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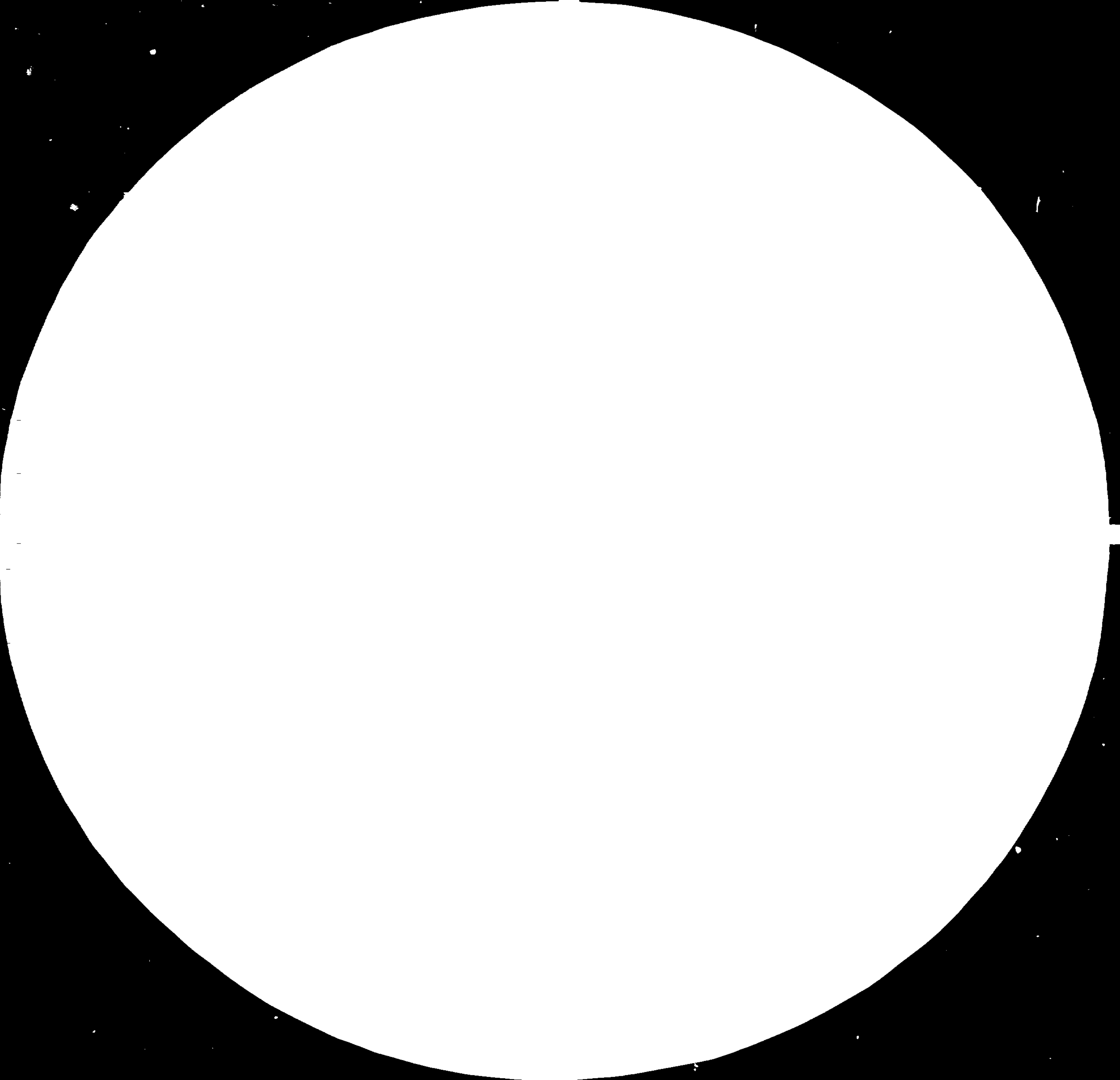

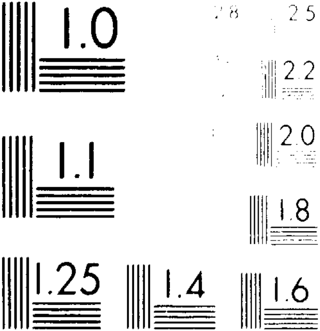
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DIRECT COAL LIQUEFACTION. Poland,

Job Description: DP/POL/77/102/11-04

Report of Visit*
to
INSTITUTE OF CARBOCHEMISTRY
Tychy-Wyry, Poland

and

CENTRAL MINING INSTITUTE
Katowice, Poland

September 2-14, 1981

by

Y. T. Shah
Expert in Coal Liquefaction

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Summary

Consulting and lecturing have been performed at the Institute of Carbochemistry, Tychy-Wyry and Central Mining Institute, Katowice, Poland from September 6 to September 12, 1981. There were five lectures entitled: (1) Structure of Coal; (2) Mechanism of Coal Liquefaction and Coal Liquefaction Processes; (3) Slurry Reactors - Part I; (4) Slurry Reactors - Part II, and (5) Lumped Kinetic Models for the Direct Coal Liquefaction given during this period. These lectures were followed by in depth discussions on each subject. Approximately 10 to 15 people attended these lectures. Some discussions and consulting help on their program were also performed.

Personnel Visited

The following personnel of the Institute of Carbochemistry were involved in most of the discussions:

Doc. Dr. Inz. Jerzy Winnicki, Director, Institute of Carbochemistry

Dr. Inz. Jan Janczarek, Deputy Director, Institute of Carbochemistry

Mgr. Inz. Adam Worsztynowicz, Chief, Group of Process Calculations

Mgr. Inz. Jerzy Swigdrowski, Chief, Installation of Plants

Mgr. Inz. Bernard Zagorski
Mgr. Inz. Alina Pilch-Kowalczyk
Mgr. Inz. M. Ferster
Mgr. Inz. W. Petyka Research Workers
Mgr. Inz. B. Robak
Mgr. Inz. J. Gridzinski
Mgr. Inz. G. Szlyzak

During the lecture at Central Mining Institute on September 12, 1981, several other visitors from Warsaw and other parts of the country were also present. The lectures and subsequent discussions during September 7-11, 1981 were all carried out at the Institute of Carbochemistry.

Lectures

During the visit, I had given the following lectures:

September 7	Structure of Coal
September 8	Mechanism of Coal Liquefaction and Processes for Direct Coal Liquefaction - Role of Catalyst on Coal Liquefaction
September 9	Slurry Reactors - Laboratory Measurements and Design and Scale-Up of Commercial Reactors - Part I
September 10	Slurry Reactors - Laboratory Reactor Design and Important Features for Cold Model Experiments - Part II
September 11	Lumped Kinetic Models for Direct Coal Liquefaction

Besides the discussions on the above topics, the following additional topics of their interest were also discussed:

1. Physical - Chemical Data Source
2. Upgrading of First Step Coal Liquefaction Products
3. Practical Hints Concerning PDU Running

All the lectures and the following discussions were based on my recent book "*Reaction Engineering in Direct Coal Liquefaction*" by Addison-Wesley Publishing Company (1981) and other published materials in technical and scientific journals. The discussions were found to be fruitful by both parties. The specific questions discussed are described in details in a later part of this report.

Character of Coal

Present Polish bituminous coal production is about 200 million metric tons/year (a metric ton, mt is equal to 1000 kg or 2205 lbs - approximately 1.1 U.S. tons). The Poles hope to mine over 300 million tons per year by the year 2000. Reserves will support such a production rate for several hundred years.

About 98% of Poland's present bituminous coal production is concentrated in the Upper Silesian Basin and averages about 1 wt% (mainly organic) sulfur. The remaining 2% of hard coal production is in the Eastern Poland; it averages 4 wt% sulfur and have been examined as possible candidates for liquefaction. Currently, only the young bituminous coals obtained from Jaworrnicko-Mikokowskie basin have been considered for the liquefaction. Brown coal whose production is about 400 million tons/year is mainly used for utility power generation. The proven Polish brown coal reserves are estimated to be 60 billion tons. The Polish economy is a coal economy in which 70% of their energy needs are supplied by coal. Polish bituminous coal deposits are deep and at most only one strip mining operation digging bituminous coal exists.

