



The effect of pressure on the catalytic upgrading of solvent refined coal
by I-Hsing Tsao

A thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

A catalytic hydrotreating (hydrodesulfurization, hydrodenitrogenation, and hydrocracking) experimental study of coal-derived liquid SRC-II was carried out at elevated pressures from 1000 psi to 2000 psi. SRC-II Light Ends Column Feed (LECF) was upgraded in a trickle-bed reactor into a liquid feedstock containing less than 0.3 wt.% nitrogen. Hydrotreating at 2000 psi extended the longevity of both commercial and MSU fabricated catalysts significantly. Results obtained from experiments carried out at various operating pressures showed that higher pressures gave better denitrogenation and hydrocracking.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

March 1983

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of a thesis submitted by

I-Hsing Tsao

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Date

Lloyd Berg
Chairperson, Graduate Committee

Approved for the Major Department

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Date

John T. Sears
Head, Major Department

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Michael Malone
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ACKNOWLEDGEMENT

The author wished to thank the faculty and staff of the Chemical Engineering Department at Montana State University for their encouragement and help. A special thanks goes to Dr. Lloyd Berg, director of this research, and Dr. F.P. McCandless for their guidance.

Appreciation is extended to Lyman Fellows for his fabrication and maintenance of research equipment, Turgut Sahin and Dr. Nam Kim for their many suggestions.

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ABSTRACT

A catalytic hydrotreating (hydrodesulfurization, hydrodenitrogenation, and hydrocracking) experimental study of coal-derived liquid SRC-II was carried out at elevated pressures from 1000 psi to 2000 psi. SRC-II Light Ends Column Feed (LECF) was upgraded in a trickle-bed reactor into a liquid feedstock containing less than 0.3 wt.% nitrogen. Hydrotreating at 2000 psi extended the longevity of both commercial and MSU fabricated catalysts significantly. Results obtained from experiments carried out at various operating pressures showed that higher pressures gave better denitrogenation and hydrocracking.

INTRODUCTION

The industrial world is in the early stages of a major energy transition. On the horizon we can clearly discern the beginning of the end of the petroleum age, and the world is starting to shift from a primary dependence on oil and gas for energy to the use of a broader, and much more diversified, mix of energy resources. Figure 1 presents a recent projection of the energy supply picture for the United States up to the year 2000 [1]. Figure 2 shows the relative contributions of various energy resources. Coal will be the most important resource as the oil contribution decreases.

COAL

Coal is the most abundant available energy resource both in the United States and worldwide. US coal production -- about 780 million tons in 1979 -- is expected to triple by the year 2000, with about 30% being used in the manufacture of synthetic fuels. Coal is a generic term covering a broad range of carbonaceous materials which differ in origin, geological age, properties, composition, and structure. Coals are classified (or ranked) as lignite, sub-bituminous, bituminous, and anthracite. This is the

