The process has been tested primarily on solvent refined coal. However, Conoco has run enough other coals through the reactor to claim that it is versatile and will accept a wide variety of coals. The coal is fed to the reactor in roughly one-to-one proportion with zinc chloride. The reactor temperature is around 700-800° F while hydrogen pressures varied between 2000 and 3500 psi. Yields of 75% distillate, based on coal (MAF) to the reactor, have been reported; this yield estimate does not include coal required to make hydrogen. Hydrogen consumption of 6-8% (based on feed coal) has been reported.

The significant fact is that two-thirds of the distillate produced is C_5-200° C, which makes it suitable for facile conversion to gasoline. By comparison, SRC II and EDS consume 5% and 4% of hydrogen, respectively, based on coal feed to the reactor. But only 48% and 34% of the respective product yields are in the distillate range, while still smaller fractions are in the gasoline range.

Catalyst losses were estimated at about a pound per barrel. This loss seems acceptable considering that zinc sells for about 40-50¢/lb. The corrosion-resistant materials of construction used are Inconel 600 and hastaloy.

The nitrogen and sulfur contents of the products are quite low. For example, 3.5 ppm S and 6.6 ppm of N in the naphtha to 400 ppm S and 150 ppm N in the resid are reported. Comparable S and N figures for H-coal and SRC are 100 times higher.

Problems which have been reported relate to the stirrer configuration, long-term corrosion, valve life, and optimization of materials. Workers at Conoco have properly emphasized the need to run the PDU for long times to facilitate estimations of corrosion data, steady-state product outputs, and general problem identifications.

Chemical mechanisms are not well understood. Carbonium ion mechanisms were proposed and ring protonation was hypothesized, but there seems to be no clear corroboration for these views. Furthermore, the precise role of hydrogen, its impact on forward rates, carbonium ion concentration, side reactions, and melt life are all unstudied.

Obvious questions are the following: How low can the hydrogen pressure be before coking sets in? What is the minimum residence time in the reactor? What is the impact of water vapor on yield, melt life, reaction kinetics? Can new rate promotors be found, e.g., BF_3?

D. Chemical Problems

The problems encountered in the $ZnCl_2$ conversion of coal all seem to arise from the novelty of the process. Specifically, how does one move molten and fairly viscous $ZnCl_2$ solutions around and avoid corrosion and galling? Obvious chemical problems concern regeneration of $ZnCl_2$ and the related problem of what to do with SO_2.

Some of the operating difficulties appear to be traceable to the lack of quantitative and qualitative understanding of the chemical processes that occur. A possible model for the "$ZnCl_2$-catalyzed" conversion of coal is that it is related to work done at Exxon by M. Siskin [J. Amer. Chem. Soc. 94, 3641 (1974)]. Siskin showed that benzene in very strong Lewis acids (TaF_5-HF) could be reduced by molecular H_2. A suggested mechanism involves abstraction of a hydride ion from molecular hydrogen by a carbonium ion. This step would be a crucial distinction between the $ZnCl_2$ conversion and other processes. There is also a plausible related model in which molten $ZnCl_2$ does not serve as a Lewis acid but rather as a Bronsted acid. The H_2O, alcohols, phenols, etc., could generate very strong acid solutions which generate carbonium ions for reduction by hydrogen.

The conversion process is remarkably selective and no explanations have been given about what the selectivity is based on. One of our members noticed that the relatively low observed gas yields, especially of butane, impugn the hypothesis that hydrocracking is the basic mechanism in coal conversion using $ZnCl_2$.

The inorganic chemistry involved in regenerating $ZnCl_2$ seems to be reasonably well understood but may well turn out to be more complex than is now believed to be the case. The approach to regeneration appears to be sound.

While we are impressed with the quoted recovery yields of 99.7%, we note that this performance has not been adequately demonstrated on a steady-state basis.

Physical properties (e.g., viscosities) of coal-H_2-$ZnCl_2$ mixtures should be measured. The solubilities of different components may be partly responsible for some selectivity in coal hydrogenation.

E. Program Recommendations

We believe that the areas of R and D represented by the $ZnCl_2$ process are important. In order to make progress in this area, the attractive and innovative technology involved must be pursued in an imaginative and inventive fashion, including work on the fundamental chemistry.

Significant information may be obtained from bench-scale tests, provided that these are carefully integrated with supporting research and analysis. Generally, FERWG members believe that this process would profit from augmented research performed by a cooperating university group.

We regard the Conoco pilot-plant housekeeping as excellent. We view the program difficulties that have been encountered as reflecting technical and engineering difficulties, as well as the lack of adequate research support, which is especially important for new and innovative technologies.

F. Historical Comment on the Z_nCl_2 Process

Hydrogenation of coal is nearly 100 years old as a laboratory curiosity and some 50 years old as a commercial reality. The step from the former to the latter was blocked until a satisfactory catalyst could be found. The early history and basic contribution of the developer (I. G. Farben) is expertly summarized in the monograph by W. Krönig: "Catalytic Pressure Hydrogenation". Krönig notes that separation of the process into two steps (liquid-phase hydrogenation followed by vapor-phase hydrocracking) made commercialization possible in the first place; the second key development was the discovery of sulfur-resistant catalysts.

In the first step, disposable catalyst is used, which is discarded with the ash (while some 90% of the organic coal substance is converted to a vaporizable oil and some gas). These disposable catalysts (usually tin or iron) are only marginally effective and, therefore, recourse was taken to some drastic operating conditions: 3,500 to 10,000 psi pressure.

The feed to the second step is ash- and metal-free; more effective catalysts could be used in bulk (usually tungsten sulfide is employed on various supports). The product from this second step, the vapor-phase, was effectively cracked down to the motor fuel boiling range.

In spite of major efforts, no significantly different catalysts for coal hydrogenation were developed for about thirty years; the same catalysts were still used in the Bureau of Mines pilot plant at Louisiana, Mo., in 1950. In the interim, the U.S. petroleum industry successfully commercialized the large scale use of supported cobalt-molybdenum catalysts for hydrocracking and hydrofixing of petroleum. When interest in coal liquefaction grew again in the U.S., these catalysts were applied to the processing of coal and coal extract. Developments sponsored by DOE now cover various systems, either based on the old I.G. Farben disposable catalysts (iron, etc.) or based on cobalt-molybdenum catalysts in a variety of configurations (circulation of donor solvent, ebullating beds, and combinations of these two). All four of the major hydroprojects are single-step systems operating at similar pressures (1,700 - 2,000 psi) and, as would be expected, their product distribution differs substantially from the old I.G. Farben sump-phase by a greatly reduced yield of vaporizable product (about 1/2 of the feed-coal); work-up of the residues is, thus, a major processing step.

Using a different version of the German sump-phase, CCDC had concentrated on a two-stage liquefaction concept, which lowered the severity of the first step to a point where <u>no</u> vaporizable product results, thus permitting operation at less than 500 psi while completely eliminating the need for gaseous hydrogen (only donor solvent is used). The resulting heavy liquid (extract) is separated by hydroclones and is then hydrocracked over cobalt-molybdenum catalysts in an ebullating bed (H-Oil process) at appropriately severe conditions, depending on the desired product boiling range.

The purpose of the foregoing comments is to show that workers on hydrogenation of coal have never been able to get around the limitations imposed on processing by inherent constraints. This observation applies to both disposable or heterogenous catalysts requiring fairly "clean" feedstock, in spite of very large efforts over many decades to get around this hurdle.

The use of molten zinc chloride was originated by Everett Gorin at CCDC about 15 years ago and opened the door to an entirely different approach. With this reagent/catalyst, it is possible to convert coal (even some of the less reactive varieties) at the H_2-pressure levels currently favored in one single step to high quality motor fuel. The conversion is amazingly selective, the yield of CH_4 is substantially lower than that obtained by other catalysts and the boiling range is "narrow" by comparison; there is effectively no residual fuel oil to dispose of. It should be noted that we are dealing with a single-stage process. If one were to list the optimum results desired from a coal-hydrogenation catalyst, one would describe those obtained with molten $ZnCl_2$.

In chemical terms, $ZnCl_2$ permits the direct conversion of the notoriously complex coal molecule to a mixture of single-ring aromatics plus isoparaffins in over 70% yield, based on MAF coal.

One of the interesting aspects of the process is the apparent suppression of carcinogens in the product. This is not a minor consideration, given the findings of various laboratories regarding the high level of apparent carcinogens in the liquids resulting from virtually all hydrogenation processes currently developed by DOE. In contrast, recent tests at MIT have shown that the $ZnCl_2$-naphtha has virtually the same lack of any significant mutagenic activity as, for example, Amoco unleaded gasoline. Given the great concern about carcinogens, this finding alone warrants real interest in this reaction.

1. The Drawbacks

One difficulty, recognized immediately and the subject of concentrated attention, is the nearly quantitative reaction of $ZnCl_2$ with the hetero-atoms in the coal (O, N, S), which requires the continuous regeneration of the melt. In principle, this is achieved by atmospheric pressure flash-distillation of the clean $ZnCl_2$ (it boils at 1,300° F). In a fluid sandbed, the heat is furnished by burning the 6-8% of unconverted coal, which remains in the spent melt, with air. At the same time, the O, N, and S compounds of Zn are reconverted to $ZnCl_2$, H_2O, N_2, and SO_2. This procedure was worked out to minimize the losses of of zinc.

The other difficulty is the corrosive nature of the system, which calls for special materials (Incolay in particular) and the inherent difficulty of handling a molten salt ($ZnCl_2$ melts at 590° F); this difficulty is particularly severe when operating at the small scale of bench tests or even at the PDU level, a fact which has admittedly not been properly weighed by CCDC.

2. The Effort to Date

The $ZnCl_2$ reaction was studied with both coal and coal extract as feed on bench-scale continuous equipment, as was also melt regeneration; the initial effort was sponsored by OCR (now DOE); $1.4 million were spent over three years. This program was followed by further R&D, mostly on catalyst regeneration; $0.4 million was spent by CCDC on this phase. In 1975, ERDA (now DOE) contracted to explore the process on the PDU scale (1 ton/day). A total of $11.5 million were spent during the next five years.

After a reconfirmation of the basic concept, the PDU was approved and this has been the main effort since 1977.

The system presented a whole series of new mechanical problems and considerable time was lost before the hydrogenation and the regeneration could finally be tested. Up to this time, the basic hydrogenation reaction had never failed to yield the products and product quality, which made the system exciting in the first place. The mechanics leave a great deal to be desired; the existing hydro-reactor uses stirrers to assure contact between gas and melt, and agitation with H_2-gas alone (sparging) would be desirable. Insofar as it is possible to tell, there exist no problems which appear beyond correction by improved engineering and adequate supporting research.

In summary then, for about $14 million spent to date, the door has been opened to a fundamentally novel type of hydrogenation system, which offers evident advantages over the known art.

Economic appraisals based on the small available data base are not very useful, but several studies which were completed all suggested some advantages compared with other multi-stage hydrogenation systems producing equivalent products.

AC-5. COMMENTS ON THE
DOW COAL-LIQUEFACTION PROGRAM
(NOVEMBER 19, 1979)

A review of the Dow coal-liquefaction program was presented at the UCSD Energy Center in La Jolla to the following FERWG members: Clardy, Furlong, Penner, Ross, Sieg, and Squires. Dr. I. Wender of DOE participated in the presentations and discussions. The presentations were made by V. May and N. Moll, who were accompanied by G. A. Klumb, Jr.

The Dow program dates back to 1973-74 when feasibility studies were performed on the processing of coal-derived oils. Initiation of coal-liquefaction development dates back to 1974. During the period 1974-78, work was performed in a miniplant, utilizing first 0.1 lb of coal per hour and then 1 lb of coal per hour. The largest unit that has been operated thus far processed 10 lbs of coal per hour. Actual experimental work was terminated in 1978. A program plan for substantial scale-up was developed during 1979, at which time both process patents and research reports were issued.

All of the work done with the Dow process involved liquefaction of Pittsburgh #8 coal (which contains about 3.5% of sulfur). The process configuration, catalyst description, product output, process variables, costing, etc. were clearly defined in handouts provided by the Dow group.

Compared with the major DOE-supported programs on coal liquefaction, this process shows two novel and potentially important and useful features involving the catalyst feed and the deasphalting system.

A. The Dow Catalyst

The Dow catalyst is a molybdenum compound. The active species formed from the catalyst feed, which is added to the slurry at a level of about 100 ppm of Mo, is probably $Mo_{1-x}S_2$. Compounds of this type are known to be good catalysts, as has been shown by Weiss (University of Munich) and others.

The procedure used to feed the catalyst to the liquefaction unit is a novel one. Thus, a water-soluble molybdenum compound [e.g., $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] is emulsified with the slurry oil and this emulsion is then added to the coal-feed stream. The ultimate particle size of the catalyst was not defined for FERWG but is probably below about one micron with composition close to MoS_2. The catalyst works effectively although the final product slate involves relatively large amounts of gas, perhaps because of the high operating temperatures (~ 470° C) used.

The catalyst cost has been estimated to be about $0.75 per barrel of oil produced. This cost may be decreased if the molybdenum is recovered from the ash (which has been classified as a good grade molybdenum ore) and proper credit is allowed for this metal recovery.

The catalyst is apparently effective in desulfurization but not in denitrification of the feed coal. FERWG members regard it as likely that the molybdenum catalyst will prove to be effective in the liquefaction of a wide variety of coals. The question of catalyst efficacy for coals with greatly different sulfur contents should be carefully investigated under steady-state operating conditions. Research to identify the active catalyst species and its performance with model compounds should also be carried out.

B. The Dow Deasphalting Unit

The very small deasphalting unit (with a three inch diameter) used in the Dow program has performed quite acceptably. A solvent deasphalting procedure is employed to produce a concentrate of mineral matter and unreacted solid in a highly asphaltic liquid; this concentrate may be gasified (e.g., by the Texaco process) to fuel gas, H_2, or both. The precise nature of the physico-chemical processes occurring in the deasphalting unit (Marangoni effect) may require elucidation. If the deasphalting unit works as well on a large scale as on a small scale, the workers at Dow will have made a major contribution to the development of improved coal-liquefaction technologies by identifying a new route and reducing the costs associated with solids-liquids separation.

The Dow claims concerning performance of the deasphalting unit should be speedily verified. Does this procedure really pull out heavy, oil-soluble compounds that cannot be readily distilled out under vacuum?

Scale-up of the Dow deasphalting unit should be regarded as a high-priority development item.

C. Process Implications

The Dow process uses a hydroclone to effect crude separation upstream of the deasphalting unit. About 75% of the recycle oil comes from the hydroclone. There is evidence from other work that this type of procedure is beneficial. Thus, the view that this recycle material, as well as some of the heavier oils recovered from the deasphalting unit, have special donor-solvent capabilities is consistent with the observation that the Kerr-McGee supercritical gas-extraction technique for separating vacuum bottoms into an organic phase and a solid residue yields an organic phase which shows beneficial donor-solvent properties.

The Dow process may offer a desirable fall-back alternative for DOE program managers in case unforeseen problems arise, for example, in connection with the SRC-II plant. Thus, the Dow catalyst could be readily introduced into the SRC-II dissolver in case difficulties are encountered with particular types of coals (such as Western subbituminous coals). Use of the Dow catalyst in the SRC-II process might also lead to more uniform product quality. This presumed potential of the Dow catalyst should, of course, first be carefully assessed in small-scale experiments.

The process scheme used by Dow allows vacuum distillation of deasphalted oil, which thus provides another possible cut for inclusion in the recycle stream used in the coal-slurrying step. Investigations on the laboratory scale to explore the efficiency of recycle mixtures (made up from cuts of hydroclone overhead plus deasphalted oil plus a vacuum distillate from deasphalted oil) could well yield improved performance for well-defined processing techniques. The definition of promising mixture compositions may then lead to potentially useful alternatives for both the EDS* and SRC-II processes.

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*Exxon has recently employed a recycle of vacuum bottoms in a modified EDS liquefaction scheme.

AC-6. COMMENTS ON NUCLEAR PROCESS-HEAT COMMERCIALIZATION STUDY, GENERAL ATOMIC COMPANY, SAN DIEGO, CA 92138 (NOVEMBER 20, 1979)

J. Watson and R. Quade presented a review of the General Atomic (G.A.) program on nuclear process-heat commercialization to the following FERWG members at the UCSD Energy Center in La Jolla: Clardy, Penner, Ross, Sieg, and Squires; I. Wender of DOE also participated in all of the discussions.