After evaluating many coals, only one coal is planned to be used in future coal liquefaction experiments. In their estimates the results will be used for another 20-25 years. Resources of this coal are enough to produce 1-2 million tons of liquid/year for 30 to 40 years. In the distant future, the bituminous coal obtained near Russian borders may also be used. The composition of upper Selesian coal that is currently planned to be used is as follows:

Nitrogen content	1.4 wt%
Sulfur content	1.26 wt% (mainly organic)
Hydrogen content	4.5 wt%
Carbon	70.20 wt%
Oxygen	9.85 wt%
Water	10 wt%
Volatile matter	34.9 wt%
Calorific value	27130 kJ/kg

The average ash content is about 15% (containing Fe-oxides, lime, ferric carbonates etc. not much FeS_2). This ash content is difficult to remove.

Program for Coal Liquefaction

Their program for liquefaction is under the charge of Professor R. Zahaczewski who is resided at Central Mining Institute, Katowice.

Early Studies (1972-1979) - CSF Approach

The Institute of Carbochemistry is operating two continuous coal liquefaction units, 120 and 1200 kg coal/day, both of which were initially modeled after the Consolidation Coal Company's CSF process which the Poles saw at Cresap, WV. The 1200 kg/day PDU contained an ebullated bed reactor for hydrogenation of the recycle solvent. Six tubular, upflow liquefaction reactors are available for operation at pressures up to 320 atm or a single stirred tank reactor for operation in the CSF mode at 40 atm. The six tubular reactors are 20 cm ID and approximately 3.5 meters long. The preheater is a hairpin-type in a furnace; it has an ID of 20 mm, a length of 160 meters, and is designed to operate up to 420°C at 320 atm. The solids separation is presently being performed uisng candle filters having an area of one square meter. Filtration was found to be a very difficult problem. Hydrogen is supplied from a water electrolysis plant (80 Nm^3/hr) adjacent to the PDU.

The 120 kg/day unit was similar to the 1200 kg/day unit with the exception that the extract hydrogenation is performed in trickle bed reactors of about 20 liter/hr capacity. Two 500 ml trickle-bed catalyst test units capable of operation at pressures up to 300 atm and 200 to 600 ml/hr were being used for extract hydrogenation and catalyst studies. Laboratory studies on coal extraction were performed in one and four liter stirred autoclaves.

The catalyst research had been on testing conventional catalysts and synthesizinq and testing new formulations. In catalyst poisoning studies, where the nitrogen content of the coal liquids was reduced to 0.1 - 0.5% and the hydrogen content increased to 10 - 12%, they determine cokinq to be the primary cuase of rapid deactivation and deposition of titanium and other metals as causing slow long-term deactivation. This was in agreement with findings in the U.S. Reaction conditions were usually 430 and 450^{0}C (2 stages) 280 atm, and 0.5 kg extract feed/liter catalyst-hr. Catalyst life was typically 500 hrs and the benzene insolubles in the product increased to 30% of the feed content after 250 hrs. The catalyst usage rate at this level of deactivation was roughly 200 kg extract processed/kg catalyst, or about 1.5 lbs of catalyst/ton of coal processed. For reference, H-Coal is designed on the basis of 1.0 lb/ton. Catalysts studied were Co-Ni-Mo, Co-Mo, and Ni-Mo, all supported on alumina. In further studies of alumina support pore structure, it was found that catalysts with a large fraction of pores in the 200-500A range had relatively high activity and seemed less susceptible to deactivation by coke deposition. A technique was developed to synthesize alumina supports used in the pore size studies.

Testing on the 1200 kg/day unit was concerned with integrated operation of the ebullated bed extract hydrogenation step with the extraction reactors. The fluidization in the ebullated bed was accomplished by gas recycle, and the liquid is not recycled internally beyond the normal backmixing caused by the gas. The extraction medium in the previous work was not derived from extract hydrogenation, but was either hydrogenated anthracene oil or a mixture consisting of hydrogenated anthracene oil, oil from distillation of the filtrate, and oil from low-temperature carbonization of the filter cake. Their coal extraction and solids separation work is being carried out in a wide variety of processing equipment. Their autoclaves ranged from 1 to 4 liters capacity and operate at 450°C and 200 atms. Their batch filters operated at 350°C and 3 atoms, while their continuous (rotary) filters operated at 350°C and up to 8 atms. They also had centrifuges (4,000 rpm) operating at 250°C and 1 atm. Their vacuum distillation capability extended down to 1 mm Hg. They also had low temperature carbonization units of 1 and 5 liters each. Finally, they had also installed hydroclones to operate at 350°C and 10 atms.

A Bran-Lubbe Pump (Type N-B31, Nr. 51-42248/73) from Hamburg, W. Germany was evaluated for pumping slurries at conditions up to 300 atm and 465°C. It was subsequently used for external slurry recirculation in an ebullated bed reactor. With this reactor option and the other two options mentioned earlier (four high pressure reactors or a single CSF-type reactor), the PDU was capable of simulating the operations of the CSF, H-Coal, EXXON Donor Solvent, and SRC II processes. This fell in line with their objectives to prepare to build and operate various coal liquefaction processes.

Recent Studies

Around 1979, the work on smaller unit was slowed down and in 1979-1980, the major effort was concentrated on the larger unit. They are presently examining the operation of the larger unit with external slurry recycling for processing Upper Selesian coal. The reactor in larger unit is 160 mm ID and 6 m in length. All the experiments are conducted for one coal, 30-35 wt% slurry (with hydrogenated ant. oil and mixture of recycle oil as liquid), Ni-Mo 1.5 mm extrudate catalyst (about 25 kg catalyst in the reactor), temperature range of 430^0C-450^0C and pressure range of 150 atm-200 atm. Slurry velocity of approximately 3 cm/sec and gas velocity of approximately 9 cm/sec are used.

The goal of the present five year program (1981-1986) is to evaluate operability of the ebullated bed externally recycled 1200 kg/day reactor. The data obtained from a smaller unit at typical reaction conditions of 25 MPa (300 atm), 450^0C 1 hr space time and 1 kg cat 2000 kg coal will be checked in this larger unit. The goal is to evaluate various scale up problems and outline design conditions for a commercial reactor whose capacity is not yet decided. The typical product distribution obtained from the run with feed of 285.5 tons/hr is as follows:

benzene (B.P. < 232^0C)	22.0 tons/hr
medium fraction (232^0C-332^0C	103.0 tons/hr
semi-coke	66.2 tons/hr
total gases	11,000 standard m^3/hr

Gases are distributed as:

		Vol. %
H_2O included	H_2	45-77%
	O_2	0.1
	N_2	0.1-1.7
	CH_4	7-24
	CO	0.1-3
	C_2H_6	7-24
	C_2H_4	∿ 7
	CO_2	0.03-14.5
	C_3H	0.5-10
	H_2S	0.1-0.25
	C_4H_{10}	1.5-3.5
Calorific Value		20000 kJ/m^3 or
		4800 Kcal/metric m^3

Finances

The total project involves PDU at the Institute of Carbochemistry with auxiliary work being carried out at eight or nine other institutes and seven high schools. The total budget is 1.2 billion zlotes/five years. The budget is allocated on a slanting scale. The director of the institute feels that while budget is not sufficient, it will satisfy very basic needs. More financial help in terms of purchasing equipment from the U.S., U.K., or Germany would be very helpful.

Future Need

The director indicated that they are going to have an evaluation of the entire program in a few months and will determine the future needs for the program. In his opinion, the two most important areas where the help for UNIDO and UNDP can be appreciated are: (a) training of people in the areas of chemical engineering, automatization, laboratory and plant analysis and (b) purchases of some equipment such as reactor. vessels, pumps, pressure let-down valves, etc. The exchange of scientific information by having young people visit countries like the U.S., U.K., Germany, Japan and Austria is needed. More papers and publications from these countries are needed in Poland. UNIDO can help in such a scientific exchange of information. Presently, visits by five to six experts in various areas (all except one from the U.S.) are planned. Apparently, I was the first visitor of this type. The director also strongly felt that the consultation help in the future is essential for the program. I understand that the next expert visit that is planned is that of Professor Pugmeir from Utah University in the area of NMR techniques as applied to coal liquefaction.

