher nitrogen content becomes the controlling factor in hydrogen treatment, since denitrogenation is more difficult to effect than desulfurization. Although the tar sand bitumen is not shown on the table, nitrogen removal is also the controlling factor in that case. Tar sand bitumens vary in sulfur from 4-5% (Athabasca) to 0.4 - 0.5% (Utah). Nitrogen contents are about 0.5% for Athabasca and 0.8 - 1.0% for Utah tar sand bitumens.

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Naphthas derived from synthetic crudes will most likely be upgraded to salable gasoline via catalytic reforming. Best yields from catalytic reforming are obtained from high naphthene content naphthas feeds. Low sulfur (<2ppm) is essential for modern catalytic reformer catalyst activity maintenance. For shale oil, arsenic must also be removed in a guard chamber before processing. Naphtha compositions from petroleum and hydrotreated shale oil, coal liquid, and coker distillate from tar sand bitumen are compared in Table 5. It is apparent that hydrotreated coal liquid naphtha is superior to typical crude oil, shale oil, or tar sand as a catalytic reforming feed stock. Shale oil naphtha would be the least desirable due to high paraffin content; both shale oil and tar sand sources would be less desirable than most crude oil naphthas. An example of gasoline yields from catalytic reforming of a hydrotreated H-Coal naphtha is shown below:

| | (Feed) | --- REFORMING SEVERITY --- | | |
		Low	Medium	High
C_5^+ Yield, Vol. %	(100.)	92.5	91.1	88.1
Research Octane- Clear	66.8	94.2	97.7	102.6
Compound Types				
Aromatics	19.4	65.8	71.7	83.3
Naphthenes	64.6	16.4	9.4	5.0
Paraffins	16.0	17.8	18.9	11.7
Hydrogen Yield-wt.%	–	2.5	3.0	3.4
-SCFB	–	1,250	1,500	1,700

Note that catalytic reforming produces substantial yields of hydrogen, which can be used in refineries for necessary hydrotreating of naphtha, middle distillate, and hydrocracking or FCC feed improvement.

Most of the experimental work reported on syncrude upgrading has concerned the extent of hydrotreating required to make salable, specification jet fuels, diesel fuels, or distillate fuel oils. Specifications for these products are shown on Tables 6 and 7. Low sulfur is common to all the specifications, while aromatics (to keep smoke point low) is only in jet fuel specifications per se. The cetane number specification for diesel fuel would not be met with a high aromatic content. Absence of nitrogen specifications is to be noted particularly, since it has not been a problem with petroleum sources; however, individual refiners generally prefer low nitrogen (roughly <1000 ppm) to eliminate instability and corrosion possibilities and trouble with air pollution due to nitrogen oxides. Certain types of nitrogen also act as poisons for catalytic reforming and catalytic cracking catalysts.

Examples of hydrogen consumption requirement to prepare low nitrogen distillates are shown in Figure 9 for shale oil and SRC-II coal liquid. More hydrogen is required for shale oil to a given nitrogen content than for SRC-II because it contains more nitrogen and also due to some hydrocracking occurring because of the heavier shale oil feed boiling range. Representative jet fuels derived from hydrotreated shale oil, hydrocracked shale oil, hydrotreated SRC-II liquid, and hydrotreated coker naphtha from Athabasca bitumen are presented in Table 8. Note that shale oil most closely satisfies the JET A specifications. Coal liquids do not meet the specific gravity specification; the coker-plus-hydrotreating product from Athabasca bitumen would require more hydrogen treatment to lower aromatics and raise smoke point.

Diesel products from hydrotreated shale fractions, hydrotreated SRC-II liquid, and hydrotreated coker distillate from Athabasca tar sand bitumen are compared on Table 9 with typical petroleum-derived diesel. As with jet fuel, the shale oil source yields the best diesel fuel as compared with specifications and typical petroleum. It will be more difficult to make cetane number specifications using coal liquids and tar sand bitumen due to their higher naphthene and aromatic contents. Paraffins make the most desirable diesel fuels.

Finally, the heavier part of the syncrude would be subjected to either fluid catalytic cracking or hydrocracking in order to obtain more valuable lower boiling gasoline and middle distillates (jet fuel, diesel, No. 2 fuel oil) and less heavy fuel oil. Fluid catalytic cracking tests by UOP indicate that feed hydrogen content is perhaps the most important variable in FCC, as shown below:

Feed	California Crude	Gas Oil from H-Coal	Gas Oil from EDS
		10. wt.% H_2 in feed	
Conversion - Vol%	-	55.	61.
C_5^+ gasoline - Vol %	-	39.	38.5
Carbon yield-Wt.%	-	10	9.5
		11. wt.% H_2 in feed	
Conversion - vol.%	-	69.	70.
C_5^+ gasoline - Vol %	-	51.	46.
Carbon - wt.%	-	8.	7.
		12 wt.% H_2 in feed	
Conversion - Vol.%	71.	78.	78.
C_5^+ gasoline - Vol.%	52.	58.	53.
Carbon - Wt.%	5.	6.5	5.

It is worthy of note that Amoco [26] has been successful in developing an entirely new improved catalyst - as commissioned by the Air Force - for production of specification jet fuels in high yields from whole shale oil. This was done by hydrocracking raw shale oil which was not first passed through a guard chamber to remove arsenic and other contaminants - as has been done in most test work.

References include the sources used to compile the foregoing data. In addition to UOP and Amoco, which were mentioned, Exxon, Chevron, Arco, Sun Oil, Mobil, and Gulf papers were used in part to assemble the data presented.

REFERENCES

1. D. E. Briggs, D. V. Addington, G. Ho, J. A. McKeen, J. A. Stirling; "Physical and Chemical Behavior of Liquefied Coal in Filtration". DOE contract No.EX-76-S-01-2550, presented at 1979 conference on Filtration of Coal Liquids, Miami, Florida.

2. _____; Operation of Solvent Refined Coal Pilot Plant at Wilsonville, Alabama". Technical Progress Report for the Period January - March, 1976.

3. _____; Analysis of SRC Pilot Plant data, TRW Final Report to ERDA, Task 12, Contract E (49-18) - 2213.

4. _____;"Investigating the Storage, Handling and Combustion Characteristics of Solvent Refined Coal". B&B Company, EPRI, October 1975.

5. E. H. Greskovich; "Chemical Characterization, Handling and Refining of SRC to Liquid Fuels". Corporate Research Department, Air Products and Chemicals, Inc., ERDA, July 7, 1976.

6. _____; "Solvent Refined Coal Process"; Monthly Report for November. The Pittsburgh & Midway Coal Mining Company 1977.

7. _____; Solvent Refined Coal Process"; Monthly Report for October. The Pittsburgh & Midway Coal Mining Co., P 5-6 (1977).

8. J. R. O'Leary, G. C. Rappe; "Scale-up of an SRC Deashing Process". CEP, May 1981.

9. _____; "Operation of Solvent Refined Coal Pilot Plant at Wilsonville, Alabama". Annual Report for January - December, 1979.

10. M. Peluso and D. F. Ogren; "Anti Solvent Deashing". CEP, June 1979.

11. R. S. Chillingworth, K. E. Hastings, J. D. Potts, H. Unger; "L.C. Fining of SRC - A logical second stage in two step coal liquefaction". 87th National AIChE Meeting in Boston, August 20, 1979.

12. R. F. Sullivan, D. J. O'Rear, B. E. Stangeland and H. A. Frumkin; "45th Midyear Refining Meetings Session on Feedstocks". May 15, 1980. API Preprint No. 41-80.