A. The High-Temperature (HTGR) and Very High Temperature (VHTR) Gas-Cooled Reactors

The HTGR and the VHTR have obvious and well documented safety advantages compared with light-water reactors. Their commercialization was, however, delayed until very recent times. Because they entered the utility market during a period of active curtailment of nuclear power in particular and of electricity generation in general, market penetration has been insignificant.

The HTGR and VHTR provide access to core temperatures up to about 950° C. These temperatures are sufficiently high to allow coal processing for liquefaction.* Since 30-40% of the coal energy is normally required for various types of coal-processing steps, nuclear process heat promises improvements of 30-40% in coal-conversion efficiency. As an example (cf. the attached hand-out), the use of nuclear heat in conjunction with the SRC-II process leads to a cost estimate of \$25.20/bbl as compared with \$29.80/bbl for jet fuel under otherwise equivalent assumptions.

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*Other reactors do not offer this option. Thus, liquid water reactors are generally limited to about 600° F and molten sodium reactors to about 1200° F. Corrosion problems are severe with boiling water reactors.

We believe that a costing study on the utility of nuclear process heat in coal liquefaction should be performed by a process-engineering group of the type that is normally called upon to perform costing studies of synfuel technologies (Fluor, Bechtel, etc.). If these evaluations turn out to be favorable, a serious reevaluation of U.S. commitments in this field (which were smaller during FY 1978 than those of the F.R.G.) may be appropriate.

AC-7. RESEARCH AT THE CENTRAL RESEARCH DEPARTMENT OF THE MOBIL RESEARCH AND DEVELOPMENT COMPANY; MOBIL'S METHANOL-TO-GASOLINE CONVERSION PROCESS, PAULSBORO, NEW JERSEY (AUGUST 16, 1979)

The following FERWG members participated in the site visit to Mobil: Clardy, Furlong, Leder, Penner, Ross, Sieg, and Squires. I. Wender of DOE also participated with the FERWG members.

A. Research at Mobil

Dr. P. B. Weisz, Manager of Mobil's Central Research Department, presented an introduction which was concerned with the strategy of hydrogen addition for gasification, liquefaction and fuel upgrading.

At Mobil, both M. Farcasiu and D. D. Whitehurst gave short talks on parts of the Mobil program on coal characterization and chemistry. There was little in these talks that was not presented in Whitehurst's very good chapter in Organic Chemistry of Coal (ACS Symposium Series, 1978).

Dr. M. Farcasiu presented a brief review of coal structure, stressing the fact that molecular groups of about 100 atoms with molecular weight of about 600 Daltons are connected by relatively weak bonds (50 to 60 kcal per mole). These bonds begin to scission at about 800° F. The chemical bonds within the molecular group of 100 atoms are stronger, in the range 80 to 100 kcal per mole. The molecular composition of these groups is approximately $C_{49}H_{43}O_{6.4}S_{0.8}$ and there are, on the average, 196 C-C bonds per coal molecule. The main problem which confronts liquefaction and gasification is the selective breaking of these bonds. For that purpose, one has available the variables of temperature, residence time in the reactor, pressure, solvent, and catalyst. There is always competition between thermal and catalytic scission. With high temperature, the selectivity of bond breaking by specific catalysts becomes poor; however, catalytic removal of heteroatoms remains effective. As a general rule, it is best to keep the residence time for thermal rupture of bonds as short as possible.

M. Farcasiu noted that the detailed chemistry presented was done with model compounds and primarily concerned the mechanism of oxygen removal under these conditions. This is a matter of some practical concern since oxygen-containing molecules are believed to be responsible for high viscosity and, in their presence, a relatively greater hydrogen consumption is needed to obtain a liquid product with reasonable viscosity. The work showed that it was possible to deoxygenate oxygenated polycyclic aromatic compounds but essentially impossible to deoxygenate simple phenols. The presumed mechanism involves a hydrogenation-dehydration process. The consequences of this observation for coal are not yet clear and the effect of catalysts on this reaction is deemed a high priority study. Farcasiu also pointed out that there were relatively few thermodynamic data for complex aromatic hydrocarbons and hydrogen at elevated temperatures. The concern is that if the hydrogen partial pressure falls too low, extensive dehydrogenation of alicyclic compounds would take place to give an aromatic char. This char could then coat and deactivate the catalysts. It is not now possible to predict a priori how high the hydrogen partial pressure must be to prevent this process from occurring. Finally, she also commented that N removal was not easily accomplished and further work on the mechanism of this reaction and the effect of catalysts were needed.

D. D. Whitehurst supported the view that the characterization of N functionalities and efficient processes for their removal were the major problem in coal characterization and chemistry. Current techniques for N removal result in excessive gas production. Whitehurst also addressed other outstanding problems in coal characterization and felt that "critical coal characteristics" were poorly understood. Questions such as the "molecular weight" of coal and the degree of polycyclic condensation are still to be answered. Another fruitful area for work he suggested is the proposition that if coal is usefully thought of as a polymer, what is the "monomer"? He did not describe methods to attack these problems in his talk or in private conversation but did feel that new analytical instrumentation would be needed.

Both Whitehurst and Farcasiu felt strongly that coal characterization and chemistry would be better served by "concentrated efforts on selected coals and the availability of documented samples of these coals." This analysis is identical to that which led to the Exxon program described by R. Neavel at Baytown during a previous site visit.

D. D. Whitehurst discussed problems involved in coal dissolution and transformation. He prefers short residence time thermal solution, followed by more selective hydrogen uptake by catalysis. This procedure requires decoupling of the thermal and catalytic processes, which is different from the approach used in the H-Coal process. Whitehurst listed the following characteristics of catalytic processes:

Process conditions are often too severe.
Both thermal and catalytic reactions occur simultaneously.
Catalysts affect the compositions of both solvent and heavy coal liquids.
Most catalysts now in use were developed for petroleum processing.
There are high levels of metals and coke precursors.

In conclusion, Whitehurst identified the following R/D needs:

i. Development of new tools and techniques for coal characterization.
ii. Identification of critical coal characteristics.
iii. Concentrated effort on selected coals.
iv. Availability of documented samples from all processes.
v. Improved utilization of hydrogen.
vi. New catalysts for transformations during liquefaction.
vii. Optimization of process conditions.
viii. Decoupling of thermal and catalytic processes.
ix. Defined specifications for fuels of the future.

B. Mobil's "Indirect Liquefaction Approaches"

W. Lee discussed Mobil's indirect liquefaction development. This is a proprietary process for the conversion of methanol to high quality gasoline employing Mobil's high-silica, small-pore ZSM-type catalysts. Process conditions are mild (775° F, 25 psig, 1.0 LHSV). The catalytic reaction is highly selective and yields 44% hydrocarbons, 56% water, and only traces of ether, methanol, carbon oxides, and coke. Heat release in the process is substantial, but can be controlled with light gas recycle for a fixed-bed reactor. Workers at Mobil are currently developing a fluid-bed version in a 4 bbl/day pilot plant and are negotiating with a German company for a semiworks fluid-bed demonstration. The hydrocarbon product is about 60% C_5^+ gasoline, the remainder being light olefins and paraffins. Of the total yield of 9 lb RVP gasoline after alkylation, 88% is produced from the hydrocarbon products. The clear octane numbers are 96.8 F-1 and 87.4 F-2.

Dr. Lee presented data for a conceptual commercial plant. These are listed below.

Feed	
Coal, MT/day	27.3
Water, g/min.	6,000
Product	
Gasoline, bbl/day	23,065
SNG, MMSCF/day	152.6
Fuel oil equivalent, bbl/day	45,560
Thermal efficiency, %	63
Investment, $M	
Gasification	1,475
Synthesis	205
Total	1,680
Gasoline cost, equity at 12% DCF, ¢/Gal.	93

According to Lee, the $0.93 estimate has been obtained on the same basis as $1.33 per gallon for gasoline by the Sasol (FT) route .

The specified Mobil technology combines proven commercial technology for coal gasification and methanol synthesis very effectively with exciting new catalytic chemistry to produce a premium product. Though still costly relative to gasoline from imported crude oil, it looks like a route that could be commercialized quickly with a high chance of success. Furthermore, improvements in coal-gasification technology over the dry-bottom Lurgi process (their base case) could reduce the major component in the capital cost. It is interesting to note that Mobil has been contacted by the Germans to build a semiworks fluid bed plant and by New Zealand concerning a fixed-bed commercial project. This U.S. invented technology may well be first commercialized outside of the United States.

C. Presentation by W. Lee of Mobil

The Mobil process for the methanol-to-gasoline process is described in Figs. AC-7-1 to AC-7-5.

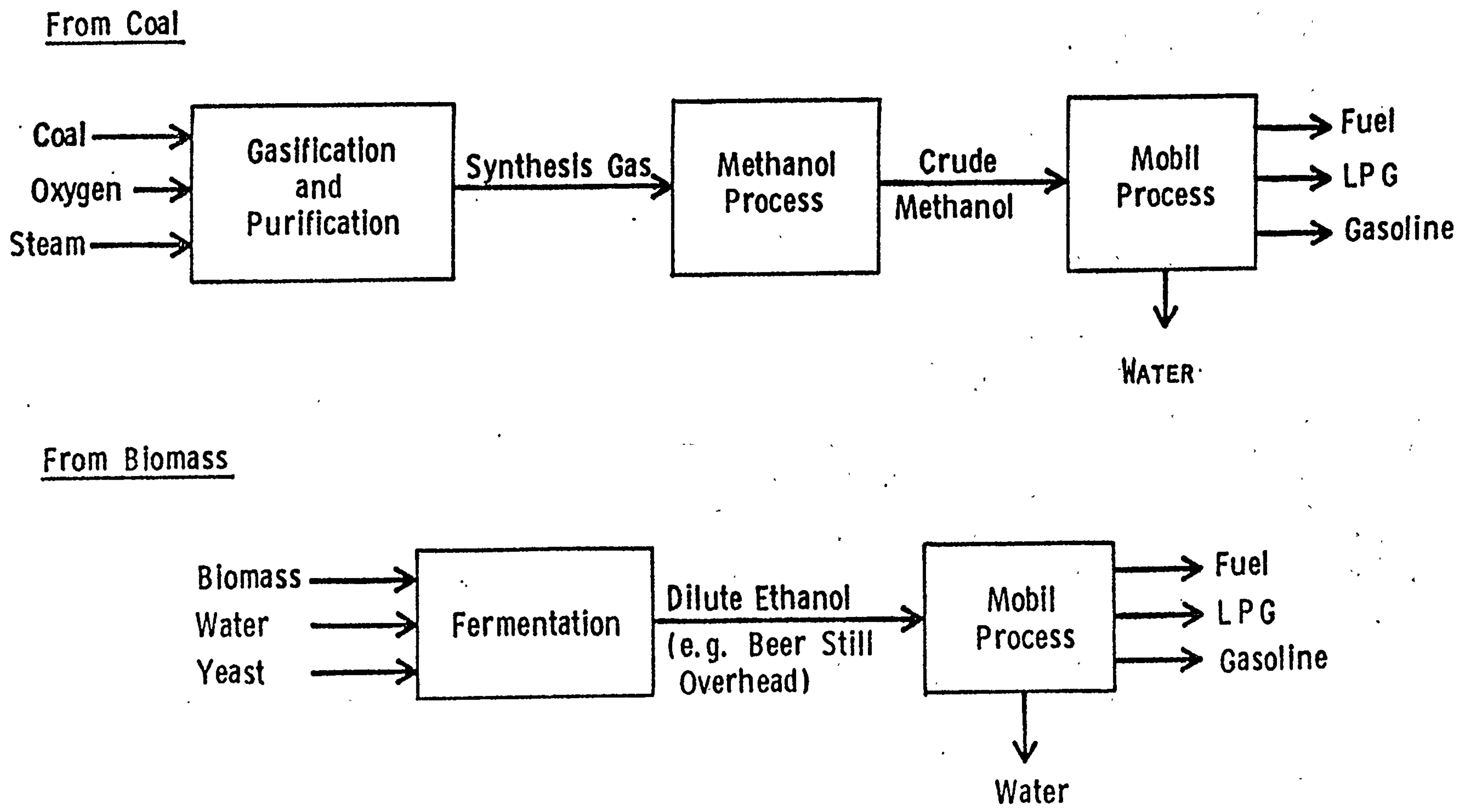

Fig. AC-7-1 Conversion of alcohols to gasoline.

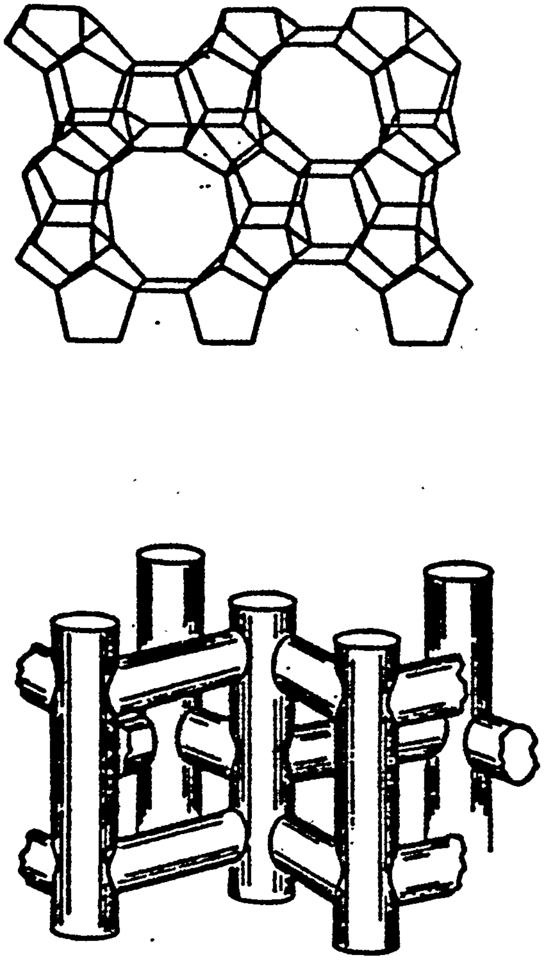

Fig. AC-7-2 The ZSM-5 structure; reproduced from Nature 272, 437-38 (1978).

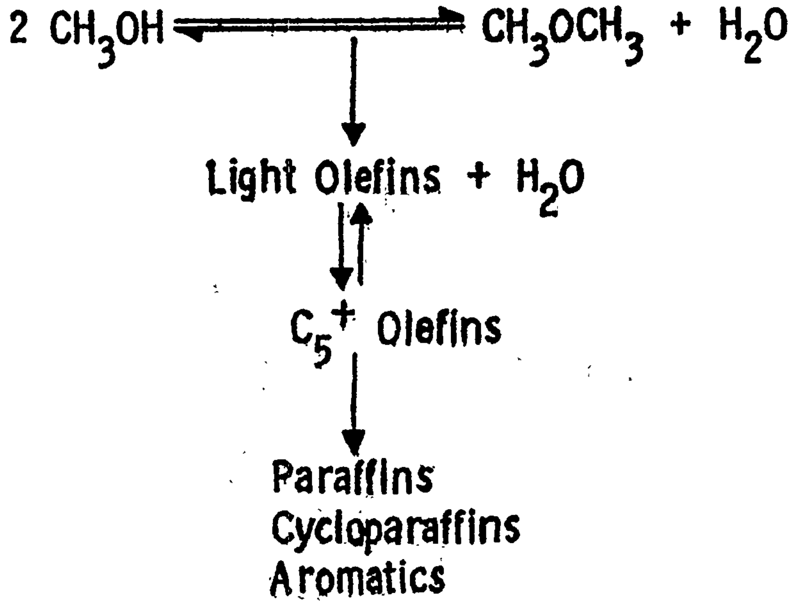

Fig. AC-7-3 Reaction paths in methanol conversion.