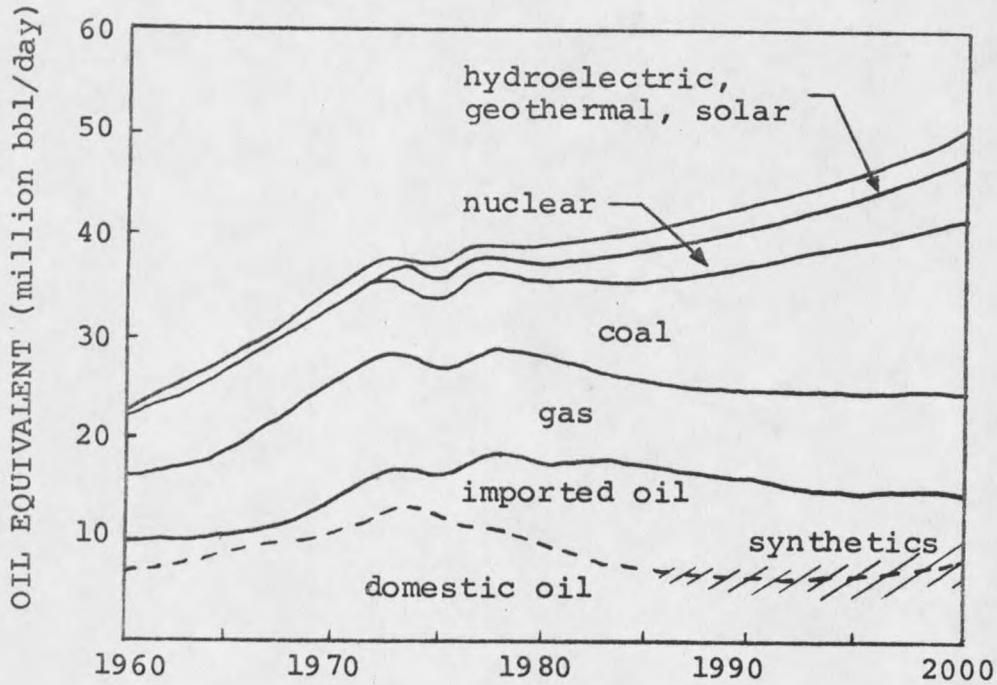


Figure 1 Changes in the total US energy supply and in the amounts of energy deriving from different sources are recorded for 1960-80 and projected for the year 2000. [1]

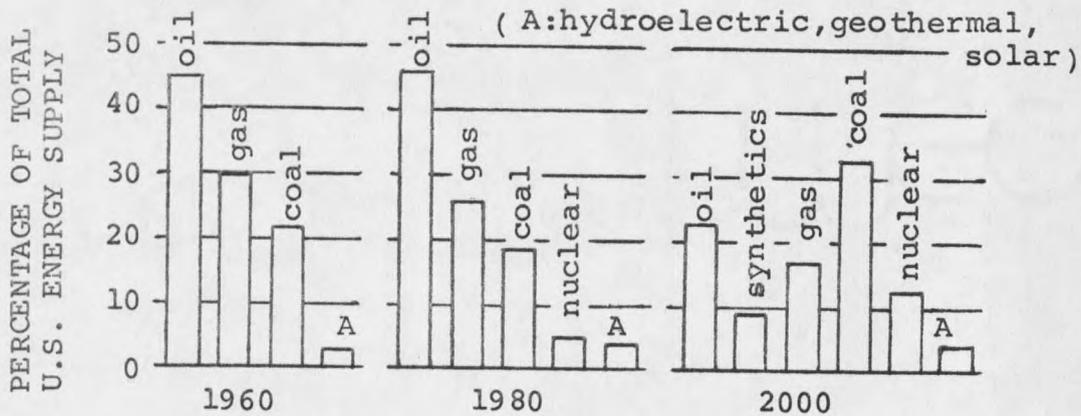


Figure 2 The contributions to the total US energy supply of the sources plotted in Figure 1.

order of increasing aromatic content and decreasing volatile matter and moisture. It is also roughly the order of increasing heat content. Wender[2] has suggested the simple structural models in Figure 3 for visualizing changes in rank.

Coal is basically an organic sedimentary heterogeneous rock with discrete inorganic inclusions and an ultrafine capillary pore-like structure. The actual organic structure of coal has been debated actively, and various molecular models have been proposed. In one such model for a bituminous vitrinite -- the principal organic component of coal -- the main types of linkage bridging the polynuclear clusters are short aliphatic groups and various kinds of heteroatom linkages, such as oxygen (ether) and sulfur (sulfide) bonds. There are also a large number of partially or wholly saturated aromatic structures, which, together with the short aliphatic bridges, impart a good deal of nonplanarity to the vitrinite structure, resulting in cavities between clusters and layers in which water or other small molecules can reside. Present also are oxygen, sulfur, and nitrogen heterocyclic structures.