13. Mark T. Atwood; "The production of Shale Oil", Chemtech. October 1973.

446

14. Thomas A. Sladek; "Recent Trends in Oil Shale - Part 3." Shale Oil Refining and some Oil Shale Problems". Mineral Industries Bulletin.

15. C. W. Matthews, Gulf Research & Development Co.; "Improvements in Oil Shale Retorts". Presented at IGT Oil Shale Symposium. October 1981.

16. R. F. Sullivan, B. E. Stangeland, H. A. Frumkin, C. W. Samuel; "Refining Shale Oil". API 43rd Midyear Meeting, May 10, 1978. Toronto

17. James W. Bunger, Kenneth P. Thomas and Samuel M. Dorrence; "Compound types and properties of Utah and Athabasca Tar Sand Bitumens"; Fuel, Vol. 58. March 1979.

18. National Research Council; "Chemistry of Coal Utilization". 1980

19. H. G. Hipkin, T. C. Lin, K. C. Lu; "Survey of Design Data Needs for Refining Synthetic Crudes", May 1981. Preliminary Report to API by Bechtel.

20. Gembicki, V. A.; "Processing Requirements and Economic Analysis of Heavy Oil and Syncrude Refining". 2nd World Congress on Chemical Engineering. Montreal, October 1981.

21. M. R. Smith and M. R. Parikh; "Bitumen Upgrading", M. W. Kellogg. August 1981.

22. Richard F. Sullivan; "Upgrading Coal Liquids". ACS Symposium Series 156, 1981.

23. R. F. Sullivan; "Refining and Upgrading of Synfuels from Coal and Oil Shales by Advanced Catalytic Processes". November 1979, DOE Contract No. EF-76-C-2315.

24. J. H. Knight, J. W. Fishback; "Superior's Circular Grate Oil Shale Retorting Processes and Australian Rundle Oil Shale Process Design".

25. D. E. Steere, W. A. McDonald and D. H. Stone. "Characteristics of Fuel Products from the Canadian Tar Sands". API Meeting, May 1981.

26. A. M. Tait & A. L. Hensley' "Jet Fuels from Shale Oil by Single-Stage Hydrocracking". ACS Symposium, Preprint, Presented at Las Vegas, Nevada, March 28 - April 2, 1982.

27. P. W. Tamm, C. A. Bertelsen, G. M. Handel, B. G. Spars, and P. H. Wallman; "The Chevron STB Oil Shale Retort". API 46th Midyear Meeting, May 1981.

28. Edward N. Coppola; "Aviation Turbine Fuel from Shale Oil". IGT Symposium, Oct. 26, 1981.

29. A. J. DeRosset, G. M. Tan, Lee Hilfman; "Upgrading Distillates from Coal Liquefaction". 44th Midyear API Meeting, May 1979.
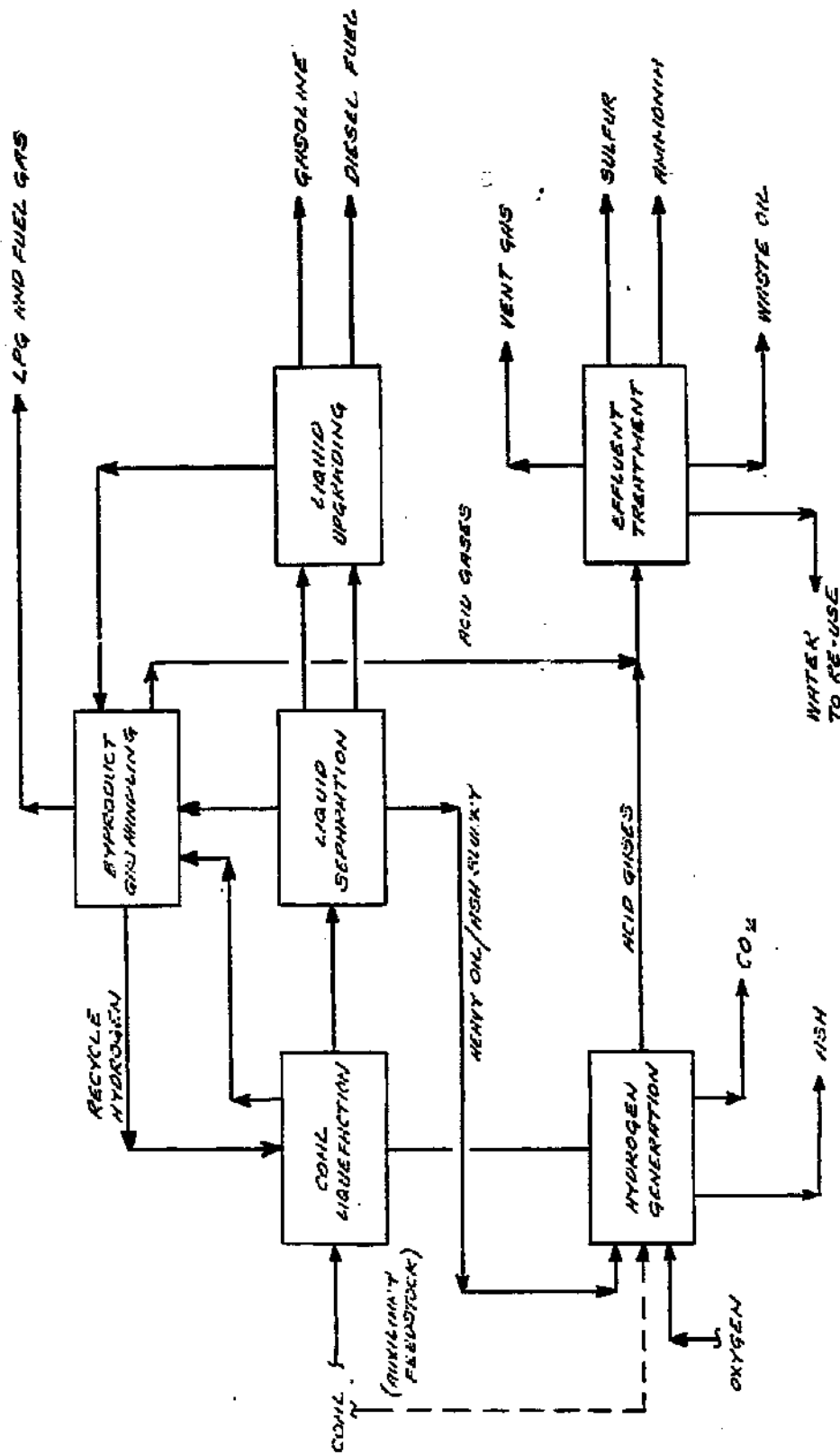
FIGURE 1

BLOCK FLOW DIAGRAM - TRANSPORTATION

FUELS BY DIRECT COAL LIQUEFACTION

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START

COAL GASIFICATION
PROCESS (CWP)
SELECTION

D-1

SOLVENT
DEASHING TO
BE USED
?