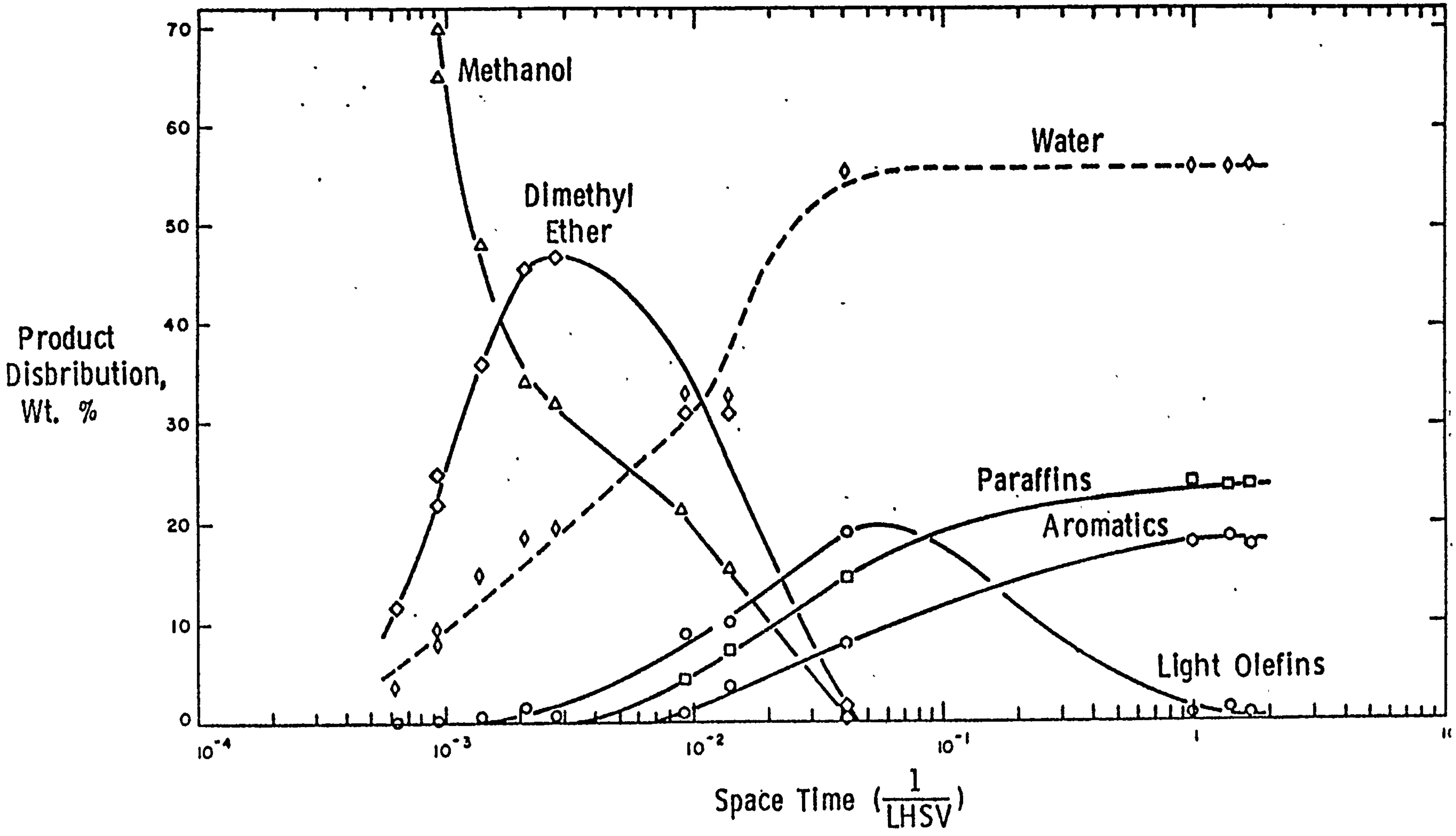

Fig. AC-7-4 Reaction paths for methanol conversion to hydrocarbons at 371°C.

Feed **Product**

$$nCH_3OH \longrightarrow (CH_2)_n + nH_2O$$

Methanol ⟶ Gasoline
Fuel Gas + Water

Material Balance: 100 Tons ⟶ 44 Tons + 56 Tons

Energy Balance: 100 Btu ⟶ 95 Btu + 0 Btu

Fig. AC-7-5 The chemistry of methanol conversion to gasoline.

AC-8.1 REPORT ON DISCUSSIONS WITH STAFF MEMBERS OF THE EXXON CORPORATION, PRINCETON, NEW JERSEY (AUGUST 17, 1979)

R. Schlossberg and L. Vernon from Exxon made presentations. These contained a substantial amount of new material.

Schlossberg noted that the primary structure in coal consists of C-C, C-H, and C-O bonds. These bonds may break by either a free radical or ionic mechanism. The secondary structure consists of weaker interactions such as Π-Π bonds and H-bonds (5 to 15 kcal per mole).

R. Schlossberg then revisited the well known Friedel-Crafts reaction on coal, specifically the reaction of coal with isopropylchloride and aluminum trichloride. By the use of mass spectroscopy, he showed that the product represented chemical attack on the coal, not dissolution of the coal in other reaction products. He also showed that the derivatized coal gave better liquefaction yields in tubing bomb experiments. Areas for future exploration suggested were the following:

i. What is the Lewis acid catalyst doing to coal?
ii. How are the alkylated products related to coal?
iii. Is the mass transport of the system being altered?
iv. Can a new, practical process be developed from these observations?

L. Vernon reported on coal liquefaction mechanism studies. He chose an appropriate model compound, diphenyl, and studied its hydrogenation at 450° C, both with and without tetralin. Bibenzyl is known to cleave into radicals with an activation energy very close to that involved in coal liquefaction. His analysis and rate studies show that direct hydrogenation can occur by a free radical mechanism in the absence of a donor solvent. In the presence of tetralin, hydrogenation occurs by H transferred from the solvent, as well as by direct hydrogenation. He presented a mechanism that is consistent with the observed kinetics and product distribution. This mechanism is, however, not unique and some alternatives (suggested by John Ross) involve ionic rather than radical reactions for the step in which tetralin is a catalyst. Vernon's work does rule out the accepted mechanism for donor-solvent action as the whole process.

AC-8.2 REPORT OF A VISIT TO THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY

(OCTOBER 11, 1979; BY S. S. PENNER)

According to J. B. Howard, the total annual research program on coal-related studies in the Department of Chemical Engineering at M.I.T. is about $\$3 \times 10^6$ per year. This program is supported by DOE, EPA, NIH, NSF, Exxon Corporation, several utility companies, and other sponsors.

A. J. B. Howard and W. A. Peters described the results of extensive studies on pyrolysis, hydrocracking, and hydropyrolysis performed in a specially designed reactor. This reactor has two perforated, electrically-heated plates between which small particles (10 µm to 1 mm) of coal, lignite or cellulose are heated at controlled rates. Temperature-time profiles and gas composition vs. time profiles are mapped. The gas analyses are performed on cooled samples that are withdrawn at defined time intervals. Pressures up to several hundred atmospheres, heating rates of 600 to 12,000°C/sec, and temperatures up to 1300° C have been utilized.

This work is fully described in the appended list of references.

I believe that it would be useful to apply Howard's pyrolysis and hydropyrolysis apparatus for routine testing of all of the coal samples that will be collected and studied by Neavel. The work at M.I.T. has thus far been restricted to studies of a Montana lignite and a Pittsburgh seam bituminous coal. The results obtained on pyrolysis rates have been correlated by using a Gaussian distribution of activation energies in a set of first-order decomposition reactions.

References

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3. D. B. Anthony, J. B. Howard, H. C. Hottel, and H. P. Meissner, "Rapid Devolatilization and Hydrogasification of Bituminous Coal," Fuel 55, 121-128 (1976).
4. D. B. Anthony and J. B. Howard, "Coal Devolatilization and Hydrogasification," AIChe Journal 22, 625-656 (1976).
5. E. M. Suuberg, W. A. Peters and J. B. Howard, "Product Composition and Kinetics of Lignite Pyrolysis," I and EC Process Design and Development 17, 37-46 (1978).
6. P. C. Lewellen, W. A. Peters and J. B. Howard, "Cellulose Pyrolysis Kinetics and Char Formation Mechanism," Sixteenth (International) Combustion Symposium, pp. 1471-1480, The Combustion Institute, Pittsburgh, Pa., 1977.
7. E. M. Suuberg, W. A. Peters and J. B. Howard, "Product Compositions and Formation Kinetics in Rapid Pyrolysis of Pulverized Coal - Implications for Combustion," Seventeenth (International) Combustion Symposium, pp. 117-130, The Combustion Institute, Pittsburgh, Pa., 1979.
8. E. M. Suuberg, W. A. Peters, and J. B. Howard, "A Comparison of the Rapid Pyrolysis of a Lignite and a Bituminous Coal," Symposium on Thermal Hydrocarbon Chemistry, Division of Petroleum Chemistry

and Fuel Chemistry, American Chemical Society, Anaheim, Calif., March 12-17, 1978.

9. E. M. Suuberg, W. A. Peters and J. B. Howard, "Product Compositions in Rapid Hydropyrolysis of Coal," submitted for publication to Fuel (1979).

B. C. N. Satterfield has performed studies on model compounds (e.g., thiophene, quinoline, pyridine) of interactions between hydrodesulfurization and and hydrodenitrification at pressures to 10^3 psia and temperatures of several hundred ° C. These studies have been performed in a continuous flow microreactor and suggest that the presence of H_2S may enhance denitrification. Current studies involve the use of nickel-molybdenum catalysts in a trickle-bed, liquid-phase reactor.

References

1. C. N. Satterfield, M. Modell, and J. F. Mayer, "Interactions Between Catalytic Hydrodesulfurization of Thiophene and Hydrodenitrogenation of Pyridine," A.I. ChE Journal 21, 1100-1107 (1975).

2. J. F. Cocchetto and C. N. Satterfield, "Thermodynamic Equilibria of Selected Heterocyclic Nitrogen Compounds with Their Hydrogenated Derivatives," Ind. Eng. Chem. Process Des. Dev. 15, 272-277 (1976).

3. C. N. Satterfield and J. F. Cocchetto, "Pyridine Hydrodenitrogenation: An Equilibrium Limitation on the Formation of Piperidine Intermediates," A.I. Ch.E. Journal 21, 1107-1111 (1975).

4. C. N. Satterfield, "Trickle-Bed Reactors," A.I. Ch.E. Journal 21, 209-228 (1975).

5. C. N. Satterfield, M. Modell, R. A. Hites, and C. J. Declerck, "Intermediate Reactions in the Catalytic Hydrodenitrogenation of Quinoline," I and EC Proc. Des. and Dev. 17, 141-148 (1978).

Satterfield is currently also working on indirect coal liquefaction using slurries in an autoclave and finely divided catalysts. The hope is to develop procedures that produce efficient conversions at greatly reduced $(H_2)/(CO)$ ratios. The apparatus has automated microprocessors with three chromatographs that allow continuous analysis of C_1 to C_{15} compounds, including the oxygen compounds formed by reaction between H_2 and CO. Contact times are seconds to minutes and a variety of catalysts will be used. The autoclave has a capacity of 1 liter but generally holds only about 300 cc.

C. J. P. Longwell has been involved in defining study programs to optimize the refining and application technologies of coal-derived liquids.

Longwell's work has involved primarily the reoptimization of aircraft turbines in a study performed for NASA. He believes that it is especially desirable to develop engines that can accept a wide spectrum of readily available fuels, especially diesel fuel. To facilitate this objective, he would like to see the development of special refineries with capacities of a few hundred barrels per day that are used to process selected fuels for engine testing from coal-derived (e.g., SRC II) and other liquids.

The current constraint of less than 20% aromatic contents on aviation fuels should be raised to 35% aromatics (i.e., the highest levels that are likely to be encountered in shale-oil-derived fuels).

Longwell's stated objective of broadening the fuel cuts usable in aviation engines requires engine development, especially the design of two-stage combustors to reduce peak temperatures and overheating of liners with sooting fuels. At the same time, engines should be developed for specialty fuels (e.g., H_2 or

H_2-derived fuels) and for accepting a very wide range of fuels (e.g., Stirling-cycle steam engines).

NASA is the primary current contractor for studies of reoptimization of combustion systems, although it is apparent that DOE also has an important role to play in this field. These studies should include considerations of fuel thermal stability and the design of burners to control fuel-nitrogen conversion to compounds other than NO_x. Thus, in aircraft engines, one should use a pilot-plant igniter for near-stoichiometric mixtures and add fuel downstream to maintain low temperatures; in boilers, it is desirable to burn fuel-rich mixtures to minimize NO_x production and then to add more air in order to burn particulate formations.

Longwell's goal is <u>fuel-system flexibility</u> for properly designed engines. With flexibility, H_2 requirements can be reduced. A 1% increase in H_2 requirements corresponds roughly to a reduction in aromatics contents from 35 to 25% and a fuel-cost increase of 10%.

D. <u>P. S. Virk</u> is exploring the utilization of the Woodward and Hoffman rules in order to define concerted reactions that will allow more efficient splitting of coal structures at greatly reduced hydrogen consumption.

<u>Reference</u>

1. P. S. Virk, "Pericyclic Pathways for 1,2-Diphenylethane Decomposition," Fuel <u>58</u>, 149-151 (1979).

AC-8.3 REPORT ON THE EPRI COAL-LIQUEFACTION REVIEW (MAY 9-10, 1979; PARTICIPANTS: S. A. ALPERT, F. LEDER, S. S. PENNER, E. REICHL, J. ROSS, R. SIEG, A. SQUIRES, J. THOMAS, L. TOPPER)

The meeting agenda is appended. Copies of all of the papers presented at the conference are available to FERWG members.

The presentations and papers dealt with empirical studies. Considerable emphasis was placed on the important hydrogen-transfer capabilities of the lighter fraction of recycled Kerr-McGee material.

Detailed evaluations and recommendations by F. Leder and by A. M. Squires are attached.