COAL TO LIQUID

The conversion of coal to clear liquid fuels requires not only a reduction in molecular weight and removal of

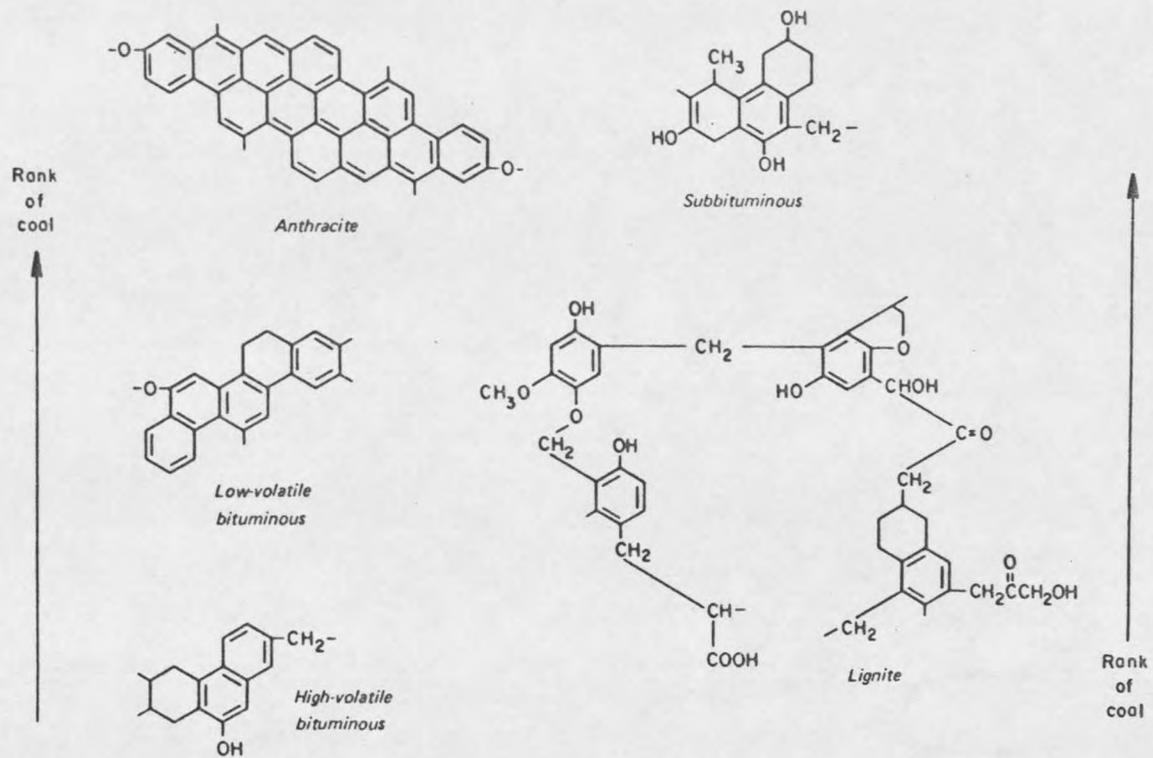


Figure 3 Representative partial structures of different ranks of coal

heteroatoms but also a substantial increase in hydrogen-to-carbon ratio. There are essentially four general methods for the liquefaction of coal: pyrolysis, gasification followed by synthesis (indirect liquefaction), hydroliquefaction (direct liquefaction), and solvent extraction. The basic technologies for each have been known for at least fifty years, and several conversion processes have been used commercially (ref. Table I). However, continued innovative research is expected to lead to more economical and more efficient technologies for the conversion and utilization of coal as a clean fuel.

Table I: Coal conversion processes dating from at least 50 years ago [1]

Gas from coal	1780 Fontana: $C + H_2O \rightarrow CO + H_2$ 1902 Sabatier: $CO + 3H_2 \rightarrow CH_4 + H_2O$
Liquids from coal	1867 Berthelot: $Coal + H_2$ 1910 Bergius: $Coal + H_2$ 1925 Fischer-Tropsch: $CO + H_2$
Chemical/tars from coal	late 1800s Coke ovens early 1800s pyrolysis

The addition of hydrogen to coal is done most simply in the solvent refined coal (SRC) process. Interestingly enough, this process was originally designed to remove ash from coal, thereby making it more economical to transport and more valuable in combustion. This involved taking the coal through a liquid phase, at which point the hot ash is separated out. But some knotty problems developed at this

point. Through a series of modifications, these problems unraveled and a new liquefaction process was born [3].