Personal Assessment of Plans and Associated Finances

If sufficient funds and the required equipment are available, the proposed program for the five year period should be able to be carried out with relative ease. The goal of the program is to obtain sufficient information for the design of a large scale process. The restriction to one coal makes the plan much more feasible. I think it is important to decide whether a catalytic or a non-catalytic process is to be developed. Even in a catalytic process, the process conditions depend upon the cost of the catalyst (i.e., disposable versus non-disposable catalysts). A decision regarding the use of a catalyst should, however, be based on the bench scale experiments on the catalyst activity as well as life expectancy. The catalyst regeneration costs would, of course, play a major role on the economics of the process.

The major reaction variables that need to be pinned down with the help of bench scale experiments are the conditions of temperature, pressure, space time and the solvent quality. Once these conditions are reasonably well fixed, the PDU unit can be used to evaluate the scaleup variables such as gas and slurry velocities, reactor length, diameter and internals (if any) and phase distribution (particularly gas) devices. The PDU can also be used to evaluate the engineering feasibility of the various process units. There is sufficient time allowed in the program to carry out these phases.

The two major problem areas in the program are: (a) availability of the required equipment and (b) flexibility in financing due to rising cost by inflation. I believe that the success in the plans would mainly depend upon these two factors.

Technical Discussions and Evaluations

During my stay at the institute, a number of technical discussions were carried out. The topics for these discussions and the important points brought about by these discussions are outlined below.

Monday, September 7, 1981

Discussion on Coal Structure and Its Relation to Liquefaction Behavior

- It is generally well known that the liquefaction behavior depends extensively upon the structure of coal. The percentage conversion (i.e., conversion to pyridine soluble materials) depend upon sulfur content, volatile matter, hydrogen/carbon ratio and vitrinite portion of the coal. A number of correlations for the percentage conversion in terms of these variables are reported in the literature, and these are reviewed in my book.* A discussion on how coal structure can be improved (through beneficiation) to get better product yield was carried out. Generally, this is not economical. However, the correlations can help explain the different behavior of coals obtained from different seams or mines. The discussion on the role of mineral matter on coal on the reactions was also carried out. It was interesting to find that they thought some mineral matter may change the chemical compounds during the liquefaction conditions. For example, CaO and MgO can be changed to $CaSO_4$ and $MgSO_4$.

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*Reaction Engineering in Direct Coal Liquefaction, Ch. 2, Addison-Wesley Publ. Co., Reading, MA (1981).

Tuesday - September 8, 1981

Discussion on Roles of Solvent and Catalyst on the Mechanism of Coal Liquefaction

It was generally agreed that the quality of the solvent affects the product distribution obtained from liquefaction. It is a good idea to improve the hydrogen donor and shuttler capabilities of the solvent coming out of the reactor before recycling back into the system. It is also recognized that, in general, the characterization of the solvent quality is a difficult task and can only be achieved in qualitative terms. The quality of the solvent is also important in the processibility of the slurry particularly in the preheater.

The main function of the catalyst is to better hydrogenate/hydrocrack coal liquid thereby producing more naphtha (low boiling liquid) yield and get better removals of sulfur and nitrogen compounds. It was realized that the present usages of $Ni-Mo/Al_2O_3$ or $Co-Mo/Al_2O_3$ are very high and expensive. The tests for the catalyst life are badly needed. They have, as yet, not evaluated the effects some disposable (cheap) catalysts on the liquefaction behavior. However, they are planning to do so in the future. It was pointed out that the main reason why many catalytic processes in the U.S. have died is because catalyst cokes readily in highly aromatic coal slurry. Also, the hydrocracking capability of the catalyst vanishes rapidly because the acidic sites are blinded by the basic coal-liquid medium. It was suggested that the route of catalytic process should be followed with caution because in the U.S. low catalyst life has put many processes to extinction.

Wednesday and Thursday - September 9 and 10, 1981

Discussion on Slurry Reactors - Parts I and II

This was the most important and longest discussion session. A number of items were discussed, some important ones are described below.

A. Physical-Chemical Data Source

At present there is no unique data source for the physical and chemical properties of the slurries under the reaction conditions. Generally, viscosity under reaction conditions vary from 0.7-1.1 cp, density from 0.9-1.3 gm/cc and surface tension as low as 5-10 dynes/cm^2. Thermal conductivity and specific heat can be estimated from the corresponding hydrocarbon system. There are no available data; the above numbers are only estimates. Presently a number of efforts are being made (e.g. Prof. Kobayashi at Rice University, Houston, Texas) to improve this data bank.

The vapor-liquid equilibrium data are also sparse. The only published work is that by Prof. K. C. Chao from Purdue University, Indiana who has published vapor-liquid equilibrium data for tetralin. These data should provide an estimate for the vapor-liquid equilibrium calculations for naphtha range materials under the reaction conditions. In the calculation of distillation fraction, Watson factor of 12 used in petroleum refinery is also used for coal-liquid. The validity of this assumption still remains somewhat questionable. More experimental work is needed in this area.

The heat of reaction can only be estimated (based on hydrogen consumption) from the data obtained from hydrocarbon systems. These are generally good estimates. Minor variations could occur depending upon the nature of coal-oil slurry.

During our discussion, it was also pointed out that thermal-physical properties of the coal-oil slurry under preheater conditions are not well known. More experimental work is needed in this area. Much of the published work carried out in this area in the U.S. is reported in Department of Energy reports.

B. Scaleup Variables

In the U.S. a number of different types of reactors for the direct coal liquefaction have been investigated. The present conclusion is that because of: (a) high degree of mixing, (b) high liquid holdup, (c) better heat transfer characteristics, and (d) flexibility in construction and maintenance, slurry reactor is a preferable mode. The major scaleup variables that need to be examined for this type of reactor are:

(a) gas distributor

(b) axial mixing of heat and axially uniform solids distribution

(c) temperature control - shutdown procedure

(d) hydrogen mass transfer in the top part of the reactor

The proper design of a gas distributor is very important (particularly in large scale reactor) in order to avoid channeling and dead zones. The distributor that may work well in a small scale reactor may not work well in a large scale reactor. The effectiveness of a particular gas distributor can be examined in cold model experiments. The proper gas distribution is very important for having good axial mixing of heat and the mixing of solids (catalyst). Since the temperature window for the coal liquefaction reactor is small, (430^0C-465^0C), good axial mixing of heat is required for obtaining acceptable product distributions. The preheater duty and the required reactor inlet temperature also depend significantly upon the axial mixing of heat in the reactor. If large catalyst particles are used, its uniform axial distribution required good axial mixing. The axial variation in the catalyst concentration can cause control problems.

The large scale reactors would be operated under close to adiabatic conditions. The control of a well mixed, adiabatic reactor is an important scaleup problem. Preliminary observations carried out in the U.S. indicate that the adiabatic coal liquefaction reactor is likely to be operated under an unstable steady state condition. Some experimental studies for the understanding of this problem should be carried out. Some work should also be carried out on the proper reactor shutdown procedure if the reactor temperature runs out of control or other malfunction occurs. Finally, under given reaction conditions it is important to note that good hydrogen mass transfer across the gas-liquid interface, particularly in the top part of the reactor (where the adiabatic reactor is at the highest temperature) occurs. The hydrogen starvation can cause coking problems in the reactor.

Choice of Laboratory Scale Reactor

Basically three types of laboratory reactors can be used for the kinetic measurements: (a) batch reactor, (b) continuous stirred tank reactor, and (c) plug flow reactor. The conventional batch reactor has problems of long heat-up and cool-down periods. A gradientless batch reactor, wherein coal is injected in a hot oil, is believed to be a workable reactor, particularly for the measurements at short contact times. There are, however, few problems in this gradientless batch reactor that need to be worked out. Most of the important ones are: (1) representative sampling, (2) uniform coal feeding, and (3) quantity of samples. The long tubular plug flow reactor can be used for the laboratory scale kinetic measurements. However, lack of mixing may cause problems with hydrogen mass transfer in the slurry as well as isothermality in the reactor. The measurement of temperature of the slurry in the reactor may be a problem due to small internal diameter of such reactors. The best laboratory reactor for the kinetic measurements is believed to be a continuous stirred tank reactor. This type of reactor has been very successfully used in the U.S.