AGENDA

Wednesday, May 9, 1979 (MAXIMUS SOUTH)

	8:00 a.m.	Registration
	8:10 - 8:20 a.m.	Rovesti's Welcome and Instructions
		Session I Chairman: Howard Lebowitz
Paper No. 1	8:20 - 9:10 a.m.	"Improved Coal Liquefaction Technology" C. J. Kulik and H. E. Lebowitz - EPRI
Paper No. 2	9:10 - 9:55 a.m.	"Response of Product and Solvent Composition to Catalyst Deactivation During Coal Liquefaction" T. O. Mitchell - Mobil R & D Corporation
Paper No. 3	9:55 - 10:40 a.m.	"Western Coal Liquefaction" H. F. Silver - University of Wyoming
	10:40 - 11:00 a.m.	Coffee Break - (Lobby Area)
	11:00 - 12:00 noon	Discussion - (Mezzanine Area)

Paper Number:	Discussion Leaders:	Rooms:
1	Art Squires	Patrician I
2	Ricardo Levy	Patrician II
3	Linda Atherton	Patrician III

	12:00 - 1:15 p.m.	LUNCH (Maximus Central) Ron Fischer - DOE Coal Liquids Refining Program
		Session II Chairman: Jerry Fox
Paper No. 1	1:15 - 1:55 p.m.	"Critical Solvent Deashing of Residual Coal Derived Liquids" H. E. Lebowitz - EPRI
Paper No. 2	1:55 - 2:40 p.m.	"Catalytic Upgrading of Regular and Short Contact Time SRC" P.J. Angevine, R.H. Heck, S.S. Shih, T.R. Stein - Mobil
(no discussion)	2:40 - 3:00 p.m.	"The Effect of Carrier Gases and Solid Heat Carrier on Tar Yield and Quality of ORC Flash Pyrolysis" S. C. Che - Occidental
Paper No. 3	3:00 - 3:40 p.m.	"Solids Formation During the Liquefaction of Western Coal" R. G. Jenkins - Penn State
	3:40 - 4:00 p.m.	Coffee Break - (Lobby Area)
	4:00 - 5:00 p.m.	Discussion (Mezzanine Area)

Paper Number	Discussion Leaders:	Rooms:
1	Nandor Herskovits	Patrician I
2	Bill Weber	Patrician II
3	Frank Tiller	Patrician III

6:30 - 7:30 p.m.	No Host Coctails - Maximum Central
7:30 p.m.	DINNER - Maximum Central Dwain Spencer - "Legislative Initiatives to Foster Commercialization of Synthetic Fuels"

Thursday, May 10, 1979 (MAXIMUM SOUTH)

	8:00 - 8:10 a.m.	Linda Atherton - Remarks
		<u>SESSION III Chairman: Linda Atherton</u>
Paper No. 1	8:10 - 8:55 a.m.	"Conventional and Short Residence Time Coal Liquefaction Using Selective Product Recycle" J. A. Kleinpeter and Francis P. Burke, Conoco Coal
Paper No. 2	8:55 - 9:45 a.m.	"Catalyst Development for Liquefying Eastern and Western Coal" K. K. Robinson and D. Kim - Amoco Oil
Paper No. 3	9:45 - 10:35 a.m.	"Properties & Liquefaction Behavior of Western Coals in Synthetic Recycle Solvents" D. D. Whitehurst - Mobil R & D Corp.
	10:35 - 10:45 a.m.	Remarks: S. B. Alpert
	10:45 - 11:05 a.m.	Coffee Break (Lobby Area)
	11:05 - 12:05 a.m.	Discussion (Mezzanine Area)

Paper Number:	Discussion Leaders:	Rooms:
1	Howard Lebowitz	Patrician I
2	Bill Rovesti	Patrician II
3	Howard Silver	Patrician III

	12:05 - 1:15p.m.	LUNCH (MAXIMUM CENTRAL) Ron Wolk - Concluding Remarks
		<u>SESSION IV Chairman: Norman Stewart</u>
Paper No. 1	1:15 - 2:00 p.m.	"Effect of Solvent Properties in the SRC Process" Bill Weber - Catalytic (EPRI), G. Styles - Southern Company Services
Paper No. 2	2:00 - 2:45 p.m.	"The Evaluation of Selective H-Coal Catalysts" A. G. Comolli, E.S. Johanson and D.T. Huibers - HRI
Paper No. 3	2:45 - 3:30 p.m.	"Liquefaction of Western Subbituminous Coals with the EDS Process" K. Trachte - Exxon
	3:00 - 3:35 p.m.	Remarks - Bill Rovesti
	3:35 - 3:55 p.m.	Coffee Break - (Lobby Area)
	3:55 - 4:55 p.m.	Discussion (Mezzanine Area)

Paper Number	Discussion Leaders:	Rooms:
1	Conrad Kulik	Patrician I
2	Heinz Heinemann	Patrician III
3	Ev Gorin	Patrician II

AC-8.3A OVERALL IMPRESSIONS OF THE EPRI CONFERENCE ON COAL LIQUEFACTION (BY F. LEDER)

- A good deal of the work is concerned with incremental improvements in existing technology.
- Fundamental studies in kinetics were not emphasized. Instead, overall yields and gross conversion rates were estimated.
- Heavy emphasis was placed on hydrotreating in solution as in SRC II and EDS technology. Pyrolysis was mentioned only briefly and Fischer-Tropsch synthesis was not discussed.
- A new development emerged, namely, supercritical extraction and fractionation of coal as developed by workers at the Kerr-McGee Corporation. This discovery is potentially important and may provide a new unit process for inclusion in other liquefaction schemes.
- A great deal of work is being generated on catalysts and on model compounds. Work on bimodal catalysts and bi-metallics provides a good base line for state-of-the-art hydrogenation technology.

Recommendation: EPRI, as well as DOE, should fund more work of a fundamental nature. Basic kinetics, reaction mechanisms and conversion routes need to be elucidated so that major steps forward will occur.

AC-8.3B COMMENTS ON EPRI COAL LIQUEFACTION CONTRACTORS' CONFERENCE (BY A. M. SQUIRES)

This Note comments upon some aspects of the recent Conference in Palo Alto, bringing in items discussed during the FERWG visit to Ft. Lewis on May 11. The emphasis will be upon (a) leads for fundamental research in coal chemistry and (b) difficulties standing in the way of such research that may require special measures to assist workers who would undertake the studies.

1. Leads for Research - Recycle of Heavy SRC Species

The Kulik-Lebowitz paper that led off the EPRI Conference contains exciting leads for fundamental work in coal chemistry to determine the precise chemical mechanisms that underlie the essentially engineering phenomena reported in the paper. In brief, the Kulik-Lebowitz paper presents a set of liquefaction data for which the simple explanation is that SRC product contains moieties of peculiarly "super" donor solvent power through their virtue as "shuttles" to convert gas-phase hydrogen onto the solubilized coaly matter. Although other, more complex explanations were attempted in the discussion of the paper, it seems most improbable to me that the simple explanation will not hold up. It should perhaps be emphasized that the Kulik-Lebowitz data show that the "super-donor" species are present in the solvent in relatively small amounts.

In the light of the Kulik-Lebowitz paper, it was interesting to learn during the visit to Ft. Lewis that the operators of the SRC pilot plant there had independently come to the belief that the SRC product itself contains moieties from coal whose return to the dissolver caused "good things" to happen. This was viewed as a benefit of the recycle stream in the SRC II Process and is independent of the benefit to be derived by recycle of ash matter and the building up of the concentration of ash matter in the SRC dissolver.

The beauty of the Kulik-Lebowitz disclosures is that the Kerr-McGee Critical Solvent Deashing Process provides a means for <u>selecting</u> those moieties in the

SRC process whose recycle to the reactor will do the most good - or will do the particular "good" that the process design engineer wishes to have accomplished for his particular process. One can visualize a whole range of processes using this new tool for different process objectives.

The Kerr-McGee Process is a new approach to the fractionation of hydrocarbonaceous matter, allowing the separation of fractions of such matter that are heavier than anything that could be distilled. Clearly, chemical engineering researchers must take note of this development, and consider its needs by way of fundamental chemical engineering research to extend its power.

From the point of view of the coal chemist, he now faces an urgent task to discover which particular species are the "ingredient X" that make Kerr-McGee "light SRC" such a good hydrogen shuttle.

The combined effect of such research may be a greater selectivity toward the ingredients whose recycle will do the most "good".

2. Leads for Research - Need for a Test Characterizing Coals for Liquefaction

On March 23, FERWG heard from Exxon about the extreme discrepancy in liquefaction behavior of two Illinois No. 6 coals in the Exxon Donor Solvent Process. The two coals, Monterey and Burning Star, give relatively good and relatively poor performance in the primary coal-dissolution step of the process, respectively, yet the two coals differ relatively little in the "classical" tests for characterizing coals. At the March FERWG meeting, Dr. John Scott urged that an important research objective ought to be the development of a test to characterize a coal for donor-solvent liquefaction. (It might be noted that the relative merit of Monterey and Burning Star coals are reversed in the H-Coal Process, compounding the sense that we need to know much more.)

The EPRI Conference brought out further paradoxes of this type in the form of data presented by Dr. Duayne Whitehurst of Mobil Research & Development Co. on the liquefaction behavior of a series of samples of subbituminous coal (from the Wyodak seam) taken from the same large drum-sample. The sub-set of samples varied enormously, both in early-time liquefaction conversions and in percentage aromaticity.

The personnel at Ft. Lewis told us of the paradoxical behavior of four lots of Pittsburgh Seam coal that had been processed in the SRC II mode at Ft. Lewis: Blacksville No. 2 and Loveridge Mine gave poor performance, and Powhatan No. 5 and Ireland Mine, good. We were not given coal characterization data on these coals, and it will be important to obtain such data to reinforce the point that FERWG will wish to make concerning research on better tests to predict such behavior.

3. Difficulties for the Researcher Who Would Do Basic Research on Coal

FERWG will need to discuss certain difficulties that stand in the way of the researcher who would undertake basic research to resolve some of the foregoing matters - especially the researcher who works in an institutional setting relatively isolated from the large coal R & D establishments.

One difficulty is illustrated by the amount of information that was coded or kept confidential during the EPRI Contractors' Conference. The reasons for this are clear: EPRI cannot be expected to reveal all of the details of the operation of the Kerr-McGee Process to secure the "light SRC's" used in the Kulik-Lebowitz studies. Kerr-McGee is performing a service to the Nation by developing its Process for use in de-ashing SRC and cannot be expected to disclose all of the details of its process to the general public. Exxon's Solvent Quality Index is proprietary information that Exxon evidently regards to have competitive value.

Given the nature of EPRI as an institution, it seems probable that the full details of its studies of recycled light SRC's will remain secret for only a relatively short time. One cannot be so confident that Kerr-McGee and Exxon will be forthcoming with additional information very soon.

Given the hard fact, however, that confidential information exists, the would-be researcher into the fundamental bases for the phenomena reported upon faces two difficulties: how is he best to plan his work, and will he be "scooped" when he is at the point of publication by revelations that make his own work seem pointless and a waste of time? (Has the latter risk deterred work on supercritical gas extraction of coals in the United States, simply because everyone knows that the National Coal Board is sitting upon such a mountain of data? It is otherwise puzzling that so little work on supercritical gas extraction of coals is underway here.)

Another difficulty has been emphasized to me by Dr. Duayne Whitehurst - both last March in a 'phone call and again at the EPRI Conference. This is the difficulty of obtaining samples of coal and plant materials from operations during which curiosities have emerged. For example, will it be possible now to obtain from Ft. Lewis or Exxon samples of coals and products made during runs on the specific coals mentioned above?

AC-8.4 CONFERENCE ON UNIVERSITY COAL LIQUEFACTION CONTRACT RESEARCH (SEPTEMBER 6-7, 1979; BY JON CLARDY)

This is an annual gathering in which all university groups with DOE funding for coal research meet. This year's format was changed to have one hour presentations by selected speakers rather than 10 minute talks by everyone and to focus on coal liquefaction. There has also been a change to decentralize the management of contracts and some levity was provided by the scramble of university researchers to meet their new managers. Abstracts and research accomplishments of all contracts related to coal liquefaction were given out and I include a copy for reference. My overwhelming impression, which was borne out by every nonspeaker I chatted with, was that very little new material was presented.

1. Ronald H. Fischer

The advanced research and development objectives are to "explore innovative process concepts having a potential for significant cost reduction in synfuels production, to provide a fundamental understanding of the chemistry of coal conversion processes, and to explore new coal chemistry". Fischer is very excited about research in this area and picked two topics on which he felt a great deal remains to be done and in which universities could contribute.

A. Disposable catalysts program for hydroliquefaction.

The motivation for this is to reduce hydrogen consumption substantially and increase liquid product yield. Current technology uses excessive hydrogen, i.e. much more than would be theoretically required to make a premium fuel and hydrogen production is estimated to be one-third of the capital cost and 35% of the operating cost of planned plants. The idea is to use the mineral matter in coal or some other inexpensive ore as coal liquefaction catalysts. He hastened to add that this was not a new idea and could be traced to Bergius. He then summarized a series of studies at Sandia that showed that a 5% pyrite addition was roughly equivalent to a 20°C reduction in temperature for a number of coals. There was also an effect of surface area - the more the better in terms of liquid yield. Of course the amount of solid added makes this unattractive for practical processes. What needs to be done:

1) _in situ_ study of iron sulfides during liquefaction
2) study of stoichiometry of pyrrhotites in residues as a function of variables
3) determination of the limitations of pyrrhotites as catalysts
4) exploratory research involving use of other inexpensive minerals as catalysts.

Pyrrhotite seems to be the approved way to describe nonstoichiometric "FeS".

Mr. Fischer also addressed outstanding research opportunities in indirect liquefaction. The stated objective of this program is "to produce transportation fuels from synthesis gas at high selectivity and efficiency". Three areas could be improved:

1) better integration of gasification and fuel forming steps
2) limit chain growth by use of shape selective catalysts
3) more thermally efficient reactions

A suggested attack on the first problem could be to use a gasifier which produces synthesis gas having a low H_2/CO ratio in conjunction with a liquefaction reactor which uses the Kolbel reaction, i.e. $3CO+H_2O \rightarrow 2CO_2+CH_2$. The advantage to this is that a separate shift reaction is not required and the overall process produces less H_2O (steam). The two processes are compared in the following scheme.

COMPARISON OF STOICHIOMETRY FOR NORMAL SYNTHESIS AND KOLBEL SYNTHESIS

	NORMAL F-T	KOLBEL F-T
GASIFICATION	$12\,CH_{1/2} + 6H_2O + 3O_2 \Longrightarrow 9H_2 + 12\,CO$	
SHIFT	$9H_2 + 12CO + 5H_2O \Longrightarrow 14H_2 + 7CO + 5CO_2$	NOT REQUIRED
SYNTHESIS	$14H_2 + 7CO \Longrightarrow 7CH_2 + 7H_2O$	$9H_2 + 12CO \longrightarrow 7CH_2 + 5CO_2 + 2H_2O$
OVERALL	$12\,CH_{1/2} + 11H_2O + 3O_2 \longrightarrow 7CH_2 + 5CO_2 + 7H_2O$	$12CH_{1/2} + 6H_2O + 3O_2 \longrightarrow 7CH_2 + 5CO_2 + 2H_2O$

The shape-selective catalyst story was essentially the ZSM-5 discussion we heard at Mobil. It was felt that this was the only way to get away from the "Schulz-Flory" distribution of products.

The need for more thermally efficient syngas conversion reactors was also discussed but this was not directly relevant to our concerns.

The question period did elicit some more details about the catalytic activity of pyrite. It has no apparent effect on the cleavage of dibenzyl into radicals, the model system that L. Vernon (Exxon) discussed with us, but does catalyze the conversion of tetralin into methylindane. This is a very poorly understood area.

2. N. Deno (Penn State) discussed the application of a newly developed and somewhat bizarre oxidation reaction to coal structure and chemistry. Normal oxidations burn off aliphatic carbons to leave an aromatic acid residue while Deno's reaction (H_2O_2-CF_3CO_2H-H_2SO_4) burns away the aromatic part to leave aliphatic acids. [I did not believe the original claims for this reaction and reinvestigated it casually. It is simply remarkable. A crudely crushed coal dumped into this reagent turns into a water-clear solution overnight!] This work is still in the exploratory stages but it appears to be quantitative and should yield some very interesting information. It may be premature to judge but, if one were forced to use Deno's work to select among the competing coal models, Given's structure is the most compatible. The Deno results are somewhat retrograde in current coal structure thinking because they require large condensed aromatic units.

3. J. Katzer (University of Delaware) talked about his work on model compounds in hydroprocessing - especially hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The HDS work showed that both hydrogenation and hydrogenolysis take place with the relative importance varying with choice

of model. The problem of HDN is much more difficult. It appears that complete hydrogenation of the heteroaromatic ring must occur followed by hydrogenolysis of the C-N bond. This latter reaction is not at all selective and substantial C-C cleavage also occurs. The problem is exacerbated by the observation that basic N model compounds such as quinoline are poisons for such hydroprocessing catalysts as $Ni\text{-}Mo/Al_2O_3$. Considerable work on HDN is needed.

4. R. Robinson (Oklahoma State University) described experiments to obtain phase equilibrium data on coal-derived fluids. The most interesting point was that at temperatures up to 400°F and pressures up to 2000 psia the parameters are well described by the Soave-Redlich-Kwong equation with empirical binary interaction parameters for the paraffin-aromatic pairs only.

5. P. Given (Penn State) summarized much of the recent work from that laboratory. The first part of his talk was a detailed excursion into statistics. They had attempted "to establish a base from which conversion, mineral matter effects, product composition, dynamics, etc., in liquefaction can be predicted from such characteristics of the feedstock as the various parameters related to rank, petrographic composition and mineral distribution." After a lengthy excursion into cluster and factor analysis the situation was far from clear and he stated that "we don't know what all of this means". He suspects that it means that the ideal of a "single band in coal metamorphosis is nonsense". Refreshing candor and possibly a cautionary note for the Exxon program.

He also described some work on the catalytic activity of coal minerals, pyrite and pyrrhotites, in liquefaction. They found pronounced effects at elevated temperatures but minerals from different coals had widely different effects. They are endeavoring to identify the crucial variables.

[As a result of Fischer's talk and this type of work the nomenclature of coal scientists has changed rapidly. There is no longer any "ash" in coal but rather "minerals".]