YES

A-1

REVISE
CWP
EFFLUENT

NO

A-2

DEFINE AMOUNTS
AND COMPOSITIONS
OF RAW LIQUIDS

FROM A-5
(FIGURE 3)

FROM A-8
(FIGURE 4)

A-5

DEFINE LIQUID
PRODUCT YIELDS
AND QUALITIES

TO D-2
(FIGURE 5)
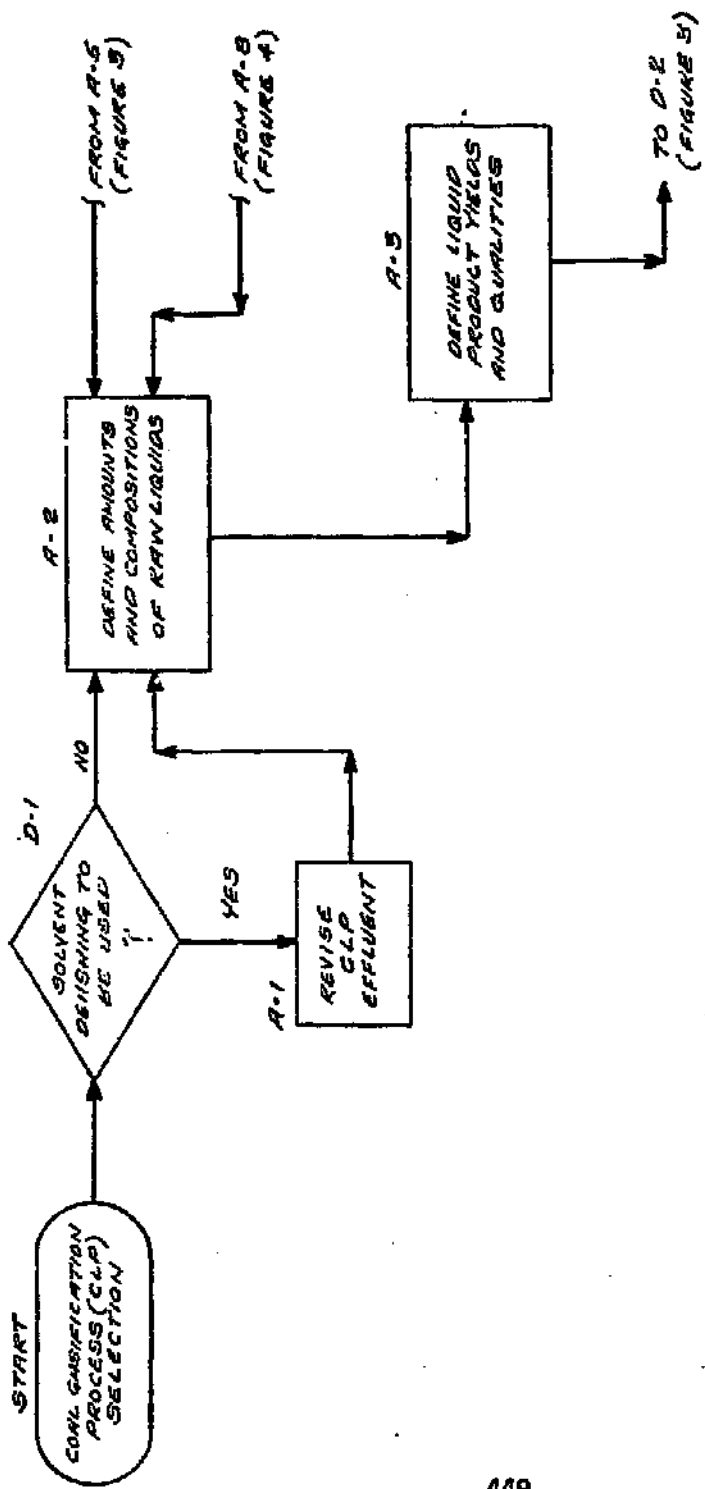
FIGURE 2

PROCESS SEQUENCE DEVELOPMENT -
DEFINITION OF LIQUID PRODUCTS

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A-7
DEFINE H2
AVAILABLE BY
GASIFICATION
OF HEAVY
OIL/ASH

TO D-8
(FIGURE 4)

A-6
DEFINE
H2 SUPPLY
REQUIRED

YES

D-2
PRODUCT
YIELDS &
QUALITIES
SATISFACTORY?

FROM A-3
(FIGURE 2)

NO

A-4
REVISE UPGRADING
SCHEME (I.E. ADD
HYDROCRACKING)

A-5
REVISE CLP
CONDITIONS
AND
EFFLUENTS

TO A-2
(FIGURE 2)