The process has two variations. In variation one (SRC-I), shown in Figure 4, crushed coal is blended with a process-derived oil and pumped through a slurry heater and reactor at temperatures of about 850°F (450°C) and hydrogen pressures of about 2000 psi (13.8 MPa). This breaks up the heavier, more carbonaceous molecular structures, producing more volatile compounds. Although the hydrogen-to-carbon ratio of the product does not differ very much from that of the coal used, considerable hydrogen is consumed (Table II) [4]. The product mixture is separated into gases and lighter oil which can be recycled to make a slurry, a heavy product called solvent refined coal (a tar-like solid used as a boiler fuel), and the unreacted coal and ash residue. The latter fraction can be gasified with oxygen and steam to make the hydrogen required. In variation two (SRC-II), shown in Figure 5, the existing ash, notably containing pyrite, is used as a catalyst to enhance conversion and the yield of a lighter distillate fraction. The product is liquid at room temperature and hydrogen consumption is greatly increased over that of SRC-I, as is the gas production. In contrast to SRC-I, the hydrogen-to-carbon ratio of the liquid is increased over that of the original coal. Figure 6 shows the hydrogen-to-carbon ratios of SRC-I and SRC-II products.

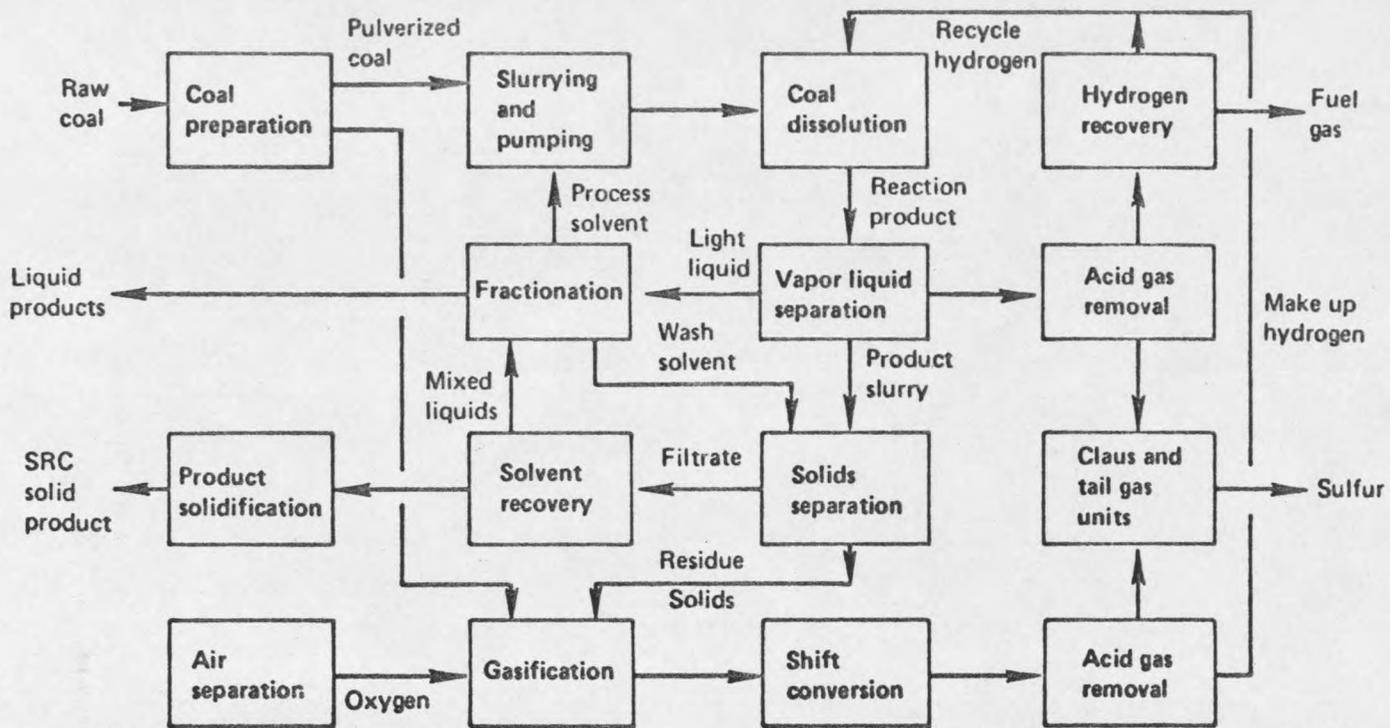


Figure 4 SRC-I process, without the addition of catalysts

Table II Hydrogen consumption and hydrocarbon yields from SRC processes

	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)
Hydrogen consumed, standard cubic feet per ton of coal ^a	7,400	15,500
Process yields, based on coal		
Light gases, pounds per ton of coal		
CH ₄	50.7	116.8
C ₂ -C ₃	62.7	163.2
Liquid hydrocarbons, barrels per ton of coal		
C ₄ -380°F	0.44	0.96
380-650°F	0.30	1.07
650-1000°F	0.16	0.20
1000°F+ (SRC)	2.47	1.11
Total C ₄ + liquids	3.37	3.34
C ₄ -1000°F liquid, vol %	26.7	66.7
Hydrogen consumed per C ₄ -1000°F liquid, standard cubic feet per barrel	8,200	7,000
Ratio of CH ₄ to H ₂ consumption, pounds per million standard cubic feet	6.8	7.5
Ratio of CH ₄ to C ₄ -1000°F liquid, pounds per barrel	56.3	52.4

^aAs received. Hydrogen externally supplied.