6. W.H. Wiser (University of Utah) described several aspects of the Utah coal program. He began with his own studies and presented his model of coal. This model was severely criticized in the question period and in my opinion many parts of it do seem to have been whimsically arrived at. He presented model compound studies with N-benzyltetrahydrocarbazole. It was not entirely clear whether this was a first or second order process or whether it occurred in the liquid or gas phase. No further comments are needed.

He also presented some nice ^{13}C NMR work by D.M. Grant. In this study both solid coal and coal-derived liquids obtained by $ZnCl_2$ treatment were studied. This work was consistent with a liquefaction mechanism that is the reverse of the Friedel-Crafts alkylation.

7. H.C. Dorn (VPI-SU) also spoke about new analytical developments. The use of high temperature ^{13}C NMR appears to be a useful quantitative technique for coal characterization and a convincing story about the use of CF_3COCl as a ^{19}F NMR reagent was given. The fluorine reagent is also useful for characterizing heteroatoms.

These analytical techniques, at present, do not show differences between coals that perform very differently in the SRC process. He reiterated the point that coal performances "may be related to subtle differences in the chemistries of the respective coals."

8. J.A. Guin (Auburn) presented work closely related to Katzer's and Given's on coal mineral catalysis. In his work on benzothiophene he

concluded that pyrite is a good hydrogenation but a poor hydrogenolysis catalyst. He also stressed that phase equibibria are not well known in coal conversion processes and most operating conditions appear to be above the critical point. He showed photomicrographs which suggested that pyrite reacts rapidly with hydrogen to give pyrrhotite and becomes quite porous. He has also done some work with Fe_2O_3 (hematite) but the effect of this is not catalytic. It does improve liquefaction yields but stoichiometric amounts (based on conversion to pyrite) are needed.

He also discussed the role of solvents and suggested NMR criteria for optimum solvent quality. The choice of optimum solvent in SRC processes is coal dependent.

9. C.N. Satterfield (MIT) discussed the advantages of a slurry reactor system in Fischer-Tropsch synthesis. His own reactor is not yet complete. He has reanalyzed literature data to show that the rate becomes mass transfer limited at higher temperatures. This result was not anticipated by earlier workers.

10. N.F. Woolsey (University of North Dakota) talked about the chemistry of preasphaltenes. The major new development appears to be the use of s-triazine as an NMR solvent. The question period reworked the point that the "molecular weights" of a coal and its conversion products are not at all well understood. There does not appear to be any agreement on how to do the gel permeation chromatography experiment. A group at PETC is investigating this and T.F. Yen (University of Southern California) claims to have done it and promises a DOE report will be released soon.

11. A. Davis (Penn State) talked about aging of coal and mineral matter catalysis. The thermoplastic behavior of coal showed dramatic changes

with 20 days exposure to air at room temperature. This was found to have little effect on liquefaction behavior. He also found that the addition of exchangeable cations to 800° chars increased their reactivity in the following order:

Na>KC>Ca>Raw>Fe>Mg>Demineralized .

AC-8.5A REPORT OF SITE VISIT TO THE LAWRENCE BERKELEY LABORATORY
(MAY 8, 1979; VISITORS: S. S. PENNER AND L. TOPPER)

Discussions were held with a number of staff and U.C. Berkeley faculty members at LBL, including A. M. Sessler, C. Judson King, H. Heinemann, G. Somorjai, T. Vermeulen, and K. Westmacott.

The LBL program on fossil-energy research is currently funded at an annual level of about $600,000 (from BES in DOE) and is expected to grow to about double this level. The work is of high scientific merit and interest and is designed to contribute to fundamental understanding of elementary processes. The Lawrence Berkeley Laboratory is unique among DOE laboratories insofar as extensive involvement of university faculty members and graduate students are concerned: about 150 U.C. Berkeley faculty members and about 450 Ph.D. students are participants in LBL studies.

Fundamental research at LBL includes the following types of studies: catalysis, separations, heat and mass transfer, phase equilibria, chemical rate processes, and combustion studies; also exploratory process research, and instrumentation development. The laboratory personnel view LBL as an under-utilized national resource in the fossil-fuel development area.

The following basic studies relating to coal mining and coal liquefaction are currently in progress: studies of catalysis on single crystals, geological and geochemical impacts of coal mining, processes for the removal of pyritic and organic sulfur prior to coal combustion, homogeneous catalysis under mild conditions, design of process configurations to take proper advantage of catalyst properties, development of novel solvents for extraction, acid-base chemistry as it relates to stripping, coal characterization, studies of pore accessability, and the relation between chemical reactivities and surface structures and properties. There are excellent and costly diagnostic facilities [e.g., electron microscopy is now being developed to achieve a spacial resolution of about 5 A in an "environmental cell" (~ 10^3 °C, 100 atm)].

Model compound studies are in progress to evaluate the role of heteroatoms. Fundamental work on catalysis deals with both Fischer-Tropsch synthesis and with direct liquefaction. Emphasis is on the relation between the microstructure of coal and gasification kinetics.

Hydrocarbon synthesis is being studied on single crystals of rhodium and iron, with particular emphasis on the role of O_2 in effecting conversions. High CO/H_2 ratios have been converted successfully without reactor plugging. Experiments have been designed to identify the possible formation of hot spots during conversion. Controlled deposition of transition metals on coals is being used to study rates of pyrolysis and hydrogenation; the role of organometallics (transition metals) on reactions involving small molecules is being defined. The product selectivity of zeolite catalysts is under investigation. Low-temperature (~ 325° C) liquefaction in $ZnCl_2$-alcohol mixtures is being studied.

Workers at LBL estimate the current extent of catalytic research in the U.S. (~ $\$15 \times 10^6$ per year, including industrial support) to be perhaps one seventh of the level of support that has been shown to be needed for the successful development of catalysts in the petroleum industry (~ $\$100 \times 10^6$ per year for 20 years).

AC-8.5B REPORT OF SITE VISIT TO THE LAWRENCE BERKELEY LABORATORY AND UNIVERSITY OF CALIFORNIA, BERKELEY

(JUNE 18, 1979; BY ARTHUR M. SQUIRES)

Persons seen:
Edward Grens
Judson King
Heinz Heineman
Gabor Somorjai
John Shinn (representing Theodore Vermeulen)
Russell Blackadar
William Gillespie
Philip Ross

I visited Berkeley on June 18 for discussions with coal scientists there on behalf of FERWG. In general, the work underway at Berkeley appears to be of high scientific quality, and much of the work is of "longrange" character, in the sense that it is speculative and not geared to produce results of immediate usefulness to a specific DOE technological program.

Coal "Depolymerization" under Mild Conditions

Vermeulen and Grens in Chemical Engineering at Berkeley have a program involving a number of students in efforts to find new ways to "depolymerize" coal under mild conditions, i.e., at temperatures below the coal pyrolysis range. For example, John Shinn (working for Vermeulen and about to complete his Ph.D. before joining the staff of Chevron Research at Richmond, CA) has obtained high degrees of solubilization of Wyodak subbituminous coal in treatments with $ZnCl_2$-methanol mixtures at 275°C under hydrogen at about 14 atmospheres. Methyl groups are incorporated in the pyridine-soluble product (not methoxy groups; the product contains appreciably less oxygen than the starting coal).

The work provides another technique for mild "depolymerization" of coal to prepare material for study by organic chemists interested in the structure of coal.

The work may also constitute a lead for improved coal liquefaction processes in which the primary coal-treating step is conducted under milder processing conditions than hitherto thought possible. The process medium for such processes would appear to require the presence of at least two ingredients:

(a) a catalyst for rupture of the "scissile" bonds that hold the coal's cross-linked macromolecular structure together; and

(b) an agent to swell the coal or otherwise improve the penetration of reactants to the interior of the coal's structure.

In John Shinn's work, the two ingredients are $ZnCl_2$ and methanol, respectively. (As mentioned earlier, methanol participates in the reaction as well as produces coal swelling.)

I regard this work as important. It points up the importance of fundamental research in the following areas:

(1) Work to identify scissile bonds and obtain measures of their bond strengths.

(2) Search and development of catalysts for rupturing scissile bonds, especially catalysts that are easier to design for than $ZnCl_2$.

(3) Studies of the interaction of coals with a wide range of liquid media: rates of penetration, degrees of swelling, heats of wetting, etc.

As a (perhaps) minor footnote to the Berkeley work, it may be noted that if methanol is to enter the pool of motor spirits or combustion fuels, the incorporation of methyl groups from methanol into coal liquids, as in Shinn's experiments, may be something to consider.

Waste Water Treatment

Judson King of Chemical Engineering notes that DOE Energy Technology is not giving much consideration today to waste water management. King urges that FERWG recommend to Energy Technology to pay more attention to water recycle and water management, with the view of discharging as little water as possible from coal conversion processes, and this water to have potential pollutants at the highest possible concentration levels. King states that biological treament will deal with only a part of the chemical oxygen demand (COD) from typical coal-processing waste waters. This means that chemical processing will be needed, and this in turn means integration of such processing with the main conversion process. King believes that not nearly enough attention is being paid today to such considerations.

Pyrolysis and Gasification Studies

Coal pyrolysis is being studied in an "environment cell" incorporated in an electron microscope, to study physical changes that accompany the coal conversion. Also, gasification is being studied in a kind of "underfeed stoker", in which a compacted sample of coal is shoved upward into the gasification zone, with rapid heating and some degree of control of solid residence time as well as gas product residence time. I was not able to observe these experiments, but from their descriptions, they appear to me to be useful.

Catalyst Studies

A large effort is underway to study catalysis on specially prepared metal surfaces of known structure. Alexis T. Bell and Gabor Somorjai are studying the Fischer-Tropsch reaction on such surfaces, and have obtained significant results. They always get a surface monolayer of carbon, but also find there must be some penetration of O-atoms into the metal lattice before it becomes Fischer-Tropsch active. It is not clear whether such O-atoms arise from the support or from CO. It is not clear whether oxygen in H_2O product comes directly from CO or via an exchange from O-atoms in the support.

Work on hydrocarbon reforming on well-characterized metal surfaces is also in progress.

Albert Levy is looking at the deactivation of Co-Mo catalysts in coal liquefaction (e.g., in the H-Coal Process). He sees a layer of vanadium sulfide and MoS_2 on a spent catalyst from oil hydroprocessing, and a layer of FeS_2 and MoS_2 on a spent catalyst from coal treatment.

Heinz Heineman plans work to try to understand why a H_2/CO ratio of about 0.6 works best in the Fischer-Tropsch reaction in a slurry phase (the Kölbel reaction), while a ratio of 2 works best in a fluidized bed.

Heinz Heineman discussed with me the potential role of zeolite catalysts in Fischer-Tropsch synthesis. (I gathered that he plans research in this area, with the object of tailoring the synthesis to give diesel fuel.)

Mobil has a commercial dewaxing process using zeolites in a hydrogen atmosphere, with some four or five commercial installations. The process uses the fact that any straight chain hydrocarbon will go into a zeolite, but immediately rearranges (i.e., aromatizes) and/or cracks, and cannot get out again except as, for example, a C_{12-} species.

Mobil's methanol-to-gasoline work and also use of zeolites in conjunction with Fischer-Tropsch synthesis rest upon this same fact. A striking result is that a <u>physical mixture</u> of an iron Fischer-Tropsch catalyst and a zeolite gave the same result as putting the iron onto the zeolite. This shows that the fragments arising from Fischer-Tropsch synthesis are mobile in the gas phase, can enter the zeolite, and cannot get out again except at permitted sizes.

Heineman told me that Sasol II has a "Mobil part", in which Mobil's dewaxing process is used to convert waxes and oxygenates to fuel oil and gasoline. He said that Sasol III may remove oxygenates from process water over zeolite catalysts.

AC-8.6 REPORT OF A VISIT TO THE COLLEGE OF EARTH AND MINERAL SCIENCES PENNSYLVANIA STATE UNIVERSITY

(NOVEMBER 13, 1979; BY J. CLARDY)

The research budget for coal research programs is roughly $\$3 \times 10^6$/year. In the groups I visited this is mostly DOE money. A breakdown of funding for various programs is given in Appendix I. A group of 30 investigators has submitted a proposal to establish a University Coal Laboratory with DOE funding.

1. P. Given is primarily concerned with coal liquefaction and characterization; Most of my time was spent with him. His most recent effort has been a massive study on the dependence of coal liquefaction on coal characteristics for a sample of 104 coals.

A sample of 104 high volatile bituminous coals from the U.S. was selected and liquefaction behavior in a simple tubing bomb system with tetralin was studied. Liquefaction was judged by pyridine solubility and yields to correlate best with volatile matter content and inversely with vitrinite reflectance. At this point, it became clear that the sample base was not homogeneous and cluster analysis was applied. The coals seem to group naturally into three clusters with S content being the most important variable and rank a secondary variable. For each cluster, the liquefaction yield could be "loaded" onto different coal characteristics.

In practice, this means that large numbers of questions can be answered but not simply. For example, suppose one wanted to know how sulphur content affected liquefaction. The analysis shows:

a) Group 1 (high rank, medium sulphur) - essentially no effect on conversion yield from organic or inorganic sulphur.

b) Group 2 (medium rank, high sulphur) - a substantial correlation of conversion with total sulphur.

c) Group 3 (medium to low rank, low sulphur) - a substantial effect on conversion from mineral matter content, no effect from organic sulphur.

This work complements the Neavel effort [Exxon] very nicely.

The other interesting point that came out of my talk with Given was the poor state of coal mineral analysis. A recent round robin of samples gave widely disparate results in various laboratories. Much better analytical methods are needed.

2. W. Spackman and A. Davis are interested in greatly expanding the Penn State Coal Data Base. The logic of this is essentially identical to that we heard for the Neavel program at Exxon. A. Davis would be personally interested in quantitative mineral matter analysis using automated microscopy, FTIR, x-ray diffraction and fluorescence, and SEM. He agrees that this field is not in good shape but expects rapid progress because of current interest in mineral matter catalysis.

Spackman and Given also have a project trying to trace the chemistry of plant materials to coal. They have approached NSF for funding of this study.

3. N. Deno has developed some interesting new oxidation reactions for coal. The work so far has been with model compounds in order to understand the chemistry involved. Serious work on coal is just starting, but very interesting results are anticipated.

AC-8.7 REPORT OF SITE VISIT TO THE UNIVERSITY OF UTAH

(DECEMBER 4, 1979; BY S. S. PENNER)

Discussions concerning coal-liquefaction technologies were held at the University of Utah with A. G. Oblad, W. H. Wiser, and R. E. Wood. Bench-scale (1/8 to 1/4 inch i.d.) experimental facilities, which have been used to examine the catalytic efficacy of a large number of metal salts in direct coal-liquefaction, were inspected.

A general philosophy on coal liquefaction was described some years ago by Oblad,[1] while essential performance details are given for more than 60 hydrogenation-liquefaction processes in another publication.[2]

The principal point made by Oblad et al relates to a problem that was previously discussed at length by FERWG members in connection with the site visit to Conoco. In brief, one should be able to find a catalyst which, in small concentrations and in well defined pressure and temperature ranges, will facilitate the efficient hydrogenation of coals by rupturing only those bonds that need to be ruptured to produce high liquid-to-gas ratios. Interesting work has been done at Utah to define both the catalyst and the desired operating conditions. While the Conoco work involved a $ZnCl_2$ ("catalyst")-to-coal mass ratio of about unity, the Utah work has been done with metal-to-coal mass ratios of about 0.03. Finely ground coals (40 mesh +) were exposed to concentrated salt solutions and were then dried before entering the preheater and the reactor under hydrogen pressure. Flow in the helical coil reactor (~ 1,800 psia, 475-525° C) tube is expected to be highly turbulent. Conversions up to 70% + were achieved at liquid to gas ratios as high as 8. The most effective catalysts found[3, 4] were $ZnBr_2$, ZnI_2 and $ZnCl_2$ in some tests while $ZnCl_2$ was found to be best in others.

Work on direct coal liquefaction using small amounts of metal salts as catalysts is currently funded by DOE at the Cities Service Corporation. University-based studies in this field were previously recommended by FERWG after the site visit to CONOCO. The ideas proposed by Oblad, Wiser and Wood appear to be well founded on extensive experience and include notions about pretreating coals to increase porosities (to $\sim 400\ m^2/g$), studying bond ruptures that are promoted by selected metal salts present in low concentrations, using moderate processing conditions, identifying the nature of the fluid-flow processes that actually occur in the reactors, etc.