Measurements of Phase Holdups and Mass Transfer Coefficient

The measurement of phase holdups (i.e., gas, liquid, and solid) is an important problem. The gas holdup can be measured via tracer technique. The solid holdup can be measured by sampling or tracer techniques. They have used Kr-79, Br-82 and La-140 as gas, liquid and solid phase tracers and have obtained successful results. At present, there are not reliable data available in the literature, particularly when the solid particles are large. The behavior of solids distribution in the column should be undertaken in the cold model experiments.

Friday - September 11, 1981

Discussion on Lumped Kinetic Models for the Direct Coal Liquefaction

At present numerous lumped kinetic models for the direct coal liquefaction have been reported in the literature. These models should be applied to their study. More analytical capabilities are needed before any more complex models can be used.

Personal Training

I feel a number of people (i.e., all research workers outlined on Page 1) can learn by visitation to a number of universities and industries in the U.S. We here at the University of Pittsburgh can entertain one researcher in the area of scaleup problems. Other institutions who may be interested in hosting Polish researchers are the University of Utah, Pennsylvania State University, Auburn University, and Colorado School of Mines. I also feel that practical training can also be best achieved by visiting industries or government laboratories in the United States. I am not sure UNIDO can work out the administrative details of such visitations. If I have some additional thoughts on the matter, I will pass it on to UNIDO.

REFERENCE PAPERS OF INTEREST

SLURRY REACTORS FOR COAL TECHNOLOGY

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ABSTRACT

In recent years, the use of coal as a raw material for the productions of hydrocarbons, liquid transportation fuels, chemical feedstocks and solid fuel is gaining importance. Three important processes for the achievement of this goal are: (1) direct coal liquefaction, (2) removal of sulfur from coal by oxydesulfurization and (3) indirect coal liquefaction or the Fischer-Tropsch synthesis. All of these processes employ three-phase slurry reactors. In this overview, a present state of the art for the models, scaleup, design and other operational problems associated with these processes are briefly evaluated.

1 INTRODUCTION

One of the major applications of the slurry reactor in recent years is in coal technology; in particular, coal refining and conversion processes. Three specific processes that are considered here are: (a) direct coal liquefaction (DCL) wherein coal is liquefied in the presence of a hydrogen donor solvent and hydrogen gas to produce a host of gaseous, (light hydrocarbons, water, CO, CO_2, NH_3, H_2S), liquid (of a wide boiling range components) and solid (unconverted coal, mineral matter etc.) products; (b) chemical cleaning of coal (CCC) via Pittsburgh Energy Technology Center process wherein the sulfur from coal is removed via oxidation in the presence of water; and, (c) Fischer-Tropsch slurry (FTS) process wherein carbon monoxide and hydrogen are reacted in the presence of a solvent and catalyst to produce a variety of light and heavy hydrocarbon products. This process utilizes the co-rich synthesis gas produced by second generation coal gasifiers.

Major advantages and disadvantages of a slurry reactor are discussed by Shah (1). In coal technology, slurry reactors are often preferred because of:

(a) high heat capacity due to high liquid holdup. This allows better mixing of heat which is desirable in all three exothermic processes described above. In direct coal liquefaction, good axial mixing is desirable because of the narrow temperature window for the smooth operation of the process. In Fischer-Tropsch process, the reactor temperature control appears to be easier in slurry bed operation than in fixed bed operation.

(b) high liquid holdup, which is desirable for the liquid phase reaction and which helps avoid coking during the reaction.

(c) in catalytic coal liquefaction (e.g. H-COAL Process) where four phases (gas, liquid, reactive coal and catalyst) are involved, slurry bed reactors appear to be the only logical alternative.

(d) one can change the catalyst effectiveness factor by suitably changing the particle size. The catalyst can be removed or added while the plant is in operation; in theory it is not necessary to shut down the plant for the purpose of replacing the spent catalyst. The packed bed reactor gets clogged easily and consequently the plant must be shut down for the catalyst to be regenerated.

(e) it is simple to construct and the reactor internals can be changed if so desired.

In the discussion of the application of a slurry reactor to each specific case the following topics will be considered:

(a) laboratory reactors

(b) models for the reactor

(c) scaleup and other design and operational problems.

2 LABORATORY SCALE SLURRY REACTORS

The major purpose of a laboratory scale slurry reactor used in coal technology is to evaluate the intrinsic kinetics of the process, free of extreneous mass, heat transfer and mixing effects. The most commonly used laboratory scale reactor is the continuous/batch agitated autoclave reactor. Kinetic studies for the direct coal liquefaction in such a reactor have been investigated by various workers and many modifications of the conventional agitated reactors have been proposed to overcome problems such as heating and cooling times, rapid coal-oil slurry injection, slurry sampling at short contact times, maintenance of constant pressure in the reactor, etc. A detailed analysis of different modifications of reactors has been given elsewhere (2), and it will not be repeated here. The kinetics of oxydesulfurization of coal has been studied either in batch or semi-batch agitated autoclave reactors using aqueous coal slurries and a comprehensive review on this subject is also available (3). This study has shown that one can use conventional agitated slurry reactors for the kinetic study of oxydesulfurization process. There is little information available on the use of an agitated slurry reactor for the FT synthesis. All the intrinsic kinetic rate measurements have been carried out in the vapor phase (4-9).

All three processes considered here are exothermic. Since slurry reactors on an industrial scale are operated under close to adiabatic conditions, a major scaleup problem is that of the thermal control of such reactors. Recently, Shah and Carr (10) have described a custom made agitated adiabatic slurry reactor, which can be used to evaluate the thermal behavior of the large scale reactors.

3 PILOT AND COMMERCIAL SCALE SLURRY REACTORS

Descriptions of typical slurry reactors used in the three processes considered here are available in the literature (4,5, 11,12). The operating conditions employed in these reactors are briefly outlined in Table 1. Some similarities in the operation of the three reactors can be noted. The reactors for both DCL and CCC processes are operated in a similar manner. In the FTS process, the liquid-solid (catalyst) slurry phase is usually stagnant. While the solid particle size in catalytic processes (FTS and catalytic DCL) can be large, in most practical situations, the solids are very fine and the slurry is considered to be pseudohomogeneous. Slurry velocities for all the three processes are either small or none. In general, the gas velocities are in the same range; however, FTS uses somewhat smaller gas velocities as compared to DCL and CCC processes.

TABLE 1

COMPARISON OF OPERATING CONDITIONS IN SLURRY REACTORS USED IN COAL TECHNOLOGY

Process	Reactor	Reactor Dimensions (cm) D	(cm) L	Solid Concen. (wt%)	Temp. T (K)	Press. P (MPa)	Slurry Space Veloc. (hr^{-1})	Gas Veloc. (cm/s)	Liquid Veloc. (cm/s)	Solids Particle Size (μm)
DCL	Coiled tube (preheater)	3-7	100-1000	33	523-673	10-15	10-20	50-100	5-21	< 70
	3 phase bubble column	30-60	200-700	33	693-738	10-17	0.5-1.0	2-4	0.08-0.4	.15-3
CCC	3 phase bubble column	2.2	183	20-26	433-503	6-8	0.5	30-120	0.06-0.5	50-1400
FTS	3 phase batch bubble column	3.8-155	70-860	up to 20	493-633	0.5-2.4	---	0.3-10	---	50

Solids play different roles in the different processes. In direct coal liquefaction, a part of the solid is dissolved in liquid (mainly in the preheater) and a part (i.e. mineral matter) may act as a catalyst for the hydrogenation reactions. In Fischer-Tropsch slurry processes, solids are catalysts. Finally, in chemical cleaning of coal, only a part of solid (i.e. sulfur) takes part in the reaction following the shrinking core diffusion/ reaction mechanism. The role of solids in the design and scaleup of the reactors for the three processes is therefore different.

The fluid properties for the three processes may be considerably different. The CCC process uses a low pH solution (containing water and the acid product) whereas both DCL and FTS use hydrocarbon like liquids. Physical properties such as surface tension, viscosity, specific heat and thermal conductivity for these two cases may be quite different. Since the FTS is a very energetic process, the reactor may also contain some internals such as heat exchangers (cooling coils) etc. Some physical and thermal properties for these systems are outlined in Table 2.