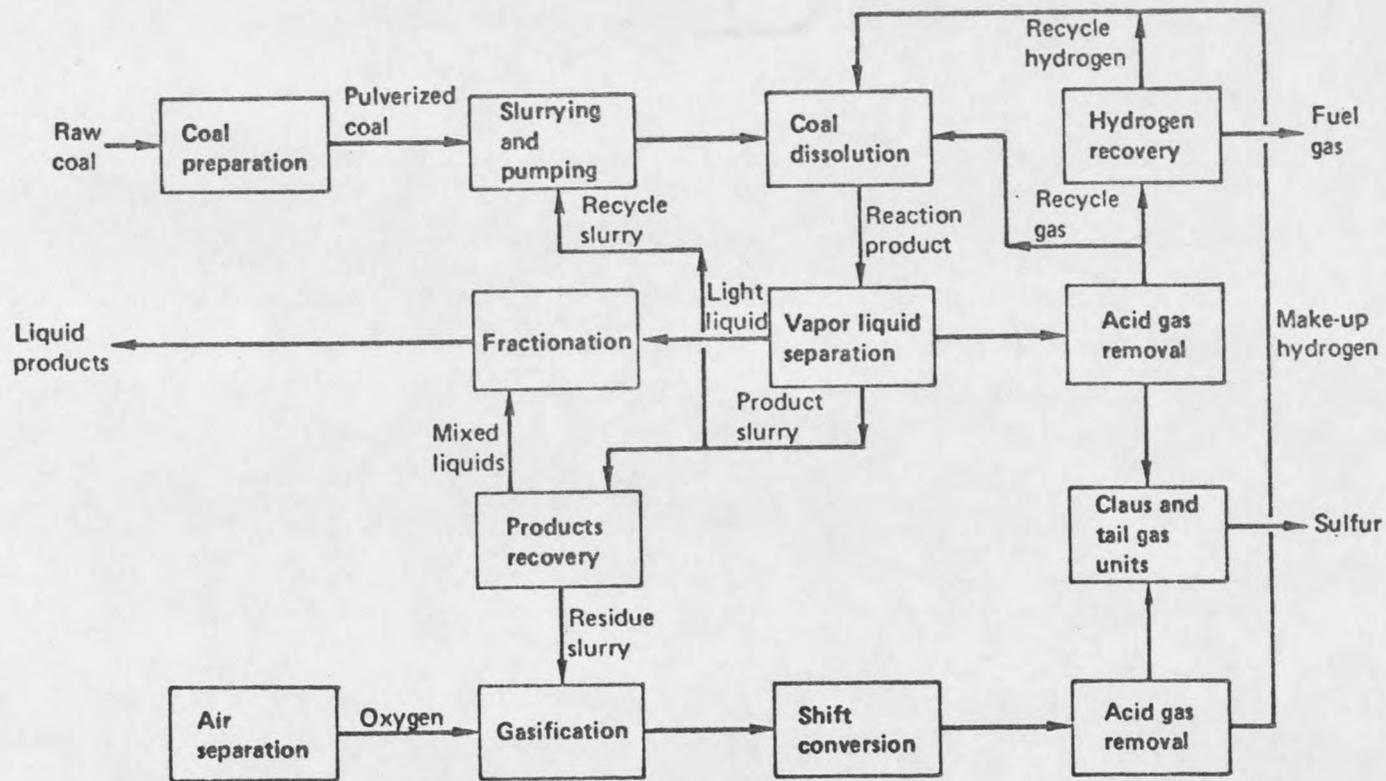


Figure 5 SRC-II process, with catalysts