450
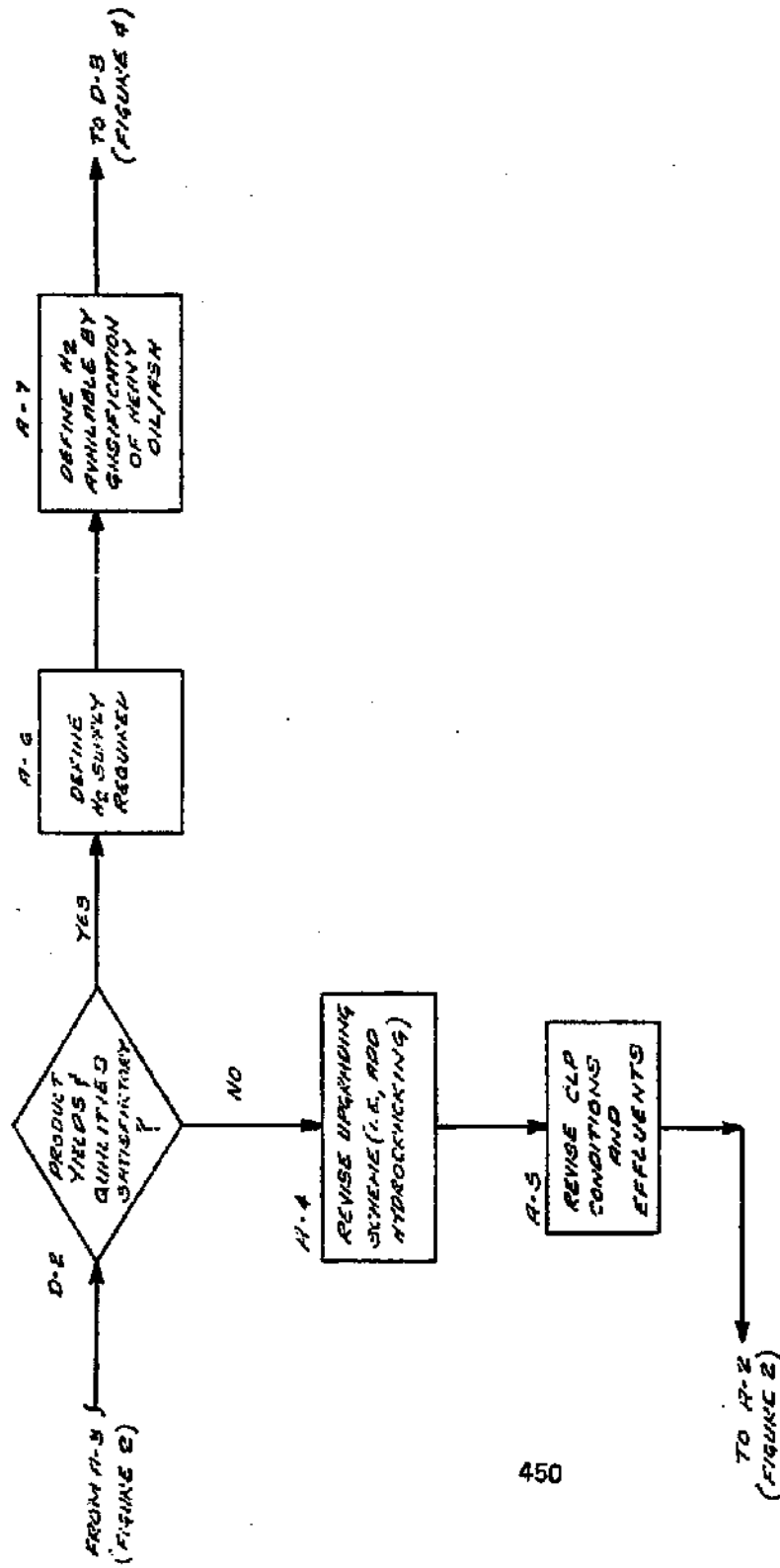
FIGURE 3
PROCESS SEQUENCE DEVELOPMENT -
DEFINITION OF HYDROGEN DEMAND
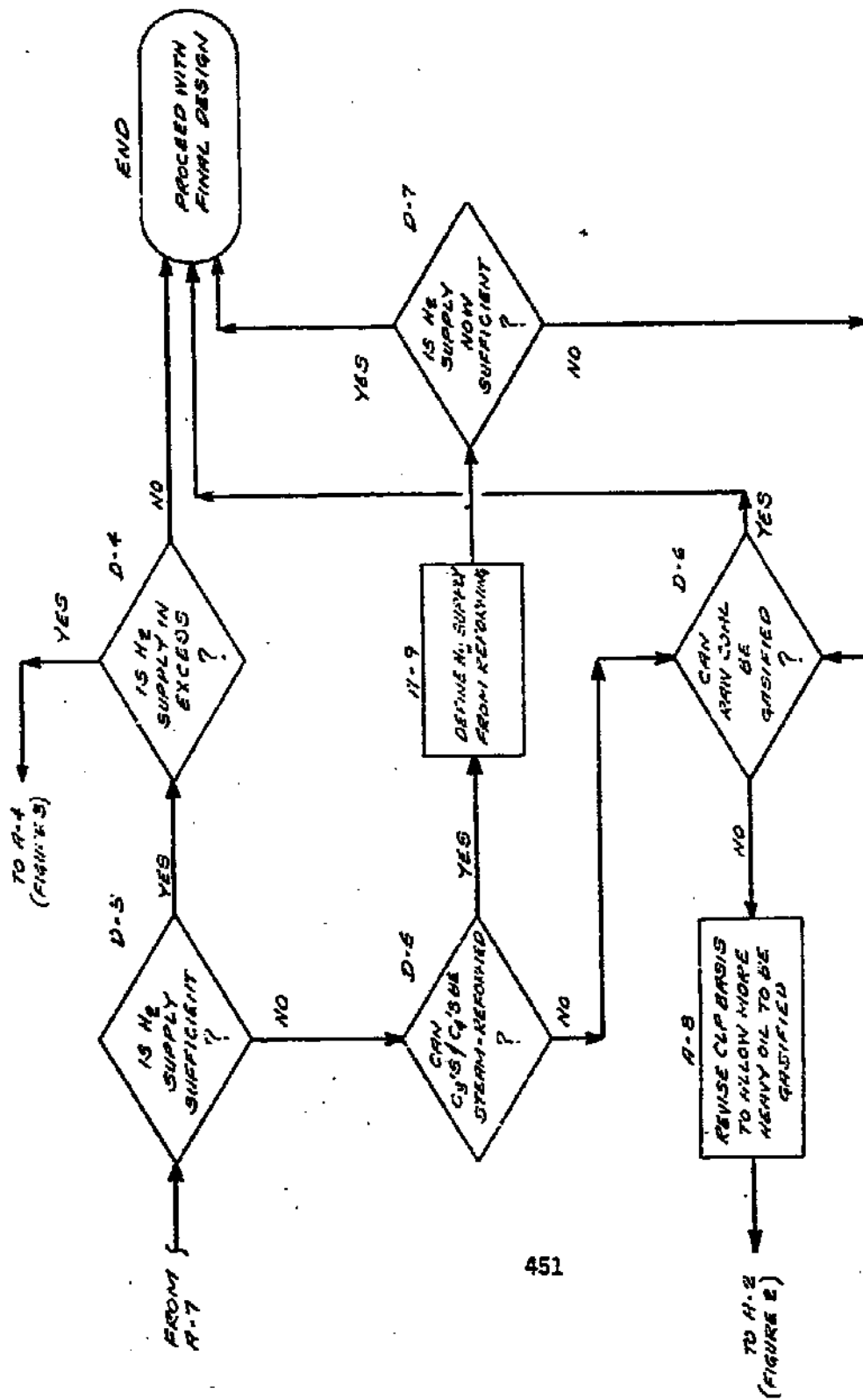
FIGURE 4

PROCESS SEQUENCE DEVELOPMENT -
SELECTION OF ALTERNATE SOURCES OF HYDROGEN

451
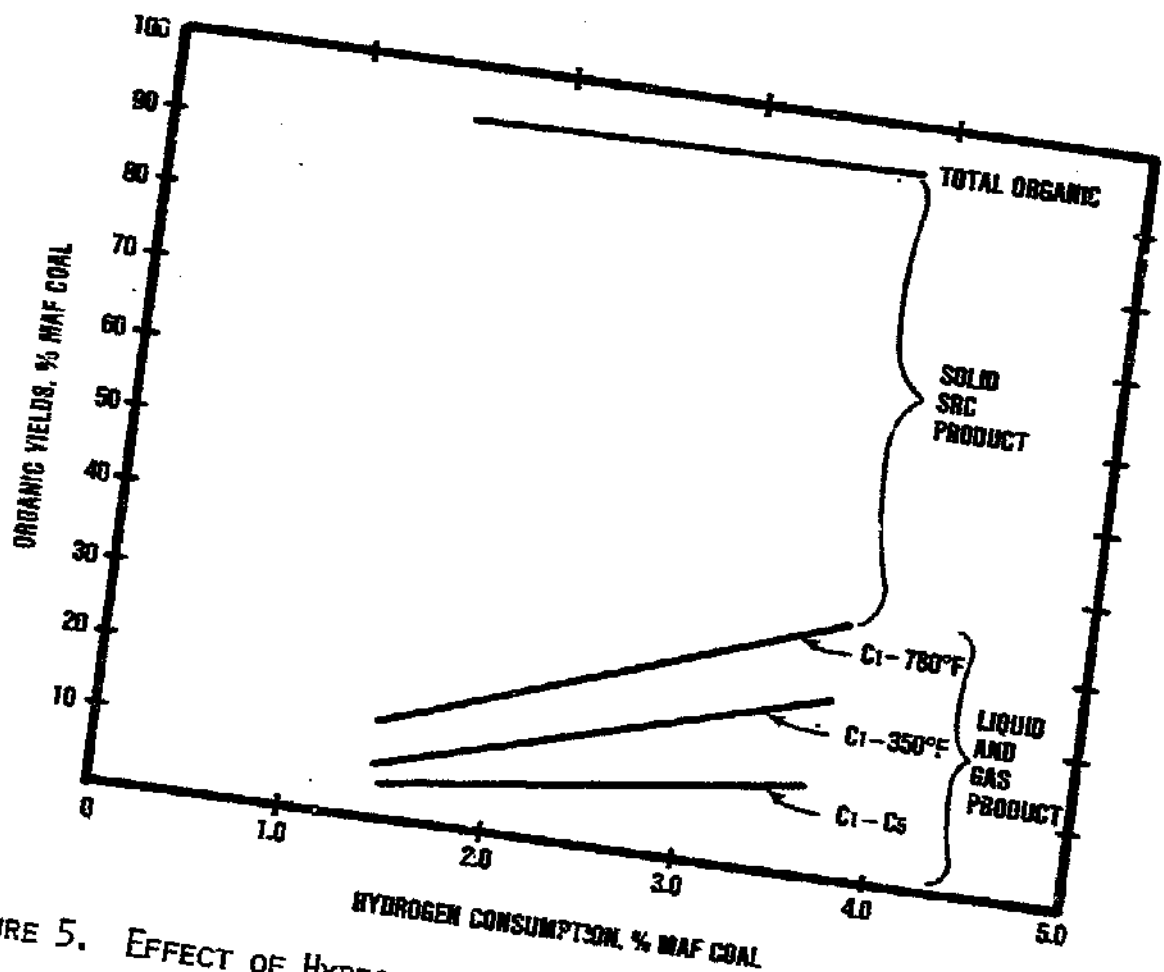
FIGURE 5. EFFECT OF HYDROGEN CONSUMPTION UPON ORGANIC REACTION YIELDS

(Extracted from Wilsonville quarterly report, January through March 1976 for Kentucky 9 and 14 coal)