One unique reactor is the preheater in the DCL process. It is a long coiled tube where the slurry is heated to the reactor temperature and as described later, for swelling coals, it may possess a peculiar thermo-hydraulic behavior. While, as described later in Table 5, available literature for various hydrodynamic, mixing, and transport parameters can be applicable to the reactors, their applicability to the preheater is questionable. More work is needed in understanding the hydrodynamic, mixing and transport characteristics of the preheater.

4 MODELS FOR THE SLURRY REACTORS

The design, scaleup and performance prediction of slurry reactors require models which must consider not only the hydrodynamic and mixing behavior of the three phases, but also the mass transfer between the phases along with the intrinsic kinetics. In the DCL and FTS processes, an axial dispersion model is applicable, with the solid phase assumed to follow sedimentation or dispersed flow model. However, in the CCC, where the solid particles take part in the reaction, dispersion model is no longer applicable. This case is evaluated with the use of the shrinking core model, wherein the solid concentration is governed by its exit age distribution.

The backmixing of the solid phase and solid concentration profile become more important when the solid loading is high (e.g. DCL process) or when the solid particles are large with significant relative slip velocity with the liquid phase. If the solid loading is low or particles are very fine, then the slurry can be assumed to be a single pseudo-homogeneous phase. In the following paragraphs, some important model features for each of the three cases are briefly outlined. A brief summary is also given in Table 3.

TABLE 2

SOME PHYSICAL AND THERMAL PROPERTIES
OF SLURRIES IN COAL TECHNOLOGY

Property	DCL	CCC	FTS
Density (kg/m^3)	1270	1150	900
Viscosity (Pa·s)	$(2-10)x10^{-3}$	$1.1x10^{-3}$	$4.5x10^{-3}$
Surface tension (N/m)	0.025	0.070	0.024
Thermal conductivity (w/m K)	0.15	0.67	0.10
Heat capacity (J/kg K)	2700	3480	2927
Heat of reaction ($kJ/mol \cdot H_2$)	50	----	290

4.1 Direct Coal Liquefaction (DCL)

The DCL process contains two steps: dissolution of coal in the preheater (accompanied by several fast reactions) and subsequent hydrogenation/hydrocracking reactions (slow reactions) in a three phase slurry reactor.

The preheater is essentially a plug flow reactor ($L/D > 100$) where the coal-solvent slurry and hydrogen gas are preheated to the liquefaction temperature. Extensive studies have been carried out to understand the exact nature of the processes, taking place in the preheater (2,11,13-16). Considerable work has also been performed to evaluate the dissolution process and its effect on thermal hydraulics of large-scale preheaters (13-16).

The processes occurring in the preheater have been conceptually divided into three regions. The first region is characterized by the length of the preheater used in heating the slurry with a decrease in the slurry viscosity until a local minimum in viscosity is reached. The slurry in this region behaves like a Newtonian fluid. The second region is characterized by a sharp increase in viscosity, corresponding to the region where the coal particles swell and form a gel with the solvent, exhibiting non-Newtonian behavior. The increase in viscosity and the pressure drop depends upon the shear rate applied on the slurry. The third region is characterized by disintegration and dissolution

TABLE 3

TYPES OF MODELS PROPOSED FOR SLURRY REACTORS

No.	Process	Model Type	Model Equation	Gas Phase Flow	Slurry Phase Behavior
1	DCL	Axial dispersion	Hydrogen mass balance	Plug flow	Partially* backmixed
		Axial dispersion	Hydrogen mass balance	Partially Backmixed	Partially backmixed
		Axial dispersion	Hydrogen mass and energy balance	Plug-flow	Partially* backmixed
		Axial dispersion	Hydrogen mass and energy balance	Plug-flow	Partially* backmixed
		Axial dispersion	Mass balance for various lumped fractions	Plug-flow	Partially* backmixed
2	CCC	Shrinking core model	Sulfur balance	Plug-flow	Partially* backmixed
		Shrinking core model	Sulfur balance	Plug-flow	Partially* backmixed

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Gas-Liquid Mass-Transfer	Overall Controlling Reaction Regime and Reference
Negligible	Chemical reaction (23)
Considered	Chemical reaction (22)
Absent	Chemical reaction (20)
Present	Depends on the turbulence in the reactor (21)
Absent	Chemical reaction (17)
Absent	Diffusion controlled (29)
Absent	(a) liquid-solid mass transfer (b) ash diffusion (c) chemical reaction (30)

TABLE 3
(Concluded)

3	FTS	Plug flow/ backmixed	Hydrogen mass balance	Plug-flow	Completely backmixed	Considered	Depends on the operating temperature (32)
		Plug flow/ backmixed	Hydrogen mass balance	Plug-flow	Completely backmixed	Negligible	Chemical reaction (33)
		Dispersion	Hydrogen mass and heat balance	Partially backmixed	Partially* backmixed	Negligible	Chemical reaction (34)

---

*Dispersion/sedimentation model used for solid concentration profile; others assume slurry as homogeneous phase.

of the coal particles into smaller molecular weight fractions and possibly some chemical reactions which give various products found in the liquefaction process. This region is also accompanied by a decline in the slurry viscosity and the average slurry density.

The preheater models are based on plug-flow behavior of both gas and the slurry phases, as the L/D ratios in preheater are usually large. Reliable estimates of the fluid properties such as viscosity and density, pressure drop across the preheater and heat transfer coefficient are needed for an optimum design of the preheater and, these have been recently reviewed by Shah (11). Parulekar et al. (17) have proposed a kinetic model for the preheater based on certain fast reactions taking place in the preheater whereas Nunez et al. (18) evaluated the hydrogen mass balance and a heat balance on the preheater.

The three phase slurry-bubble column-reactors used in the DCL process have been modeled by using an axial dispersion model. The height to diameter ratio employed in such reactors is usually in the range of 5-20 and the axial dispersion model is applicable to both liquid and solid components in the slurry phase. Since the average coal particle size in the reactor is usually believed to be less than 5 μm (19,22), liquid and solid phases are believed to form a homogeneous slurry phase. The gas phase has been assumed to be the plug flow in the models proposed by some workers (17,20,21) while others considered the gas phase to be partially backmixed (22). Several lumped parameter kinetic models have been proposed for the DCL process and their details are given elsewhere (2,11).

An axial dispersion model for an isothermal reactor with partially backmixed liquid phase and the gas phase as plug-flow has been described by several investigators (23,24). The overall reaction rates were expressed in terms of the gas phase hydrogen concentration thereby eliminating any gas-liquid mass transfer resistance for the hydrogen transfer. The solids distribution was accounted for by the hindered-settling conditions. In the range of operating variables examined, the predictions from the above model qualitatively agreed with the performance of several pilot-scale plants. Lee et al. (22) proposed a dispersion model based on the axial-dispersed flow for both gas and liquid phases. The slurry in their case was treated as a homogeneous phase and the solid distribution was not taken into account. The model parameters were estimated from the correlations proposed for the case of no solid suspension (two-phase system). The coal dissolution, hydrogenation and hydrodesulfurization were considered as the key reactions, in the model. Also, the effect of mass transfer on the liquefaction process has been investigated. The model predictions were found to be in good agreement with the experimental facts of the Wilsonville pilot plant. Their analysis also indicated that the Wilsonville pilot plant operated in the kinetically, rather than the mass transfer controlled regime. Unlike the models proposed by other investigators (23,24) where the velocity variation was also taken into account, the above model assumed that all velocities and holdups remain unchanged throughout the reactor.

Commercial reactors are invariably operated under close to adiabatic conditions and for understanding the thermal behavior of such reactors, an energy balance along with the mass balance needs to be considered. Models have been developed (20,21) to investigate the thermal behavior of such reactors, based on the axial dispersion model. The model equations assumed that the heat generation depends on the hydrogen consumption; the hydrogenation/hydrocracking reactions are believed to be the most energetic of all the reactions taking place in the reactor. The hydrogen mass balance assumed the presence as well as the absence of the gas-liquid mass-transfer resistance. The hydrogen consumption and temperature rise predicted for the case where there is no mass transfer resistance was shown to fit the experimental data measured in the Fort Lewis SRC-II pilot plant very well (21).