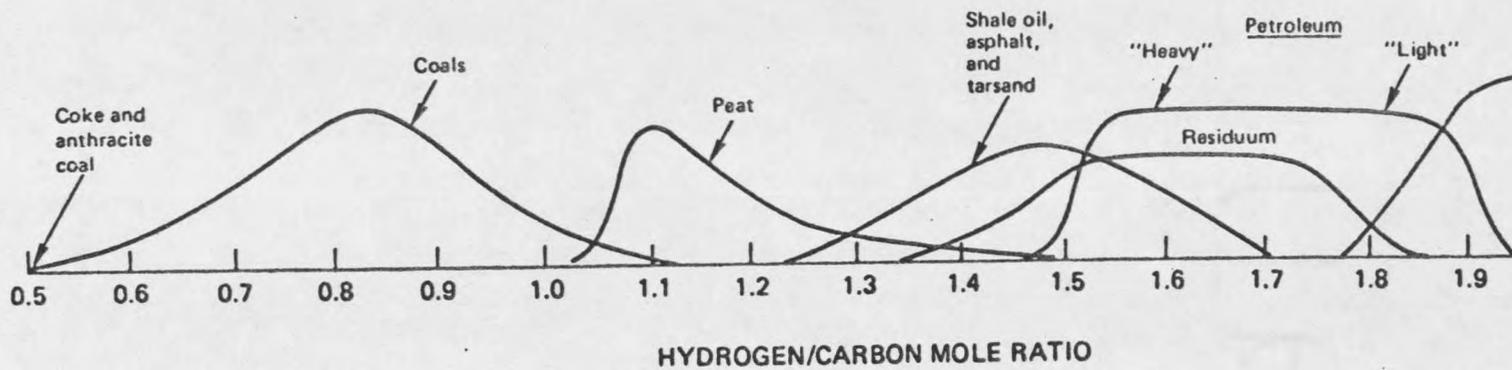
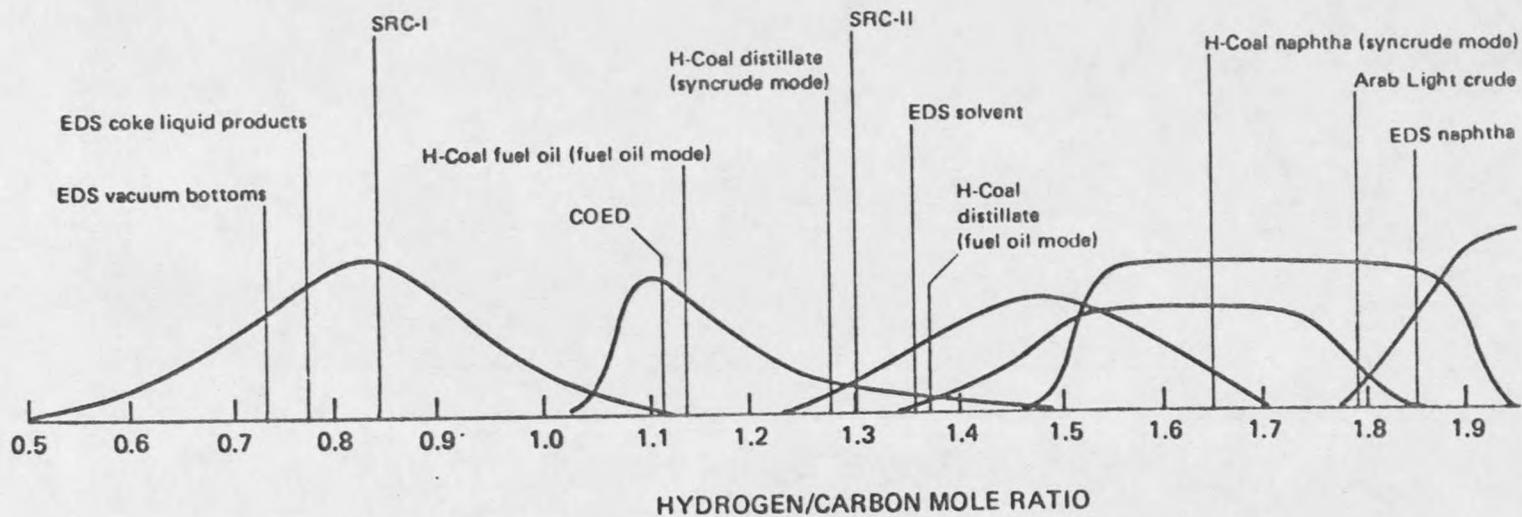