*Moisture and ash free (MAF)

Chart labels:

ORGANIC YIELDS, % MAF COAL (y-axis): 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100

HYDROGEN CONSUMPTION, % MAF COAL (x-axis): 0, 1.0, 2.0, 3.0, 4.0, 5.0

TOTAL ORGANIC

SOLID SRC PRODUCT

C_1 – 780°F

C_1 – 350°F

C_1 – C_5

LIQUID AND GAS PRODUCT

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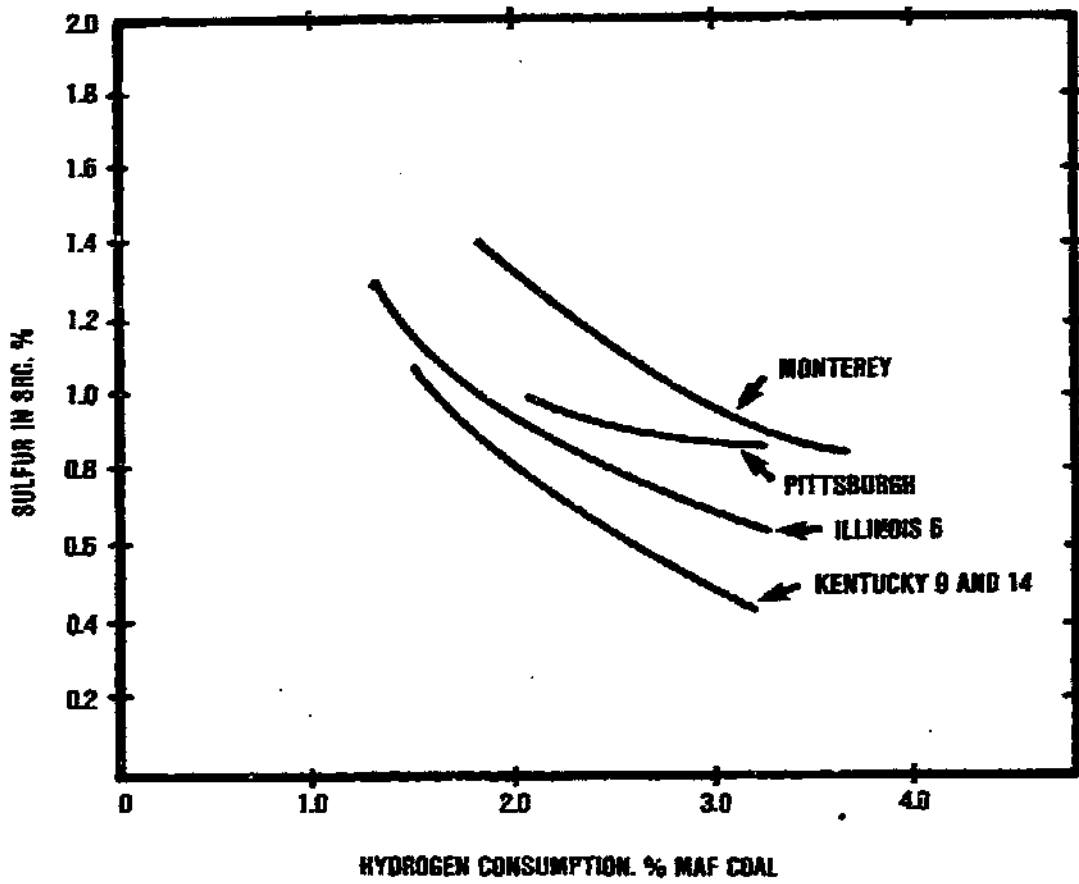
FIGURE 6. EFFECT OF H_2 CONSUMPTION ON SULFUR IN SRC

(Extracted from Wilsonville quarterly report. January—March 1976 for Kentucky 9 and 14. Pittsburgh and Illinois 6 coal)

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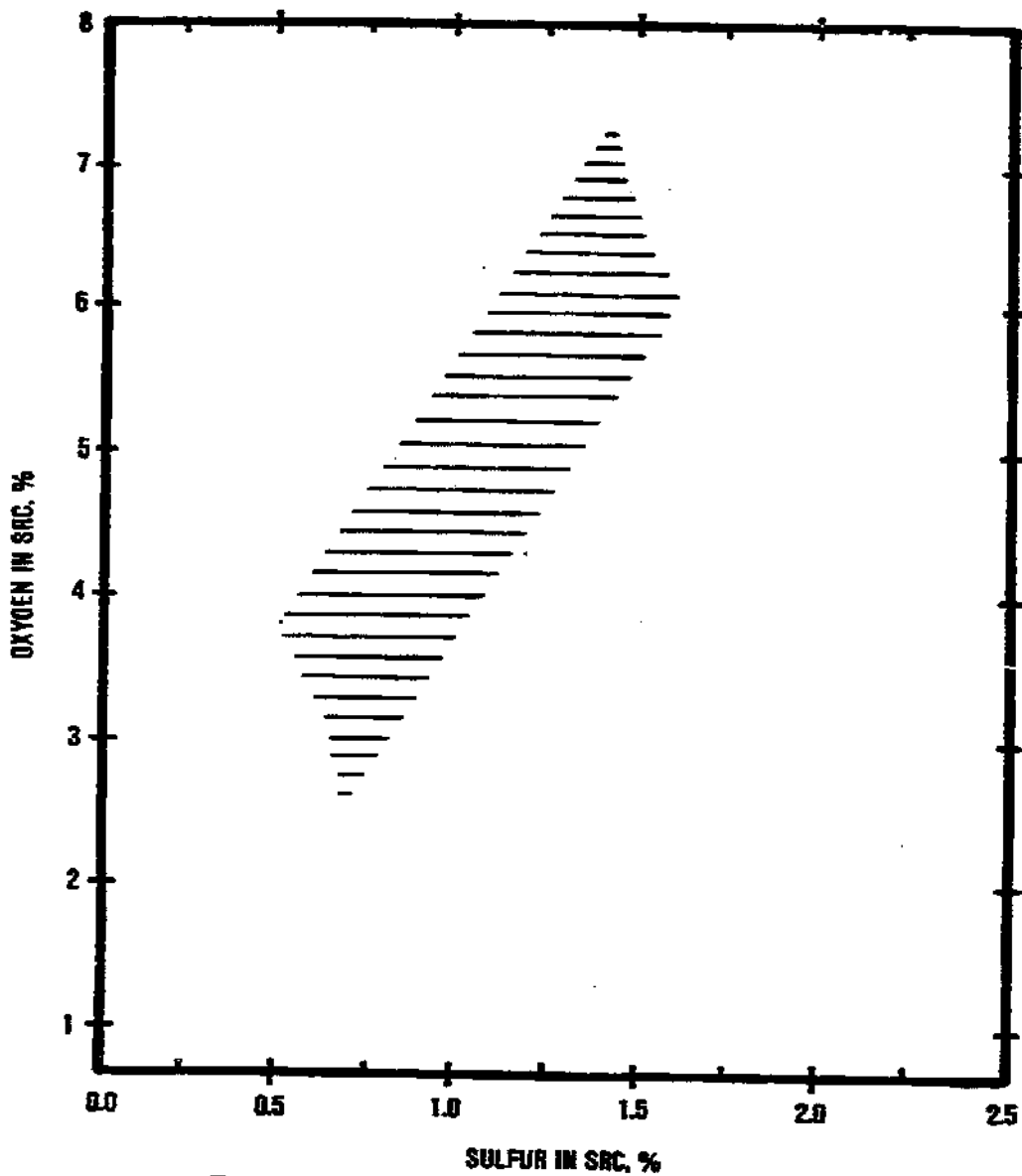
FIGURE 7. SRC OXYGEN CONTENT VS. SRC SULFUR CONTENT
(Extracted from TRW. Inc.. Report on Analysis of SRC Pilot Plant data. Task 12, Final Report. E
(49-18)-2213-TAS-012)