4.2 Chemical Cleaning of Coal

Slurry reactors are used in the chemical cleaning process, wherein, the sulfur in coal is oxidized by air in an aqueous slurry. Unlike other two cases considered here, in this process the solids react keeping the size constant. In general, for such a type of reacting system, the resistance to the overall reaction could be the oxygen mass transfer at the gas-liquid and/or, liquid-solid interface, oxygen diffusion through the product (ash formed during the reaction) layers, chemical reaction or a combination of the above resistances. Mathematical models for such cases have been proposed by various investigators based on the shrinking core mechanism (25-29). Unlike various applications where the solids act as a catalyst in the slurry reactor, in chemical cleaning of coal, we come across a situation where the solids take part in the reaction; the usual dispersion model is not applicable and a model based on the exit age distribution of the solid particles has been developed.

Ruether (29) examined the case of oxydesulfurization for completely backmixed stirred tanks in series assuming the diffusion-controlled mechanism. The reaction in the particles was described by the shrinking core model. The results obtained on the conversion as a function of residence time were shown for various number of reactors in series. The procedure to calculate the conversion for a system having a distributed particle size has also been discussed (29).

Joshi et al. (27) investigated the kinetics of oxydesulfurization of coal assuming two alternative mechanisms, (a) continuous reaction model, assuming fine pyrite particles to be uniformly distributed in the coal particles and (b) shrinking core model where pyrite particles are assumed to be free and separate from the coal particles. The applicability of the above models were examined (25) by studying the effect of coal particle size and solid loading. It was shown that the rate controlling step in the pyrite oxidation is the intrinsic chemical reaction between the dissolved oxygen and pyrite particles. The rate constants were evaluated using the shrinking core model.

Joshi et al. (30) proposed reactor models based on the shrinking core mechanism. Since the particles take part in the reaction their role was evaluated based on the residence time distribution. For extremely fine pyrite particles, (< 100 μm), it has been shown (31) that the RTD of the solid and liquid phases can be assumed to be identical and the RTD of the solid phase is given by the diffusion-sedimentation model. Various rate controlling steps that were considered are: (1) gas-liquid mass transfer; (2) liquid-solid mass transfer; (3) ash diffusion; (4) chemical reaction; and, (5) intraparticle diffusional resistance (for particles encased in the coal matrix).

Experimental studies on the oxydesulfurization process have shown that in the practical range of operations the gas-liquid and liquid-solid mass transfer resistances are negligible (25-27). Further, it has been shown (25) that more than 85 wt% of pyrite exists in the liberated form and the intraparticle diffusional resistance can be ignored. Joshi et al. (25) also investigated the effect of particle size in the range (< 72-1410 μm) and found that the reaction is kinetically controlled.

Joshi et al. (30) developed an isothermal model for the reactor, considering the steps (3) and (4) and predicted results of conversion as a function of dimensionless residence time. It was observed that the reaction/dispersion model based on the shrinking core mechaism, with chemical reaction as the rate controlling step gave good agreement with the experimental results.

4.3 FT Synthesis

In recent years, FT synthesis has been gaining importance for the manufacture of transportation fuels. There is very little information available on the kinetics, modeling and design of a slurry reactor for the FT process. The intrinsic kinetic rate measurements have been carried out in the vapor phase. However, under certain conditions, various investigators (4-7) have suggested that the rate is independent of the CO partial pressure, and since the water content is generally low due to the water gas shift reaction, the rate is expressed only in terms of the H_2 consumption. The simplified rate expression has been used in the analysis of the FT synthesis in slurry reactors (32,33,34).

Satterfield and Huff (32) have developed a model based on the plug flow of the gas phase and completely backmixed liquid phase and the model equation is based on the summation of mass transfer and reaction resistances. These authors analyzed the data of Schlesinger et al. (35) and the pilot plant scale data of Farley and Ray (36) and concluded that the overall rate is equally influenced by mass transfer and reaction resistances at normal operating temperatures (around 503 K) and the mass transfer resistance becomes increasingly more important at higher temperatures.

Deckwer et al. (33) proposed a model for a laboratory scale slurry reactor which is essentially the same as that proposed by Satterfield and Huff (32) with the only difference that their model accounts for the contraction in the gas volume. The experimental data of various investigators were analyzed and the estimated rate constants were correlated to the iron content in the slurry which is believed to be the intrinsic catalytic component. The authors concluded that the FT synthesis is predominantly controlled by the chemical reaction provided the reactor is operated at the relevant industrial conditions and that mass transfer limitations could be important only at very low gas velocities, high catalytic concentrations and for very active catalysts.

In the design of industrial scale slurry reactors agitated by the sparging of gas, one deals with large diameter columns with length to diameter ratio usually in the range of 5 to 20. In these cases, the backmixing of all three phases may be important and a dispersion model for the reactor, considering only an overall kinetic and variable gas flow rate has also been developed by Deckwer et al. (34). The results of their computations are briefly summarized in Table 4. As mentioned above, there is a difference in the conclusions of Satterfield and Huff (32) and Deckwer et al. (33) about the mass transfer limitation. The latter authors reduced the interfacial area by 50% and the space time yield reduced by less than 4%. In addition, the values of gas holdup was reduced by 50% (with a corresponding reduction in the interfacial area by 50%) and this resulted in an increase in the liquid volume and consequently an increase in the conversion and space time yield. This led them to conclude that the FT synthesis is largely controlled by chemical reaction and significant mass transfer limitations can be expected only at very low gas velocities or if the catalyst activity and/or concentration are increased. The use of very high catalyst concentration is however not recommended as this could prove detrimental to the favorable hydrodynamic conditions (31,37). Also, the computations indicated that the space time yield runs through a maximum value depending on the gas velocity and this optimum gas velocity agreed well with that used in the Rheinpreussen-Koppers demonstration plant. Other results of the simulations were also found to be in accordance with practical experience. They have presented a diagram of space time yield and conversion as a function of the reactor diameter and length from which the design and estimation of the production capacity of a FT slurry reactor can be made.

TABLE 4

EFFECT OF OPERATING VARIABLES ON THE CONVERSION AND SPACE TIME YIELD IN FT SLURRY REACTORS

Increase in Variable	STY	X_{CO+H_2}
Pressure (0.5-3 MPa)	Increases	No influence
Column dia. (1-5 m)	---	Slight decrease
Particle dia. (25-200 μm)	No influence	Slight decrease
Sup. gas vel. (0.5-12 cm/s)	Goes through a maximum	Slight decrease

4.4 Estimation of Model Parameters

In the modeling and design of reactors, reliable estimates of the various model parameters such as holdup of the three phases, mass and heat transfer coefficients, physical and thermal properties, etc. are required. The values of these parameters depend on the prevailing flow regime, operating conditions and the type of the reactor internals used (if any) in the reactor.

There are as yet no theoretical correlations capable of predicting the viscosity, pressure drop and heat transfer coefficient in the preheater. Some empirical correlations for this purpose are available in the literature (11,13-16,38). The hydrodynamic characteristics of three phase slurry reactors have been extensively reviewed (1,39,40,41). Suitable correlations have been suggested for the estimation of model parameters encountered in the three processes discussed here (11,22,30,34). Recently, the physical and thermal properties of coal liquids have been investigated and correlations have been given, which should be useful in the estimation of the model parameters for the DCL process (42). Deckwer et al. (43) have investigated the hydrodynamic properties of FT slurry process at the relevant operating conditions and correlations for a number of model parameters have been suggested (34,43). Table 5 summarizes some of the correlations useful for the model parameter estimations for the three processes considered here.

5 SCALEUP AND OPERATIONAL PROBLEMS

Various factors should be considered during the scaleup of slurry reactors such as flow regime, backmixing in the different phases, temperature control, controlling regime of the overall reaction, etc. Details of the effects of various factors on scaleup are available in the literature (1,11,21,30,34). In this section, some of the factors which influence the scaleup of slurry reactors as applied to coal technology are briefly mentioned. Table 6 summarizes some of the important scaleup factors.

In all three processes, studies on laboratory or pilot plant scale have shown the overall reaction is generally kinetically controlled. However, under the prevailing flow regimes in the commercial reactor, the mass transfer effects may be prominent and should be considered. The thermal behavior of the DCL and FTS reactors is an important factor which needs special attention. To avoid loss in product selectivity, low product yields, and coking or repolymerization reactions, a thorough temperature control is needed either by means of quench (DCL process) or cooling coils (FTS process). The solid phase backmixing in the CCC process has to be particularly considered as the conversion is expressed in terms of the particle exit age distribution. All three processes are operated under severe conditions and proper selection of the reactor diameter and the height to diameter ratio is necessary for an economical design and scaleup. The material of construction or proper reactor lining material is important, particularly in the CCC process as sulfuric acid is produced in reaction process.