The ultimate challenge, <u>for selected types of coals</u>, remains direct hydropyrolysis under the proper conditions. In this hydropyrolysis, the mineral matter that is normally present in coals will serve the required catalytic functions to effect proper and efficient bond ruptures.

<u>References</u>

1. A. G. Oblad, "Catalytic Liquefaction of Coal and Refining of Products," Catal. Rev. - Sci. Eng. <u>14</u>(1), 83-95 (1976).

2. J. M. Lytle, B. C. B. Hsieh, L. L. Anderson, and R. E. Wood, "A Survey of Methods of Coal Hydrogenation for the Production of Liquids," Fuel Processing Technology <u>2</u>, 235-251 (1979).

3. R. E. Wood and W. H. Wiser, "Coal Liquefaction in Coiled Tube Reactors," Ind. Eng. Chem., Process Des. Dev. <u>15</u> 144-149 (1976).

4. L. L. Anderson, R. E. Wood, and W. H. Wiser, "Clean Liquid Energy from Coal," Society of Mining Engineers, AIME, Transactions <u>260</u>, 319-321 (December, 1976).

AC-8.8 REPORT OF SITE VISIT TO THE SOLVENT REFINED COAL PLANT OF THE PITTSBURGH & MIDWAY COAL MINING COMPANY

(DECEMBER 20, 1979; BY A. BEERBOWER)

The writer visited the Solvent Refined Coal Plant of The Pittsburgh & Midway Coal Mining Co. on December 20, 1979, to interview Mr. D. R. Canfield, Engineering Supervisor. The purpose was to investigate the nature and extent of the erosion problems in the SRC-II pilot unit.

OBSERVATIONS

1. LET-DOWN VALVE EROSION is typical of that caused by abrasion from fluid-borne particles. The sketch in Fig. AC-8.8-1 shows the pintle rod and tip. The pintle itself is not greatly damaged. Erosion centers on the 0.25 in. lead tip, which is deeply fluted. Since the sealing takes place upstream on the conical surface of the pintle, loss of control is very gradual. Canfield feels that the problem will be less severe on larger units because of the use of wider openings and more reserve metal. The pintle and tip are made from cobalt-cemented tungsten carbide. It has been found that the erosion decreases with lower cobalt content.

2. FEED PREPARATION AND MIXING problems are limited and are largely related to the fineness of grinding in the ball mill. The mill feed is pre-ground to under one inch and the product as used is normally such that 80% will pass through 200 and 100% through 100 mesh.

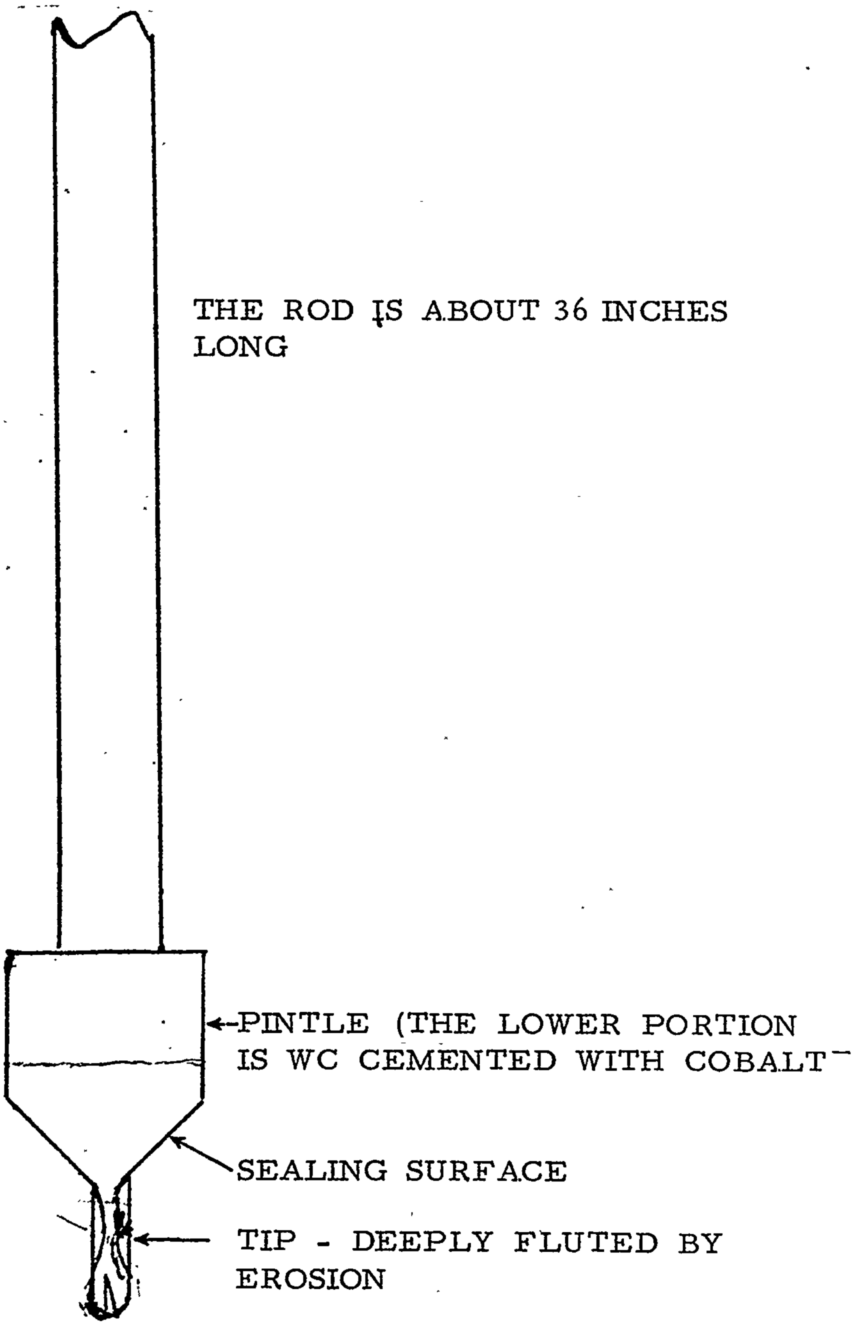


Fig. AC-8.8-1 Valve rod with pintle; the rod diameter, pintle and tip are drawn to scale.

This fineness gives minimal erosion in the system, but there are penalties which can be overcome by coarser grinding. The problem is basically one of economic balance. Fine grinding requires a good deal more energy, largely in reducing the size of rock particles; slow milling leads to a thick slurry and no settling. Coarser grinding causes more erosion and settling, but does permit faster grinding, better heat transfer in the preheater, and better life of the balls in the mill. Canfield did not feel that research was required on feed preparation. In this context, "coarse" means 100% through 60 or 80 mesh.

3. LINE PLUGGING is an occasional problem, but is not really chronic. Canfield felt that it was probably associated with the use of electric heaters. It is well known that such heaters lead to growth of deposits from hot spots since temperature excursions may occur which result in coking at the sides of the spot. Canfield showed a radiograph of a pipe that was just about solid; it was nominal 4 in. (4.5 OD, 0.67 wall, 3.16 in. ID). The usual method of detection involves measurements of pressure drops, but these generally occur too late for the effective use of preventive measures. Ultrasonic methods have been used to detect coke build-up, with limited success. There is a hot oil system in the unit but this is apparently not hot enough to be useful.

4. PUMP EROSION is not a serious problem since the plunger pumps that are currently in use minimize erosion. Research

on centrifugal pumps (cf. Rockwell International, EPRI AF-853, Project 775-1, Final Report, September 1978) is judged to be adequate. If pumps fail, multiple plunger pumps will surely be usable for scale-up.

5. FRACTIONATOR CORROSION is the most serious problem at the SRC-II unit. This difficulty has been investigated with little success. Progressively more expensive alloys have been used. The erosion rates, based on coupons hung in a tower, are:

> low carbon steel, 1.0 in./year;316 stainless
> steel, 0.2 in./year; Hastelloy G, 0.02 in. /year
> Hastelloy C, negligible.

Since the tower is two feet in diameter and about 60 feet high, alloy cost is a big factor. Certain zones appear to be hardest hit. Electron probe analysis showed nickel sulfide, but no chlorine. In many cases, there were no deposits to analyze since only bright metal remained. The tower has been steamed out when it is down, but this process did not affect the corrosion.

6. FLOW PATTERNS in the reactor were not important for the work, since there was no experience with bogging or other malfunctions of this type. There has been some use of tracers, but not for flow-pattern studies.

IMMEDIATE SUGGESTIONS

I offered the suggestions detailed below.

1. LINE PLUGGING could be detected by a gamma-ray probe such as the AccuRay from Industrial Nucleonics. The hot oil systems can be operated up to 700°F if they are properly equipped with seal pots, which prevent air from sucking back; the trapped air is soon reduced to nitrogen.

2. TOWER CORROSION may be due to trace amounts of chloride that are too low for the electron probe to detect. Chlorine can be volatilized from NaCl by two processes. Oxidation of sulfur compounds to sulfonic acids, which are non-volatile, can release HCl. Enough air could be leaking in through pump-shaft seals, etc. to provide the necessary oxidant if the sulfur is in a suitable combination. In that case, substantial injection of NaOH into the feed should help. On the other hand, a reducing situation in the tower could release NH_3 which would carry off chlorine as volatile NH_4Cl. Chloride tends to stay close to the metal and act as a "catalyst" or carrier, dissolving metal and releasing it to the oxidant such as sulfur. If this is the problem, steaming would not be sufficient. The tower should be chemically cleaned (e.g., by Dowell, Inc.) after the source of chloride has been removed.

3. FLOW PATTERNS should be measured by using radiotracer techniques [J. M. Ausman, A. Beerbower and R. E. Olsen, Chemical Eng. Progress Symposium Series, Part VIII, No. 28, Vol. 56, pp 72-75 (1960)].

RESEARCH RECOMMENDATIONS

It is evident that the pintle-valve design makes it vulnerable to erosion by liquid-borne particles. Redesign to eliminate sharp changes of direction should improve the life of the pintle tip greatly. The use of WC that does not employ a cobalt binder is also a possibility.

Pretreatment of the coal by using the Charmbury "benefication" process to remove most of the shale and pyrites by floatation would solve a whole set of problems, possibly all of those attributed to erosion and perhaps even part of the tower corrosion.

A new investigation of the tower corrosion problem would be rewarding. Since the trip, I learned from Jim Keiser at Oak Ridge that Wilsonville is experiencing similar difficulties since changing to the same feed as that used at Dupont, WA (Fort Lewis). Investigation of carbonyl sulfide (COS) formation from air, coal and sulfur is specifically suggested. This is a very active gas (b.p. ~ 0°F) and is not detected by the usual gas analysis. It can cause heavy corrosion leading to powdery FeS or Fe_2OS, which would be suspended colloidally in the bottoms.

AC-9.1 SITE VISIT TO ROCKWELL INTERNATIONAL, ENVIRONMENTAL AND ENERGY SYSTEMS DIVISION, FLASH HYDROPYROLYSIS PROJECT

(FEBRUARY 25, 1980)

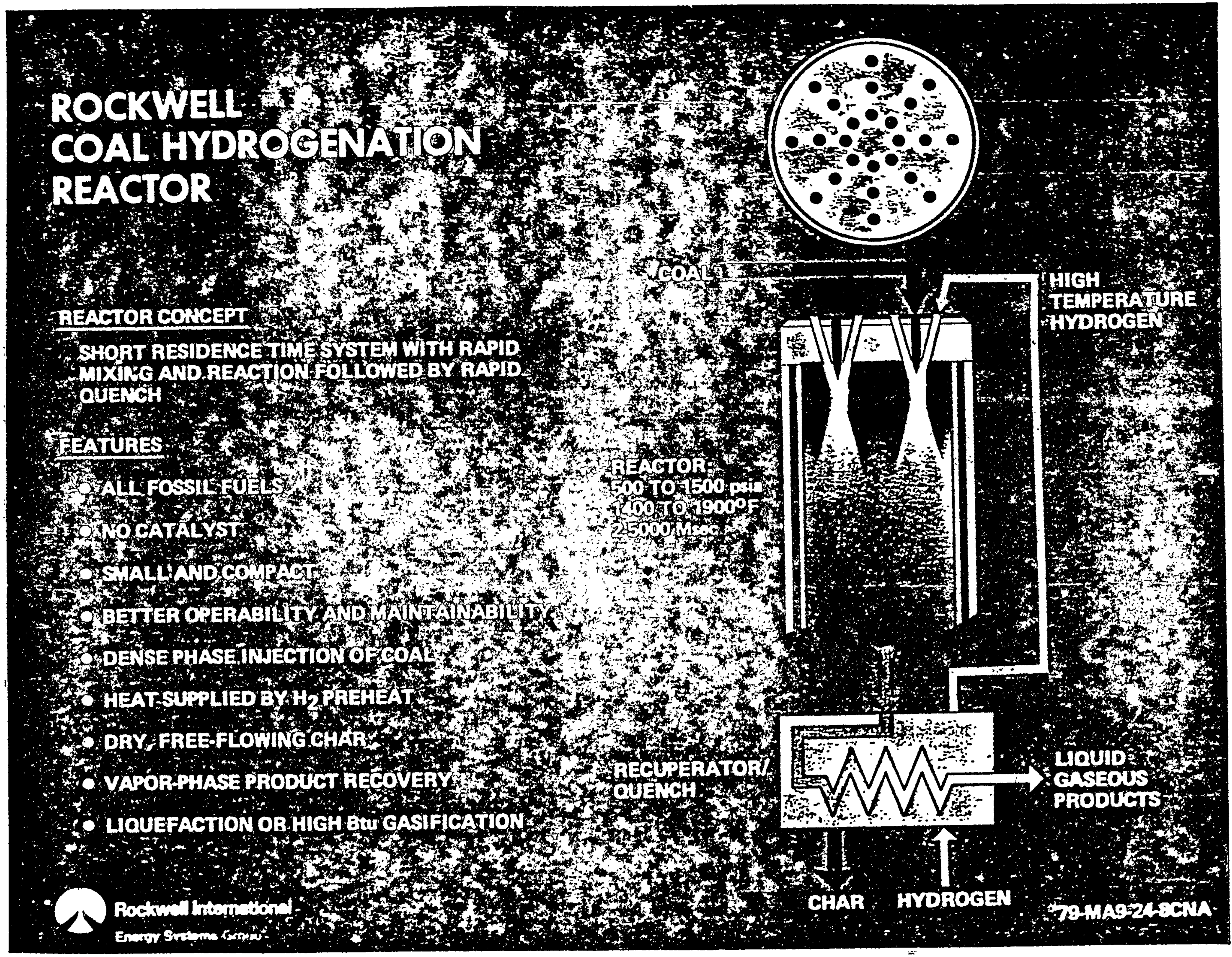
The following FERWG members visited Rockwell International on February 25, 1980: J. Clardy, S. S. Penner, and R. P. Sieg. Discussions were held with C. L. Oberg, A. Y. Falk, C. A. Trilling, and D. R. Kahn of Rockwell.

A. Process Description

A schematic diagram of the Rockwell coal-hydrogenation reactor is shown in Fig. AC-9.1-1. This system involves adaptation of rocket technology to coal pyrolysis for the production of liquids. Injection occurs through many impinging jet orifices (with impingement angles of approximately 30° between a central stream of comminuted coal and high-temperature hydrogen gas). The developed system is expected to show the following characteristics of rocket reactors: very high mass-flow rates through relatively small reactors, unit sizes that are readily scaled by replication of injector elements and reactor diameters, successful pyrolysis of a very wide variety of coals ranging from bituminous coals to peat.