TABLE 1
PROPERTIES OF SYNCRUDES DERIVED FROM COAL

	Arabian Light Crude	Pittsburgh Seam SRC-II Syncrude	Illinois H-Coal Syncrude	Wyodak H-Coal Syncrude	Rerun Illinois H-Coal*	EDS Syncrude Texas Big Brown Coal	COED Syncrude Pittsburgh SRC-I Coal	Synthoil
Gravity, °API	33.4	18.6	25.8	35.1	28.2	29	-14.6	-7.4
Aniline Point, °F	375	-	<30	<32	-	61.3	-	-
Molecular Weight	-	132	147	~130	136	-	-	-
Viscosity, CST at 100°F (122°F)	2.6	2.196	1.645	1.225	-	1.484	-	-
Ramsbottom Carbon, Wt %	0.44	0.70	0.29	0.23	0.30	0.57	-	-
Hot C_7 Insolubles, Wt %	-	0.0469	0.35	0.060	0.0054	0.13	-	-
Ash, PPM	100	40	90	<20	<20	30	-	-
Pour Point, °F	-15	<-80	-	-	-	-	-	-
Bromine No.	-	70	42 ?	26 ?	31 ?	38 ?	-	-
Maleic Diene No., Cg12/g	-	30.7 ?	10.4 ?	3.19 ?	-	-	-	-
Carbon, Wt %	85.0	84.61	86.96	86.20	86.13	86.4	87.80	82.9
Hydrogen, Wt %	13.1	10.46	11.39	12.74	11.44	11.2	6.1	7.3
Sulfur, Wt %	1.7	0.29	0.32	0.04	0.14	0.110	0.89	0.43
Oxygen, Wt %	0.1	3.79	1.80	0.86	1.96	1.92	4.52	2.1
Total Nitrogen, Wt %	0.1	0.85	0.46	0.17	0.33	0.30	2.04	0.9
Iron, PPM	<3	7.6	22	9.0	<1	30	96.0	6800
Arsenic, PPM	-	-	-	-	-	-	-	-
Chloride, PPM	-	50	32	3	34	-	60	-
Hydrogen/Carbon Atom Ratio	1.84	1.47	1.56	1.76	1.58	1.56	0.83	1.06
H_2O PPM	-	6000	2217	<500	-	-	2200	-
Watson K	12.12	10.12	10.43	10.88	10.28	10.62	-	-
TBP Distillation, °F								
51/5	112/219	56/189	56/177	53/156	101/175	53/164	159/943	-
10/30	287/472	241/379	213/333	173/261	181/194	203/317	1017/1161	-
60	655	424	404	354	335	370	[23]	-
70/90	875/-	473/562	476/508	429/535	417/508	452/662	-	-
95/99	-	648/820	654/765	602/705	638/689	799/-	-	-
Paraffins LV %	-	6.4	4.4	9.5	5.4	-	-	-
Olefins & Naphthenes	-	29.2	40.2	46.6	40.3	-	-	-
Aromatics	-	64.4	55.4	44.0	54.3	-	-	-
Reference No.	12	12	12	12	12	19	23	18

* 13 LV % Bottoms Removed From the Illinois Syncrude by Distillation

FIGURE 8[(12)]