6 SUMMARY

The salient features of the slurry reactors used in three coal refining and conversion processes and the models developed for each case have been discussed. Considerable pilot plant

TABLE 5

TYPICAL CORRELATIONS USED FOR THE ESTIMATION OF MODEL AND DESIGN PARAMETERS (11,30,34,43)

Parameter	Correlation	Process
Dispersion coefficient	$E_L = 0.00108\ D^{1.4} u_G^{0.3}$ (SI units)	DCL, FTS
	$E_S = E_{SL} = 0.38\ D^{1.33}\ g(u_G - \varepsilon_g V_{b\infty})^{0.33}$ (SI units)	CCC
Heat transfer coefficient	$St = 0.1\ (Re\ Fr\ Pr^2)^{1/4}$	FTS
Gas-liquid mass transfer coefficient	$k_L Sc^{2/3} = 0.31 \left(\frac{\mu_L \Delta\rho g}{\rho_L^2}\right)^{1/3}$	DCL, FTS
Solid-liquid mass transfer coefficient	$Sh = 2 + 0.545\ Sc^{0.33}\ Re^{0.264}$	FTS
Liquid-solid Interfacial area	$a_s = \frac{6(1-\varepsilon_G)\rho_{SL}}{d_s \rho_s} C_s\ (cm^{-1})$	FTS
Gas-liquid interfacial area	$a = 4.5\ u_G^{1.1}\ (cm^{-1})$	FTS

TABLE 6

POSSIBLE SCALEUP PROBLEMS IN SLURRY REACTORS IN COAL TECHNOLOGY

Operating Variable	DCL	CCC	FTS
gas velocity	Not important	Not important	Important
gas-liquid mass transfer resistance	Should be low	Not important	Not important (in the normal range of operation)
backmixing			
- gas phase	Not important	Not important	Important
- liquid phase	Not important	Not important	Not important
- solid phase	Not important	Important	Not important
distributor design	Important	Important	Important
heating/cooling	Important	Not important	Important
multiple temperature steady states	Important	----	Important
- reactor startup and shutdown problems			
material of construction	Important	Critical	Not important

scale data are available for the DCL process, while for the CCC and FTS processes, data for reliable design and performance prediction of large scale slurry reactors are lacking. All the processes follow complex reaction mechanisms and the models developed so far assume overall kinetic expressions. A better understanding of the kinetics is needed for the reliable design of these reactors.

NOMENCLATURE

a	gas-liquid interfacial area
a_s	liquid-solid interfacial area
c_s	concentration of solid in the slurry
d_s	solid particle diameter
D	reactor diameter
E	dispersion coefficient
Fr	Froude number
g	acceleration due to gravity
k_L	gas-liquid mass transfer coefficient
L	reactor length
P	pressure
Pr	Prandtl number
Re	Reynolds number
Sc	Schmidt number
St	Stanton number
T	temperature
u_G	superficial gas velocity
$V_{b\infty}$	average terminal rise velocity of bubbles
X	fractional conversion
ε	fractional holdup
ρ	density

Subscripts

g	gas phase
L	liquid phase
S	solid
SL	slurry

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DIRECT COAL LIQUEFACTION

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ABSTRACT

This paper presents a brief state of the art review of direct coal liquefaction. The review includes important pilot scale processes available for the liquefaction and a brief description of the structure of coal and the chemistry, mechanism and available lumped kinetic models for the liquefaction process. It also includes some discussions on the role of catalysts during coal liquefaction and on the use of model compounds for the understanding of coal liquefaction kinetics. Reactor design aspects are covered in a separate paper and will not be repeated here.

1 INTRODUCTION

The production of liquid fuels from coal can be divided into three broad categories: pyrolysis, indirect liquefaction and direct liquefaction. In pyrolysis, coal is heated in the absence of air to a temperature such that it gives off liquids and gases leaving a large amount of char. In indirect liquefaction, coal is gasified and the resulting gases are catalytically converted to liquid fuels.

This paper deals with the subject of solvent extraction and hydrogenation of coal (i.e. direct liquefaction). The main purpose of liquefaction is to produce clean fuel (both liquid and solid), eliminating the mineral matter and heteroatoms from the parent coal. Most of the processes aim towards high liquid yields. In all processes, crushed coal, mixed with the process solvent is contacted with hydrogen gas under pressure. The reaction products, after cooling, are separated from remaining solids. Different processes use different separation schemes. A large number of coal liquefaction processes are currently being developed. Some of the important ones are briefly described below.

2 PROCESSES

2.1 The SRC-I Process

In this process, pulverized coal, dissolved in a process-derived solvent, is reacted at high temperature and pressure in the presence of hydrogen. In the dissolution step, the coal molecules are fragmented, freeing organic sulfur and light hydrocarbons which are evolved as gases. The undissolved solid residue is then separated from the liquid stream which is distilled to recover process solvent and to produce an additional side stream of light liquid fuel products. The remaining heavier liquid is solvent refined coal (SRC) which, if cooled to ambient temperature, becomes a solid. The undissolved solid residue, supplemented with additional feed coal, is sent to a gasifier to produce the hydrogen required by the process. The clean residue from the gasifier is expected to be environmentally acceptable (1-3).

2.2 The SRC-II Process

In this process, the pulverized coal, dissolved in a recycle slurry containing process solvent, SRC, and undissolved solid residue is reacted at high temperature and pressure in the presence of hydrogen. In the dissolution step, the coal molecules are severely hydrocracked to gaseous and liquid fuels. A major portion of the sulfur and some nitrogen and oxygen are converted via hydrogenation to hydrogen sulfide, ammonia and water. The cooled reaction products are physically separated to recover fuel gases, liquid fuel products, and a product slurry containing solvent, SRC and undissolved solid residue. Product slurry, after removal of recycle slurry for the coal dissolution step, is distilled to recover additional liquid fuel products from the residue slurry. The residue slurry is sent to a gasifier to produce the hydrogen required by the process and additional quantities of fuel gas are also produced. The clean residue from the gasifier is expected to be environmentally acceptable (2-4).

2.3 The TSL (Two Stage Liquefaction) Process

In contrast to the SRC-II Process, where coal dissolution and coal and solvent hydrocracking are achieved non-selectively in a single unit under largely non-optimal thermal conditions, the TSL process minimizes unnecessary degradation of solvent and lighter boiling range material through staged processing of segregated streams, thereby decreasing the hydrogen consumption. In this process, pulverized coal is thermally upgraded to a low ash and low sulfur content SRC fuel product using conventional SRC-I technology. The resulting hot and fluid SRC, after separation of by-products, and gaseous and liquid fuels, is charged to an LC-Finer for conversion to the specified grade liquid and solid fuel products. In the LC-Finer, the hot SRC dissolved in an internally produced solvent, is catalytically hydrocracked in an expanded bed of catalyst in the presence of hydrogen at elevated temperature and pressure. In the hydrocracking step, the SRC is selectively cracked to gases and distillate fuels. A major portion of sulfur and some nitrogen and oxygen are converted via hydrogenation to hydrogen sulfide, ammonia and water. Following conversion, the cooled reaction products are physically separated to recover fuel gas, liquid fuel products, LC-Finer solvent and unconverted SRC (5,6).

2.4 The EXXON Donor Solvent (EDS) Process

This process is designed to maximize liquid products. The feed coal is crushed, dried and mixed with hydrogenated recycle solvent (i.e. donor solvent) and fed to the liquefaction reactor along with gaseous hydrogen. The reactor is upward plug flow type operating at 723 K and approximately 10-13.6 MPa total pressure. The reactor effluents are separated by a series of distillation steps into gaseous, liquid and solid products. The recycle solvent is hydrogenated in a fixed bed catalytic reactor employing "off-the-shelf" hydrotreating catalysts.

The heavy bottoms from vacuum distillation may be sent to a FLEXICOKING unit along with air and steam to produce additional distilled liquid products and a low quality fuel gas for process furnaces. Light hydrocarbon gases coming from the distillation unit are steam reformed to produce hydrogen. The total liquid yield is thus a blend of streams from liquefaction and flexicoking.