B. Process Characteristics

The coal-pyrolysis reactions leading to liquid products are nearly thermoneutral. Residence times used in the reactor typically fall in the range 50×10^{-3} to 5 sec. A variety of coals has been tested successfully. The coal is not pretreated. Seventy to ninety percent of the coal passes a 200 mesh screen. A separate catalyst is not used. A 1 ton/hour reactor has an inside diameter of 3 inches and a length of 5 feet; for this throughout, 8 impinging injector sets



ROCKWELL COAL HYDROGENATION REACTOR

REACTOR CONCEPT

SHORT RESIDENCE TIME SYSTEM WITH RAPID MIXING AND REACTION FOLLOWED BY RAPID QUENCH

FEATURES

- ALL FOSSIL FUELS
- NO CATALYST
- SMALL AND COMPACT
- BETTER OPERABILITY AND MAINTAINABILITY
- DENSE PHASE INJECTION OF COAL
- HEAT SUPPLIED BY H_2 PREHEAT
- DRY, FREE-FLOWING CHAR
- VAPOR-PHASE PRODUCT RECOVERY
- LIQUEFACTION OR HIGH Btu GASIFICATION

Rockwell International
Energy Systems Group

79-MA9-24-8CNA

Fig. AC-9.1-1 Description of the Rockwell coal-hydrogenation process for coal liquefaction through pyrolysis.

are used. The longest test duration has been about 3 hours. No indications of significant erosion problems were observed. Temperature measurements have been made near the reactor wall with thermocouples.

With the presently used system, it is difficult to differentiate between mixing phenomena and hydrogenation. The bulk density of the product particles is about one half of that of the inlet coal. Substantially equivalent results have been obtained with the following carrier gases for the coal: N_2, H_2, He, CO_2. Adequate preheating of H_2 is assured by using both electrical heating and partial combustion with O_2. Test durations have been limited by problems encountered on separating liquids from char in a spherical chamber; it is hoped that this problem will be alleviated by replacing the spherical char-settling chamber by an appropriately designed conical chamber.

C. Contract History

The original DOE contract extended for a period of 55 months (August 1975 to February 1980) and was funded at a level of $4,550,944. An extension contract is expected to allow program continuation around the end of March 1980. In the meantime, the facility has been shut down since the beginning of February and the operating crew members have been assigned to other tasks.

D. Results and Future Studies

A reliable method of coal feeding has been demonstrated; the coal flow rate is directly dependent on the overall pressure drop. High mixing efficiencies between gas and coal are important and have been achieved by using appropriate kinetic energy ratios at injection (≈ 6). The liquid yield reaches a maximum value of about 37% near a reactor temperature of 1500°F while total carbon conversion increases to over 62% at 2000°F. The Rockwell coal-pyrolysis data generally agree with results derived from smaller scale laboratory tests. While total carbon conversion to gas and liquid is not sensitive to reactor residence time, the liquid yields decrease quite rapidly with increasing reactor residence times. The effects of reactor pressure on conversion have been found to be small. The liquid-product yields include about 45% of toluenc, benzene and naphthalene. The product gas is largely methane (70 to 90%) with very small amounts of CO_2 (~ 3%) and the balance made up by CO. The percentage by weight of H_2 consumed relative to the weight of coal pyrolyzed lies between 1 and 7%, depending on reactor residence time and temperature (both of which lead to increasing hydrogen consumption as they are raised).

AC-9.2 COAL PYROLYSIS AT THE OCCIDENTAL RESEARCH CORPORATION*

The following discussion is based on the Occidental Research Corporation (ORC) "Flash Pyrolysis" Process, which has been under development at ORC since 1969 and has been tested at the 3 tpd scale.

A. Process Description

The process will be described with reference to a conceptual commercial design. Figure 9.2-1 shows a block diagram of the overall process while Fig. 9.2-2 emphasizes details of the pyrolysis section.

The commercial design involves processing of 22,444 tpsd of coals with 10% moisture and 8.5% ash (W. Kentucky #9 seam bituminous coal). The char produced amounts to 10,317 tpsd at 11,900 BTU/lb and is sufficient to fuel a 1000 MW power station adjacent to the pyrolysis plant. Based on a raw liquid yield of 35% (MAF basis), the yield of hydrorefined oil products is 31,200 bpsd (i.e., approximately 1.7 bbl/ton of MAF coal).

Washed coal is received at the plant by unit train and is stacked in open storage piles. Coal is reclaimed from storage and fed to the coal preparation plant where it is crushed, ground and classified to -60 mesh particles, and dried.

Pulverized coal is transferred to the flash-pyrolysis reactor, where it is contacted with a circulating stream of 1400°F char at 5 times the coal-feed rate. The coal is heated to about 1075°F in a fraction of a second and produces oil, gas and char. The oil and gas products are separated from the char and quenched in 1.5 seconds. A portion of the char product (~ 7 wt. % of the feed coal) is burned in a transfer line burner to reheat the circulating char stream which supplies heat for pyrolysis. The net char product is cooled and sent to

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*This report has been prepared by FERWG member F. Leder and critically reviewed by the following FERWG members: J. Clardy, S. S. Penner, and J. Ross.

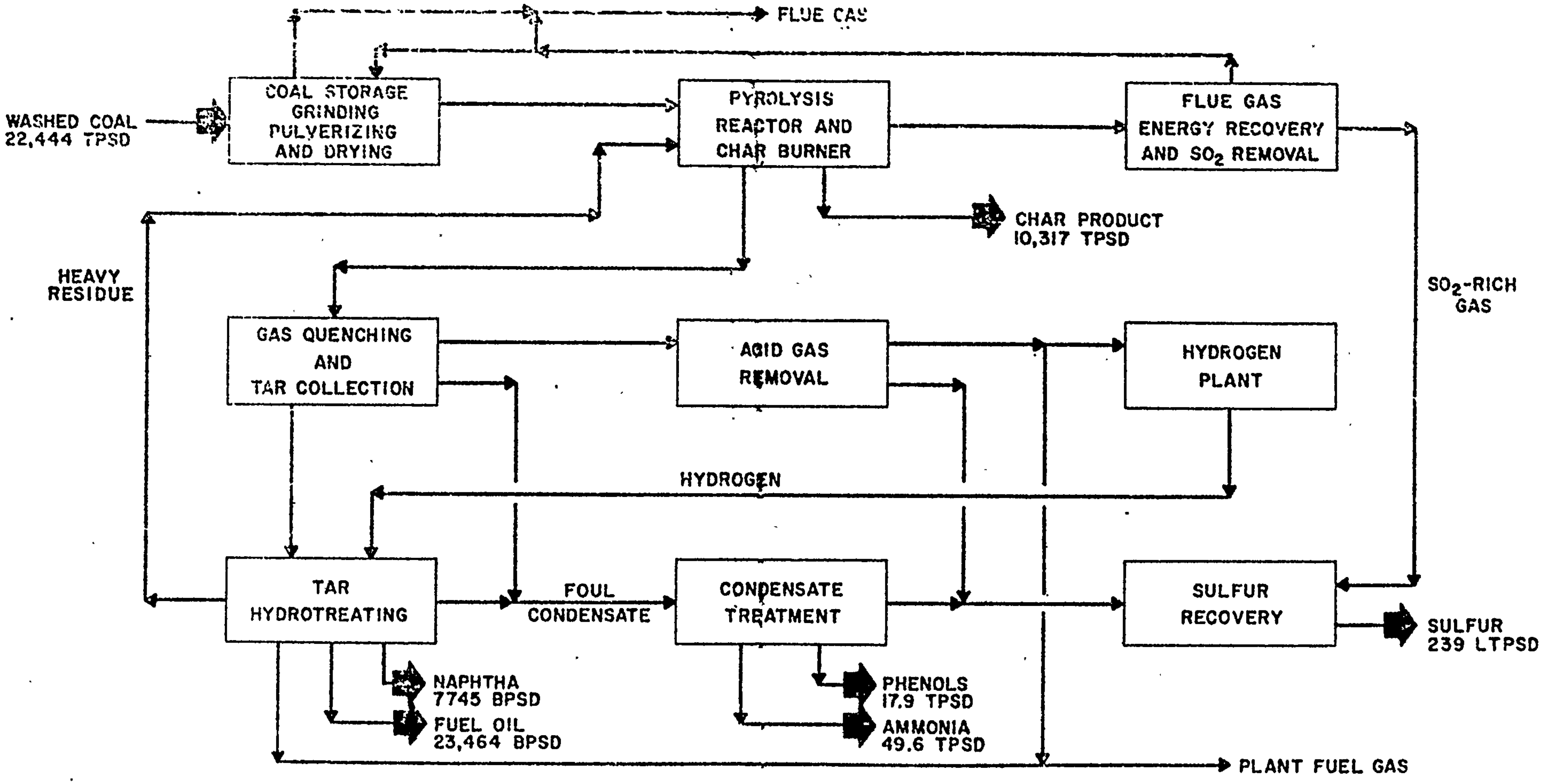

Fig. 9.2-1 Schematic diagram of the ORC flash-pyrolysis process.

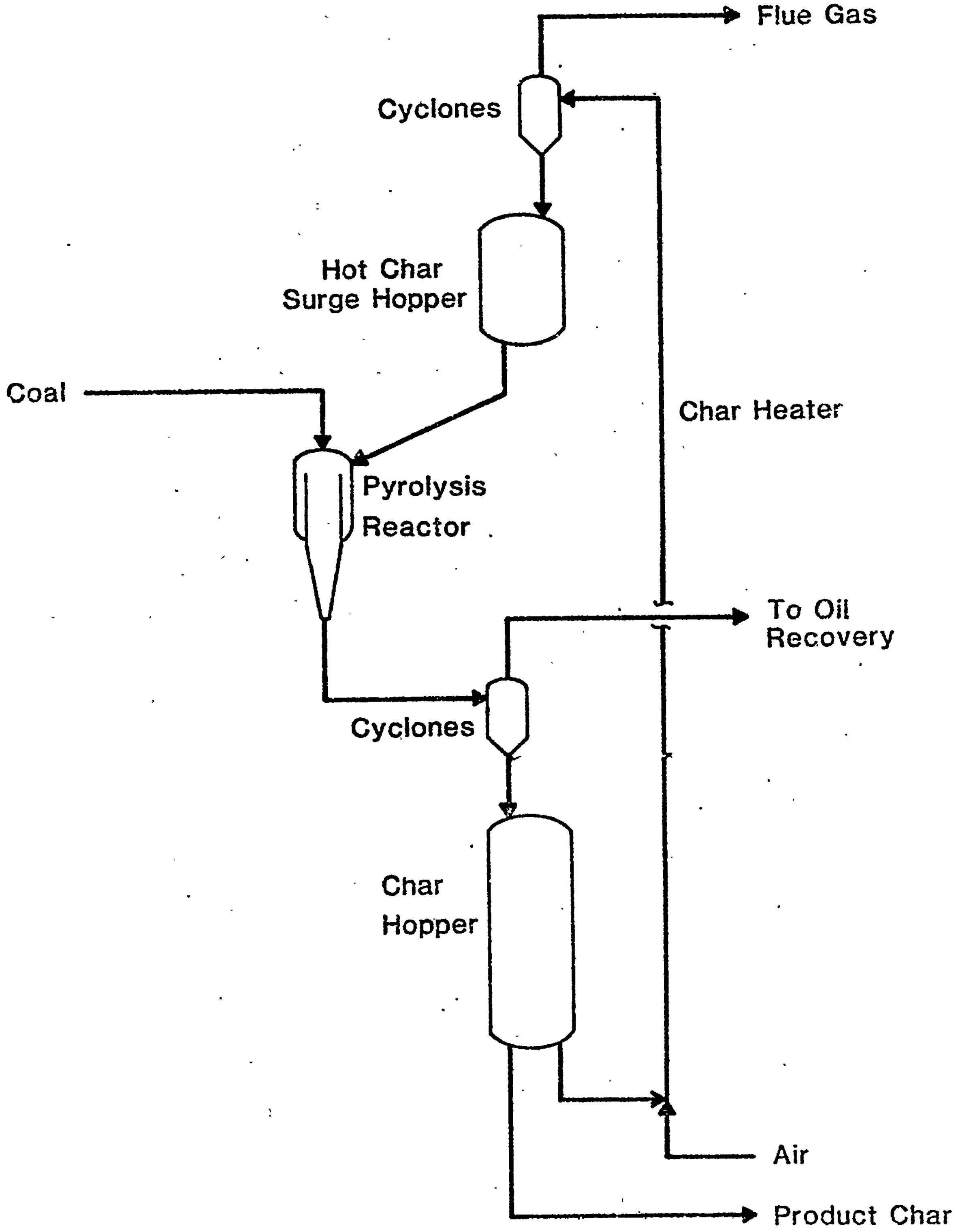

Fig. 9.2-2 A schematic diagram of the flash-pyrolysis section.

storage. Energy is recovered from the flue-gas before it is desulfurized and released to the atmosphere.

Hot vapors from the pyrolysis section are quenched and cooled to recover oil and gas fractions. Oil is fed to the hydrotreater, where low-sulfur fuel oil is produced. Dry gas is compressed and is partly used (after removal of sulfur compounds) as feedstock for hydrogen production by steam reforming and partly as plant fuel.

Hydrotreating of the raw oil in an ebullating bed reactor yields 7745 bpsd of -250°F, 49° API, 0.07% naphtha and 23,464 bpsd of +250°F, 4.6° API, 0.5% S fuel oil. The hydrogen consumption is 1700 SCF/bbl. The high boiling fraction of the oil product from the hydrotreater contains char fines that are entrained in the pyrolysis section. The oil is recycled to the pyrolysis reactors, where it is converted to char and lighter oil products.

Elemental sulfur, anhydrous ammonia, and phenols are recovered by conventional acid-gas removal and water treatment.

B. Performance Data

A 3 tpd PDU was operated under ERDA contract to test the process (1975-78). The liquid-yield and quality for two coals are summarized in Table 9.2-1.

The yields of 35% MAF from the bituminous coal and 22% MAF from subbituminous coal correspond to more than twice the Fischer assay oil contents of these coals without hydrogenation.

The liquid yield decreases with increasing residence time, as is shown in Fig. 9.2-3. The reported peak yields occurred at a residence time of 1.5 seconds, which corresponds to the commerical design point. The curves of Fig. 9.2-3 may be fitted by a first order devolatilization/cracking reaction model (see below).

Table 9.2-1 Liquid yields obtained by workers at Occidental Petroleum in flash pyrolysis; data characterization.

Coal		
Rank	Bituminous C	Subbituminous C
Source	W. Kentucky No. 9	Big Horn, Wyoming
Yield		
Wt. %	35	22
Bbl/ton	1.7	1.1
Analysis		
Ultimate, wt. %		
C	80.3	77.6
H	7.0	7.2
N	1.4	1.2
S	2.1	0.4
O	9.2	13.6
Atomic H/C	1.05	1.12
Gravity, °API	-12.6	-9.8

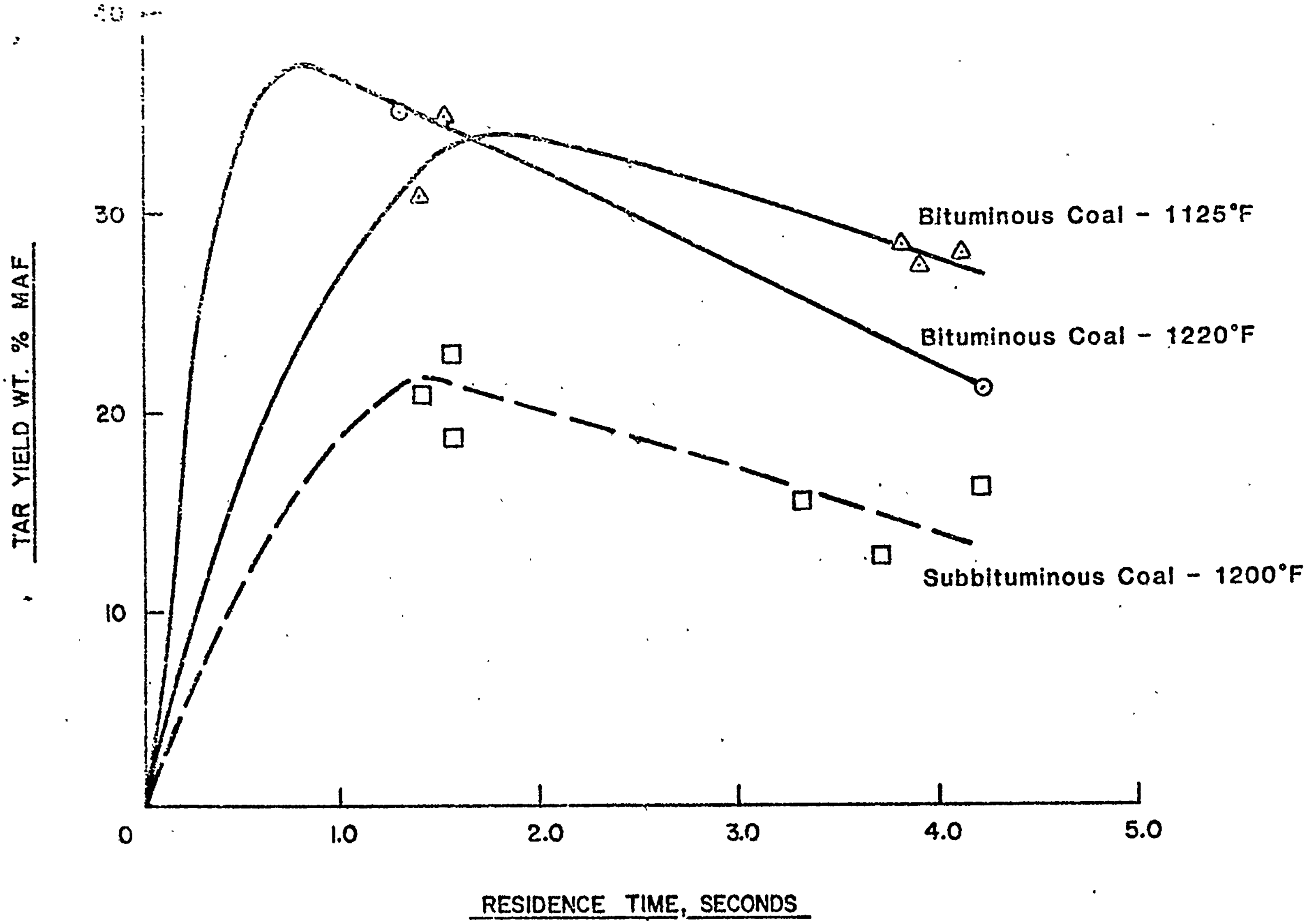

Fig. 9.2-3 Flash-pyrolysis liquid-yield data as functions of residence time.