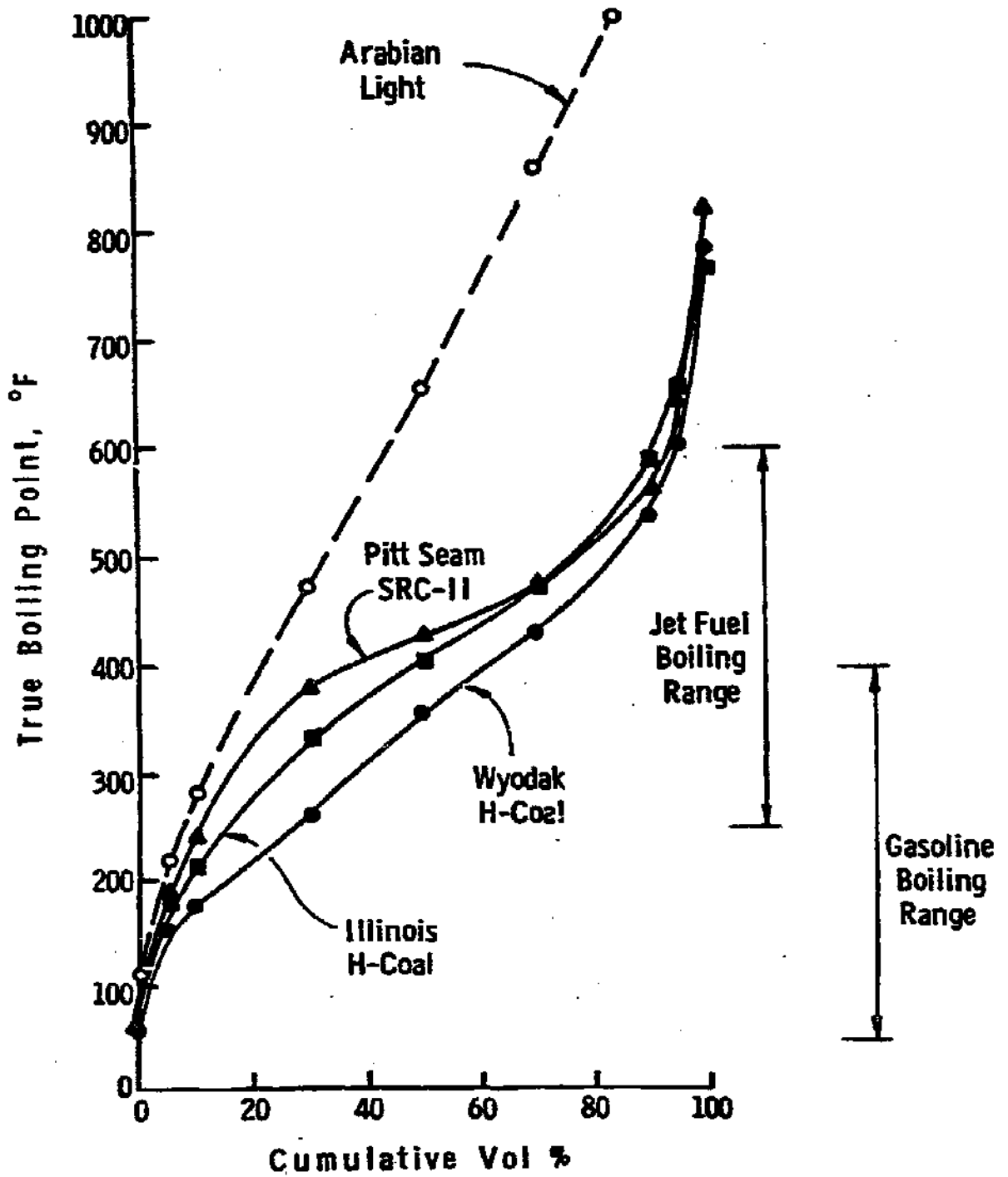## TRUE BOILING POINT DISTILLATIONS FOR ARABIAN LIGHT AND SYNTHETIC CRUDES

TABLE 2

PROPERTIES OF CRUDES DERIVED FROM COAL, OIL SHALE, TAR SANDS

	Arabian Light Crude	Pittsburgh Seam SRC-11 Syncrude	Paraho Indirect Mode Shale Oil	Athabasca Tar Sand Bitumen	Atmospheric Residue from KHAFJI Crude Oils	Coker Liquid from Athabasca Bitumen
Gravity, °API	33.4	18.6	20.2	11.6	14.7	26.5
Aniline Point, °F	-	-	-	-	-	-
Molecular Weight	375	132	326	568	255**	
Viscosity, CSt at 100°F (122°F)	-	2.2	(24.45)	6380*	-	
Ramsbottom Carbon, Wt %	2.6	0.70	2.5	16.11	11.0	
Hot C_7 Insolubles, Wt %	0.44	0.0069	0.2		6.4	
Ash, PPM	100	40	300	200		
Pour Point, °F	-15	<-90	+90		45	
Bromine No.	-	70.7 ?	51	-	-	
Maleic Diene No., Cg12/g	-	30.7 ?	40.6	-	-	
Carbon, Wt %	85.0	84.61	84.3	82.57	83.87	
Hydrogen, Wt %	13.1	10.46	11.3	10.28	11.01	
Sulfur, Wt %	1.7	0.29	0.66	4.86	4.30	3.3
Oxygen, Wt %	0.1	3.79	1.16	1.78	-	
Total Nitrogen, Wt %	0.1	0.85	2.18	0.47	0.27	
Iron, PPM	<3	7.5	70	-	-	
Arsenic, PPM	-	-	28	-	-	
Chloride, PPM	-	-	<0.2	-	-	
Nickel, PPM	-	60	-	112	32	
Vanadium, PPM	-	-	-	180	93	
Hydrogen/Carbon Atom Ratio	1.84	1.47	1.60	1.48	1.58	
H_2O PPM	6000	6000	-	-	-	
Watson K	12.12	10.12	11.32	11.68	12.10	
TBP Distillation, °F						
St/5	112/219	56/189	183/347			180/245
10/10	287/472	241/379	453/610			275/440
50	655	424	736			560
70/90	875/-	473/562	842/963			650/750
95/99	-	642/820	-			795/-
Distillate Yield				Wt %	Wt %	
IBP-380°F Naphtha				3.0	5.8	
380-650 Distillate				14.30	41.0	
650-1000 VGO				27.30	53.2	
1000+ Bottoms				55.40		
Paraffins LV %		6.4	16.8			40.70
Olefins		29.2	30.4			10.97
Naphthenes						included in paraffins
Aromatics		64.4	47.5			48.33
Reference No.	12	12	12	17	21	25

* Poise
** CST at 150°F

TABLE 3

COMPARISON OF HYDROGEN CONTENTS [22]
OF PETROLEUM, SHALE OIL, COAL SYNCRUDE
AND TAR SAND BITUMEN

FEEDS

- Petroleum	11 to 14.5%
- Shale Oil	11 to 12.0%
- Coal Syncrude	9 to 10.0%
- Tar Sand Bitumen	10 to 11.7%

PRODUCTS

- Boiler Fuel	9.0 to 12.0%
- High Octane Gasoline	11.0 to 15.5% *
- No. 2 Fuel Oil	12.0 to 14.0%
- Jet Fuel, Diesel Fuel	13.5 to 14.0%

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*The low hydrogen content may represent a highly aromatic catalytic
 reformate; the high hydrogen content would represent highly iso-paraffinic
 gasoline components of alkylate and FCC gasoline.

TABLE 4

HETEROATOM CONTENT OF TYPICAL PETROLEUM
(ARABIAN LIGHT), COAL SYNCRUDE, AND SHALE OIL (Ref. 22)

	Petroleum	Coal Syncrude	Shale Oil
Naphtha (C_5-400°F)			
%S	0.3	0.1-0.2	0.9
%N	-	0.2-0.8	1.6
Atm. Gas Oil (400-650°F)			
%S	1.4	ca. 0.2	0.7
%N	.01	0.4-1.0	1.6
Vacuum Gas Oil (650-1000°F)			
%S	3.0	0.4-0.7	0.7
%N	.07	1.0-1.5	2.2
Vacuum Residue (1000°F$^+$)			
%S	5.0	-	0.8
%N	0.3	-	2.3

TABLE 5

PROPERTIES OF NAPHTHA DERIVED
FROM SHALE OIL, SRC-II AND BITUMENS

	Typical Petroleum	Hydrotreated Shale Oil		Hydrotreated SRC-II		Hydrotreated Bitumen Coker Distillate
Boiling Range -°F,	C_5-300	C_5-180	180-300	C_5-180	180-300	C_5-300
Gravity °API	66	85	58	61	52	71
Sulfur, PPM	30	-	-	-		1
Group Type -LV%						
Paraffins	43	90	89	30	7	69
Naphthenes	46	9	11	67	90	25
Aromatics	11	1	Trace	3	3	6
Octane No. (F-1,clear)	63	70	51	81	66	58

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TABLE 6

SPECIFICATIONS OF JET-A, JP-4 & JP-8

TEST	JET A SPECIFICATION ASTM D 1655-78
Gravity, °API	37-51
Smoke Point, mm	>20
Freeze Point, °F	<-40
Thermal Stability, JFTOT at 260°C	No. 1 or No. 2 Δ P <25 mm
Aromatics, LV %	< 20
Existent Gum, ppm	< 7
Cu Strip Corrosion, 2 Hr at 212°F	No. 1
End Point, D 86, °F	< 570
Flash Point, °F	>100

TEST	MILITARY JP-4-SPEC	MILITARY JP-8-SPEC
Gravity (°API)	45-57	37-51
Freeze Point (°F)	-72 Max	-58
Combustion (BTU/LB)	18,400	18,400
Flash Point (°F)	-	100 Min
Aromatics (Vol. %)	25 Max.	25 Max.
Olefins (Vol %)	5.0 Max.	5.0 Max
Hydrogen (Wt. %)	13.6 Min.	13.6 Min.
Sulfur (Wt. %)	0.4 Max.	0.4 Max.
Nitrogen (PPM)	-	-