Figure 6 Hydrogen/carbon ratios for various hydrocarbon sources, end products and products of coal liquefaction [4]

LIQUID PRODUCT OF SRC-II

The SRC-II product cannot be considered as a single product from the process. Various products of SRC-II process are produced in different plants. Of major concern to this research are the products from the SRC-II process operated by Pittsburg and Midway Coal Mining Company (P&M). Properties of P&M's SRC-II Light Ends Column Feed (LECF) are shown in Table III. The chemical constituents of SRC-II liquids products are complicated. Unlike conventional petroleums, coal-derived liquids are characterized by the presence of significant quantities of polynuclear aromatic hydrocarbons and heteroatom-containing polynuclear aromatics [5,6]. These differences in chemical composition necessitate that synthetic crudes be subjected to hydrogenation/hydrogenolysis in order to remove most of the polynuclear aromatic hydrocarbons and sulfur-, nitrogen-, and oxygen-containing aromatic compounds prior to refining.

UPGRADING SRC-II LIQUID PRODUCT

The most effective way to use SRC-II liquid products at first may be to replace petroleum fractions now being used for boiler fuels with solvent refined coal that has undergone a minimum of refining. The petroleum fractions now used in boilers could then be refined to lighter products. If SRC-II liquids are put through a mild to moderate hydrotreating step to stabilize them and remove

Table III Properties of SRC-II Light Ends
Column Feed (LECF)

% Carbon	—*
% Hydrogen	—
% Nitrogen	0.67
% Sulfur	1.21
% Oxygen	—
% Ash	0.02
Sp. Gravity 60/60 F	0.983

ASTM D-86 Distillation	F
IBP	122
5 %	217
10%	288
20%	381
30%	446
40%	488
50%	541
60%	577
70%	611
80%	660
90%	727
95%	795
End point	956

* Data not available