The char tended to crack which reduced the yield. The use of char-to-coal ratios, in combination with inert transport gas, led to yields as low as 5%. Reactive gases (e.g., steam and CO_2) have been shown to be effective in terminating undesirable reactions that result in low yields.

The raw liquids are heavy and hydrogen-deficient. More detailed characterization is needed. The available results suggest that higher liquid yields do not necessarily lead to substantially heavier liquids.

Limited work has shown that the liquids may be hydrogenated catalytically. A 28° API syncrude was produced by using fixed-bed hydrotreatment on the liquids derived from subbituminous coal over a commercial Co-Mo catalyst; the H_2 uptake was 3100 SCF/bbl. Nitrogen removal of 80% and sulfur removal of 96% were obtained, as well as 98% conversion of asphaltenes and asphaltols to oil. The need for more work, particularly with bituminous-coal-derived liquids, is apparent.

C. Comments on the Pyrolysis Process

Pyrolysis is analogous to fluid, catalytic cracking. It is a simple procedure using proven technology. Application of the product char as a heat carrier is a distinctive feature of the ORC process. This method of heat supply leads to high through-put, is easily scaled up, avoids dilution of product gas with combustion products, and eliminates the need for an oxygen plant. The use of low-pressure service simplifies the design and feeding of solids. Application of the ORC technology to coal and solid-waste pyrolysis in the PDU was generally straightforward. However, the handling of bituminous coal required a special reactor design. The pneumatic transport of char represents a significant departure from the technology used in petroleum fluid coking and cracking to achieve fluidization.

Efficient cyclones are needed to minimize the loss of char fines to the oil-collection system. The cyclone volume accounts for about half of the vapor-phase residence time. A short residence time, higher efficiency gas-solid separations procedure would be a significant process improvement.

Reliable means must be found to perform rapid pyrolysis of caking bituminous coals because these coals produce the highest liquid yields on pyrolysis. Nearly all bituminous coals are moderately or highly caking and tend to plug pyrolysis reactors. Preoxidation or slow stagewise heating to reduce the caking tendency ameliorate this problem but leads to low liquid yields, as was noted earlier.

An entrained flow reactor was designed to handle caking coals without pretreatment and was tested in the PDU with some success. Continuous runs, with durations of up to 22 hours, were achieved with optimal yields. However, the reactor was subject to sudden irreversible fouling and forced shutdown as a result of erratic char flow. Smooth pneumatic transport of char to the reactor is of crucial importance. Since fluctuations and upsets can be expected in practice, additional engineering development will be necessary to achieve a commercially reliable design.

The char yield from rapid pyrolysis of bituminous coal is approximately 50%. Both the heating value and the sulfur content of rapid pyrolysis char are about the same as of the parent coal. Char utilization as a solid fuel therefore requires desulfurization or SO_2 control, as for the parent coal. At ORC, both char desulfurization and combustion have been studied.

AC-10. COSTING OF COAL LIQUIDS

A working group was convened at the UCSD Energy Center (on January 24 and 25, 1980) for discussions on the costing of coal liquids, to compare methodological aspects in costing, and to identify key R&D programs that might lead to reductions in product costs. F. Leder (part time) and R. P. Sieg of FERWG served as co-chairmen of the discussions and S. S. Penner participated on a part time basis. Participants included J. S. Morrison (Exxon Research and Engineering Company, P.O. Box 101, Florham Park, N.J. 07932), R. Nene (Gulf Research & Development Co., P.O. Box 2038, Pittsburgh, Pa. 15230), B. K. Schmid (Gulf Mineral Resources Co., 1720 So. Bellaire, Denver, Co. 80222), N. G. Moll and G. A. Stuart (Dow Chemical Co., Midland, Mi. 48640), R. T. Struck and W. E. Clark (Conoco Development Co., Research Division, Library, Pa. 15129), and R. N. Quade and J. F. Watson (General Atomic Co., P.O. Box 81608, San Diego, Ca. 92112). W. Häfele (International Institute for Applied Systems Analysis, Laxenburg, Austria) also participated on a part-time basis.

Carefully prepared presentations were presented on the EDS, SRC-II, Dow, and $ZnCl_2$ processes for coal liquefaction.

Important cost areas include costs for off-site utilities, hydrogen production (about 15% of total costs in the EDS and SRC-II processes and perhaps 28% in the Dow process), and costs for bottoms processing. The use of off-peak power to produce hydrogen may be a desirable procedure. Generally, hydrogen production by electrolysis will be competitive with operations of a balanced plant only if capital costs for electricity generation are less than about $\$300/kw_e$.

Häfele discussed an interesting proposal to use independently generated H_2 (e.g., from solar or breeder-reactor power stations) as an "integrator" over the long term. This type of procedure is clearly desirable when hydrogen costs are low and will have the potentially important beneficial effect of reducing atmospheric CO_2 input. There was general agreement with Häfele that a systems integration program dealing with the efficacy of off-site hydrogen use should be implemented.

Research recommendations derived from the discussions by the working group on the costing of coal liquids are summarized in Chapter IV of the main text.

APPENDIX D:

COMMENTS BY REVIEWERS

A preliminary version of this report was sent to outside reviewers. In most instances, the comments and corrections suggested by the reviewers were incorporated within the final document. In those cases in which the reviewers' comments could not be easily accommodated, letters for direct inclusion in this report were requested. These are reproduced here without change.

We are especially indebted to the following reviewers for calling needed corrections to our attention: W. R. Grimes (Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830), P. H. Kydd (Vice President/Technology, Hydrocarbon Research, Inc., P.O. Box 6047, Lawrenceville, New Jersey 08648), M. Orchin (Professor of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221), D. K. Schmalzer (Manager, Technology Development, The Pittsburg & Midway Coal Mining Co., P.O. Box 3396, Englewood, Colorado 80155), and R. H. Wolk (Project Manager, Clean Liquid and Solid Fuels, Electric Power Research Institute, 3412 Hillview Avenue, P.O. Box 10412, Palo Alto, California 94303).

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March 13, 1980

Prof. S. S. Penner
Department of of Applied Mechanics and
Engineering Sciences
University of California, San Diego
La Jolla, California 92093

Dear Professor Penner:

I am sorry to tell you that I have not had the time to give your assessment (FERWG-11, March 1980) the attention that it deserves. I agree that most, and probably all, of the many needs you identify are real and pressing. I have, accordingly, only a few comments to make.

I would probably have put more emphasis than you seem to upon porosity, internal suface and pore size distribution in coals and the changes in these properties upon heating, chemical treatments, etc.

I am not certain that I see a pressing need for further study of "equilibrium solubilities of coal in various (conventional) solvents" (p. 21). I do feel that the U.S. needs considerable study of coal extraction by super critical solvents (and this could perhaps include "equilibrium solubility" though at such temperatures some thermal effects obtain and I am not sure what "equilibrium" is).

I should like to have seen more attention given to indirect liquefaction processes since these may offer the best possibilities for relatively near-term conversion of coals to clean liquid fuels. You do include discussion of them on pages 4 through 8, but, though you have noted several pertinent points, you seem to have missed an opportunity to provide some (to me) important specific advice. As you note, coal gasification is expensive (in an energy sense); second generation gasifiers - such as the Lurgi Slagger or the Texaco - will operate, for improved energy efficiency, with minimal steam and oxygen feeds, and their output gas will have H_2:CO ratios in the range 0.6 to 0.7. Such ratios are far below those needed to avoid catalyst degradation via carbon formation in commercial Fischer-Tropsch or methanol synthesis. One can, of course, use the water-gas shift reaction to obtain the necessary H_2:CO ratio, but there is an energy penalty in this. The ability to use low H_2:CO ratios directly in Fischer-Tropsch or other synthesis is very desirable. It is this desirability that leads to interest in the slurry-phase Kölbel reactor which may markedly assist with this problem. The Kölbel-Englehardt synthesis, which under carefully controlled conditions can use CO:H_2O mixtures, represents the extreme in this regard and would also seem to be worthy of some study. Along these same lines, I feel that additional study of gas cleanup at high temperatures and pressures might also be a rewarding venture.

Thank you for the opportunity to review the output of your study, which I consider to have been well and carefully done. I regret that I have not been able to be of real assistance to you.

Very truly yours,

W. R. Grimes/nyw

W. R. Grimes

WRG:nyw

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Cincinnati, Ohio 45221
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DEPARTMENT OF CHEMISTRY

March 18, 1980

Dr. S. S. Penner,
Professor of Engineering Physics
University of California, San Diego
La Jolla, California 92093

Dear Dr. Penner:

I have gone through your "Assessment of Long-Term Research Needs for Coal-Liquefaction Technologies" rather rapidly and find it an outstanding and comprehensive document with much valuable summary material.

In addition to a number of errors, which have been corrected in the final document, I wish to offer the following comments concerning the discussion on p. AC-185.

The work of Deno could be made much more valuable if it were complemented by the results of oxidations with reagents that oxidize side chains and not rings, e.g. $KMnO_4$ and HNO_3. Taken together, these two oxidation techniques would be more revealing than either alone. I am not as sanguine as most people seem to be about the ultimate power of Deno's technique. I am sure ambiguities will arise because alternate structures can give the same product. Furthermore, the knowledge that alkaline $KMnO_4$ oxidation provided about the aromatic nuclei and the degree of substitution of rings (H. C. Howard, work in the 1940's) was very powerful but fell far short of elucidating the constitution of the clusters in coal.

I certainly enjoyed reading through your report and want to both congratulate you and thank you for sending me a copy of it.

Sincerely yours,

Milton Orchin

Milton Orchin
Professor of Chemistry

MO/jcc

ELECTRIC POWER RESEARCH INSTITUTE

EPRI

March 26, 1980

Dr. S. S. Penner
Mail Code B-010
University of California San Diego
LaJolla, CA 92093

Dear Dr. Penner:

I appreciate the effort that the FERWG-II group is making in contacting outside reviewers to insure that the final report on Assessment of Long Term Research Needs for Coal Liquefaction Technologies is both comprehensive and correct. Your prompt attention to correcting several items that I noted during our recent telephone conversation is an example of this attitude.

There are several research areas, in addition to those covered in the report, that I feel need further consideration. These include:

- Product utilization test programs
- Residue gasification
- Analytical workup procedures for raw liquefaction products
- Prior basic research work funded by OCR, ERDA and DOE
- Iron phenolate identification and impacts
- Centrifuge development

Product Utilization Test Programs

The proper economic optimization of a given process always involves the values that are assumed for the products resulting from that process. Test programs are required to establish values for various coal liquefaction products in relation to alternative materials. Coal liquefaction products are inherently lower in hydrogen content than comparable materials derived from petroleum. Product hydrotreating can be utilized to increase the hydrogen content to any desired level. However, it is not clear yet that the hydrogen content standards established for petroleum based fuels are necessary for coal derived liquids. Performance tests on large scale equipment are required to establish the compositional requirements for coal liquids.

Since coal liquefaction products can contain rather large percentages of nitrogen, up to about 2.0 wt%, their combustion with normal techniques can generate NO_x emissions which are above the stringent levels now being promulgated. Improved combustion techniques of the type that utilize staging can reduce NO_x emissions considerably. However, the risk in taking this approach is the potential generation of smoke because of the relatively low hydrogen content of the fuels.

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Basic research is required on staged combustion of high nitrogen/low hydrogen fuels to establish reaction mechanisms on a quantitative level. This will enable predictive models to be developed which will determine proper combustion conditions which simultaneously minimize smoke and NO_x formation. If confirmed in large scale tests, the cost of this approach can then be measured against the alternative concept of severe product hydrotreating to establish the same goals.

Residue Gasification

Hydrogen and/or fuel gas generation from liquefaction residues requires a large part, perhaps 30%, of the total investment in a coal liquefaction plant. In view of this massive financial requirement, research should be carried out either to improve reliability or reduce investment. The most significant area requiring further research is the rate of degradation of residues as a function of time, temperature, amount of diluent, and amount of solids. Each of these items is determined by and can be controlled independently by the liquefaction process. Therefore, some tradeoffs could be calculated if a good data base existed on the behavior of liquefaction residues as a function of composition at elevated temperature.

Other areas requiring better definition are refractory life as a function of gasification zone operating temperature and coal ash composition and temperature measurement in the gasification zone at levels of 2200-3000°F.

Analytical Workup Procedures

The analysis of coal liquefaction products depends to a significant degree to how the product is handled prior to reaching the analyst, whether certain materials are removed by distillation prior to being subjected to solvent extraction, and finally to the solvents that are used and the sequence in which those extractions are carried out. Almost every individual laboratory working in this country has developed its own procedure for analyzing products. In some cases specific procedures may be significant to the development of a given process concept and therefore these procedures can be justified.

Sample exchanges between laboratories often do not yield comparable results. This situation makes it extremely difficult to utilize literature information on product yields for comparison purposes. Therefore, a reasonable effort should be devoted to developing standard procedures for handling and analyzing coal liquefaction products.

Basic Research

A large number of projects devoted to collecting basic data have been funded over the years by OCR, ERDA and DOE. A compendium of this work would be extremely valuable in setting priorities for new projects.

Iron Phenolates

The role of iron phenolates in coal liquefaction is not well understood at this time. It is certainly worthy of a definitive program on the chemistry of formation, analytical identification procedures, and reactivity with structural steels, vessel linings, and catalytic surfaces.

Catalyst deactivation due to iron deposition in catalyst pores or on external surfaces may involve phenolate intermediates. Corrosion of distillation towers handling streams boiling in the 350-600°F range may also involve compounds of this type.

Centrifuges

A significant amount of mechanical development work was carried out on centrifuges at the Wilsonville SRC plant. This work led to the successful utilization of a titanium bellows seal in a solid bowl centrifuge that allowed operation at temperatures and pressures of interest. It should be pointed out that in all cases the centrifuges that have been used for the separation of solids from coal liquefaction products have not been designed for the severe temperature levels that are required.

There may be applications involving the separation of solids from low viscosity products for which centrifuges may prove to be the best choice.

I hope that these comments prove useful in identifying additional areas for future research.

Very truly yours,

Ronald H. Wolk

Ronald H. Wolk
Project Manager
Clean Liquid and Solid Fuels

RHW:sg