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TABLE 7

DIESEL FUEL AND NO. 2 FURNACE OIL - SPECIFICATIONS

Property	Diesel Specifications ASTM D 975-78		
	No. 1D	No. 2D	
	All Climates	Typical Climates	Cold Climates
Cetane No.	>40	>40	>40
Cloud Point, °F	Varies	Varies	<10
Sulfur % wt.	0.5	0.5	0.5
Flash (P-M), °F	>100	>125	>125
Ash, Wt %	<0.01	<0.01	<0.01
D 86, 90%, °F	<550	540-560	<560
Viscosity at 40°C, cSt	1.3-2.4	1.9-4.1	1.7-4.1
Viscosity at 100°F, SUS	<34.4	32.6-40.1	-
Cu Corrosion	<No. 3	<No.3	<No.3
Aromatics	-	-	-

Property	No. 2 Fuel Oil Specifications D 396-78	
	Typical Climate	Cold Climate
Gravity, °API	>30	>30
Flash, °F	>100	>100
Pour, °F	<20	<0
D 86, 90%, °F	540-640	640
Viscosity at 100°F, cSt	2.0-3.6	1.8-3.6
Cu Corrosion	<No. 3	<No. 3
Sulfur, ppm	<5000	<5000
Aromatics, LV %	-	-

FIGURE 9 [(12)]

PRODUCT NITROGEN VERSUS
HYDROGEN CONSUMPTION

Product Nitrogen, ppm

Paraho Shale Oil

SRC-II

Chemical Hydrogen Consumption,
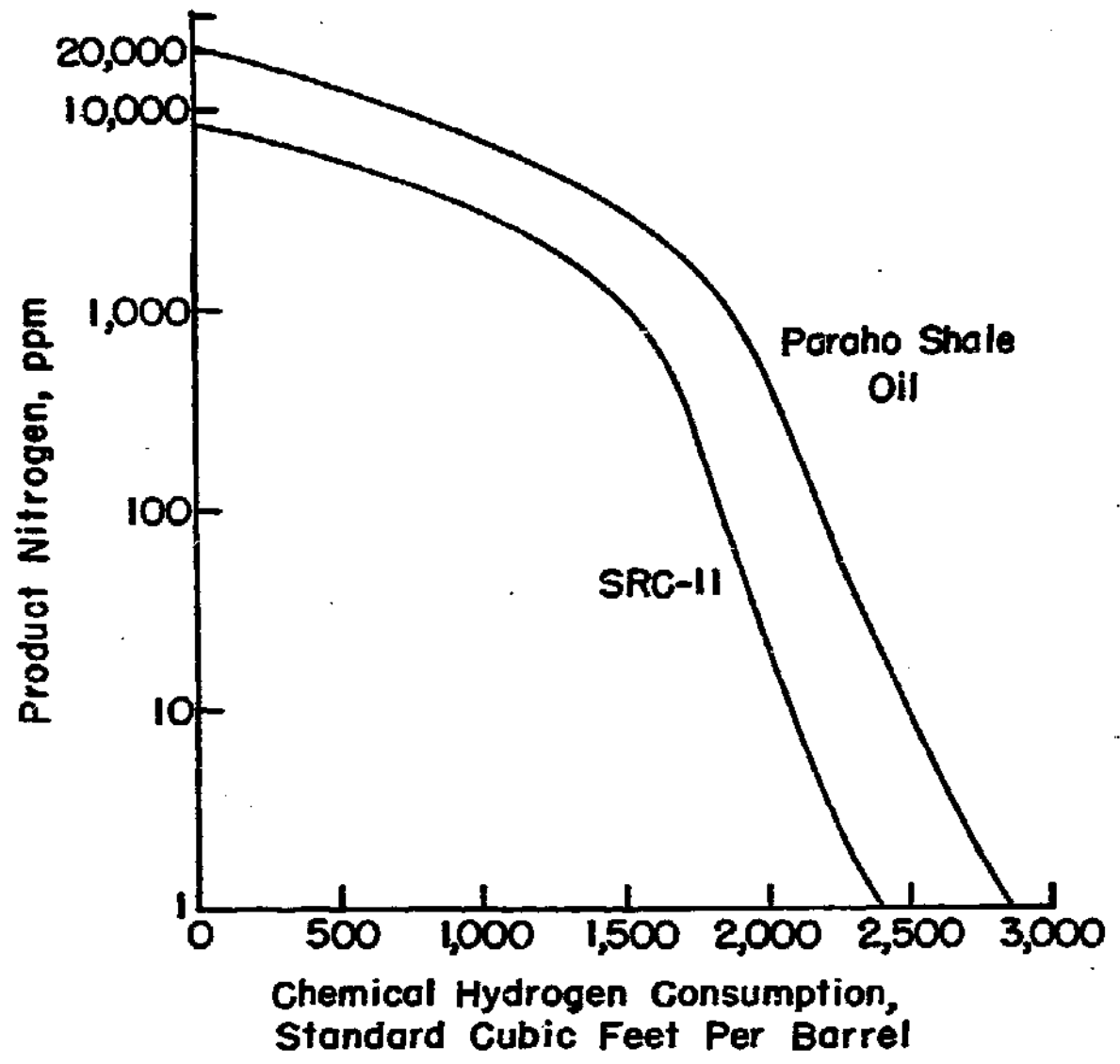Standard Cubic Feet Per Barrel

TABLE 8

PROPERTIES OF SELECTED JET FUELS DERIVED
FROM SHALE OIL, SRC-II, AND TAR SAND BITUMEN

	Acceptable Petroleum Jet A	350-500°F Hydrotreated Shale Oil *	300-535°F Hydrocracked Shale Oil	300-550°F 250-570°F Hydrotreated SRC-II **	280-545°F Hydrotreated Coker Distillate (from Athabasca Bitumen)
Gravity, °API	37-51	42	47	33-36	39
Group Type, LV %					
Paraffins		35	55	3-4	--
Cycloparaffins		45	40	93-87	--
Aromatics	<20	20	5	4-15	32
Smoke Point, mm	>20	21	35	20-23	13
Freeze Point, °F	-40	-42	-65	-75 to -95	<-77
Nitrogen	*	2	0.1	0.1	4

	*	**
Catalyst	ICR-106	ICR-106
Catalyst Temp., °F	750	775
LHSV, hr⁻¹	0.5	0.6
Total Pressure, PSIG	2,499	2,199
H₂ Pressure, PSIA	2,306	1,83?
H₂ consumption SCF/Bbl	3,109	1,9?

*In addition, severe stability requirements mean that heteroatom content must be very low (usually the nitrogen content is less than 10 ppm for petroleum-derived jet fuel).

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TABLE 9

PROPERTIES OF SELECTED DIESEL FUELS DERIVED
FROM SHALE OIL, SRC-II AND TAR SAND BITUMEN

	Typical Petroleum	350-650°F Hydrotreated Shale Oil	350-600°F Hydrotreated Shale Oil Coker Distillate	350°F+ Hydrotreated SRC-II	310-630°F Hydrotreated Coker Distillate (Athabasca Bitumen)
Gravity, °API	>30	38	41	29	26
Cetane No.	>40	46**	48	39	34
Pour Point, °F	<+15	-5	-20	-55	<-59
Group Type, LV %					
Paraffins		37	41	4-7	-
Naphthenes		44	41	70-93	-
Aromatics		19	18	2-23	44
Nitrogen, ppm*	*	350	350	0.1-0.5	25

*Heteroatoms must be removed to level required for stability (usually <500 ppm N for petroleum).

**Estimated.

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