2.5 The H-COAL Process

The "H-COAL" process was developed by Hydrocarbon Research Inc. to convert all types of coal to high octane gasoline, petrochemicals, LPG, low sulfur distillate fuels and low sulfur heavy boiler fuel oil.

Hydrogen and a slurry of coal and recycle oil are introduced to a plenum chamber at the bottom of the ebullated bed reactor operating at 10-20 MPa and 700-755 K. They pass up through a

TABLE 1

TYPICAL COMPARISON OF DIFFERENT LIQUEFACTION PROCESSES

	SRC-I	SRC-II	EDS	H-COAL
Operating Conditions				
1. Coal (type)	Western Kentucky 9/14	Western Kentucky 9/14	Ill. No. 6, Wyodak	Any Type
2. Reactor pressure (MPa)	10.3	13.34	10.3	12.1-12.6
3. Reactor temperature (K)	724	734	722	726
4. Hydrogen consumption (wt% maf coal)	2.4	4.8	4.3	3.8-5.25
Typical Product Yield (wt% maf coal)				
1. C_1-C_4 hydrocarbon gas	3.7	18.4	7.3-9.3	8.6-11.8
2. Light oil	5.1	14.2	---	16.9-23.6
3. Middle & heavy oil	8.0	28.2	33.3	18-23
4. Ash	9.6	--	---	10.9-11.67
5. Unreacted coal	5.4	6.6	---	6.3-7.5

distributor tray into the ebullated bed of cobalt molybdate catalyst. Since there is a sharp interface at the top of the catalyst bed, the catalyst level is detected by sending a beam of gamma rays through the reactor. The catalyst replacement system used here continuously removes the carbon deposited on the catalyst particles, avoiding a build up of pressure across the bed, a problem otherwise serious in other conventional units.

Table 1 presents a comparison of different liquefaction processes with respect to their operating conditions and product distribution.

3 ON THE STRUCTURE OF COAL

Coal structure has been studied using techniques like pyrolysis (7-10), alkylphenol determination (11-17), liquefaction and oxidation (18-21). After a considerable effort in this area, the compositions of some typical bituminous and subbituminous coals have been approximated as (19).

Bituminous: $C_{50.8}H_{43}O_{4.8}S_{0.8}N_{0.6}$

Subbituminous: $C_{48.4}H_{42.4}O_{8.6}S_{0.07}N_{0.5}$

Along with carbon and hydrogen, oxygen is the most abundant heteroatom found in coal in functional groups such as phenols, carboxylic acids, ethers etc. Sulfur is present as thiophenes, sulfides, disulfides and thiols while nitrogen is present as pyridines, quinolines, carbazoles and pyrroles.

3.1 On the Mechanism of Coal Liquefaction

Coal liquefaction has been assumed to be occurring in three steps: dissolution, hydrogen transfer and hydrogenation. Whitehurst et al. (21) have given a conceptual picture of coal dissolution in which the weak bonds (activation energy $\leq$ 210 kJ/mole) are broken at low temperatures ($\leq$523 K) and extracts of up to 40-50% of bituminous coals are obtained. As the temperature is raised to about 673 K, the formation of free radicals takes place. If hydrogen is available at this stage from the organic matrix or from the solvent (donor), these radicals will combine with the hydrogen forming stable species with molecular weights varying in the range of 300 to 1000. However, if there is insufficient hydrogen, the radicals will recombine forming high molecular weight compounds and coke. Han and Wen (22) presented a three step mechanism. Farcasiu et al. (23) have also presented similar explanations giving the name 'asphaltols' for preasphaltenes.

Oele et al. (24) described the extraction of Dutch bituminous coals at temperatures from 473 K to 673 K. They have shown that the extractive disintegration can be compared with a thermal decomposition requiring activation energies of 80 to 160 kJ/mol. According to them, the extraction process is greatly governed by the following factors.

1. Extraction Rate and Agent: Initially, the extraction process proceeds rapidly and becomes slow after a few hours (25). An extracting agent is effective if at 473 K the liquid is capable of dissolving 20 to 40% of a bituminous coal. Effective extracting agents are pyridine, picolines, aliphatic amines, ethylenediamine, phenol, cresol, o-phenylphenol, acetophenone, furfural etc. while benzene, trichloroethylene etc. are less effective.

2. Particle Size of Coal: In less effective solvents, coal of 1 μm particle size yields thirty times as much extract as coal of coarser particle size. With less effective solvents, the retarding action on the diffusion path through the already extracted part of coal particles increases to such a high value that further penetration of the solvent becomes very difficult.

3. Temperature of Extraction: Since it is generally assumed that coal constituents behave like a gel which is held together by secondary valancey forces, this gel shows only a limited degree of swelling at low temperature. Although there are insufficient data to verify a clear cut demarkation line, extraction with phenolic solvents becomes appreciable at temperatures above 473 K.

Morita et al. (26) pointed out that the extraction rate parameters calculated by many workers under different hydrogen pressures on the basis of isothermal and isobaric conditions may be erroneous. In batch experiments, the hydrogen absorption rate showed curious behavior. They carried out experiments at temperatures up to 713 K, residence time from 120 secs to 7200 secs and initial hydrogen pressures from 5 MPa to 11 MPa and observed that the absorption of hydrogen was initiated at about 573 K. When the temperature reached 713 K, the hydrogen pressure began to decrease at constant rate. Also, there was a tendency for the increased extraction rate and lower coke formation with the increased initial hydrogen pressure. For coals rich in oxygen (approximately 30%), hydrogen pressure was found to have little effect on the extraction rate.

4 LUMPED KINETIC MODELS FOR COAL LIQUEFACTION

Kinetic modeling of the coal liquefaction is complex because the liquefaction process depends on many variables viz., temperature and pressure of the reactor, nature and amount of solvent, presence of mineral matters and/or externally added catalysts and also the nature and rank of coals. The process is further complicated as samples of coal from the same seam differ in their response to various operating conditions.

Coal is a nonhomogeneous material and its liquefaction produces a very large number of products. A completely detailed kinetic analysis involving all chemical species is therefore impossible. All the studies reported in the literature evaluate kinetic models using different types of lumped reacting species. A number of different types of reaction paths are evaluated. Unfortunately, the kinetic parameters evaluated for a certain coal under particular conditions vary significantly from that of a different coal under identical conditions. It is therefore obvious that the models developed in this manner do not possess global applicability and their use is limited. Several kinetic models have been reported in the literature and these have been reviewed by Lee (27) and Shah (28). Here we only summarize them in some order of their intricate details as shown in Table 2. For the details the reader is advised to refer to the original references.

5 CATALYSIS IN COAL LIQUEFACTION

The study regarding catalysis in coal liquefaction can be broadly divided into two groups: (1) effects of mineral matter present in the coal slurry itself and (2) effects of externally added catalysts.

In either mode, the catalyst (or mineral matter) serves to: (a) improve the liquid yield, including enhancement in the hydrogenation and hydrocracking rates and (b) improve heteroatom removal.

Inherent coal minerals are readily available and inexpensive catalysts for liquefaction, hydrogenation/hydrocracking and heteroatom removal reactions. In recent years, experimental work has been carried out to determine: (a) liquefaction behavior of various coals with different mineral matter contents, (b) liquefaction behavior by adding various mineral matter in or to a particular coal or by reducing the mineral matter contents of a coal by some physical means and (c) liquefaction behavior in the presence of a variety of externally added catalysts. Some of these studies are briefly described below.

Given et al. (44) studied the liquefaction behavior of a number of vitrinite rich coals in batch autoclaves at 658-698 K and 8.6 MPa hydrogen pressure. In one set of experiments,

TABLE 2

SUMMARY OF LUMPED KINETIC MODELS FOR COAL LIQUEFACTION

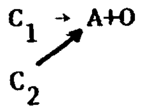
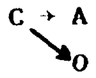
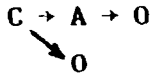
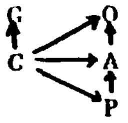
Kinetic Scheme*	Coal	Solvent	Catalyst	References
$C \rightarrow A \rightarrow O$	Pittsburgh Anthraxylon	None	SnS, NH_4Cl	Weller et al. (29)
	Spitsbergen	None	Ca-Cu-Cr	Falkum and Glenn (30)
	Pittsburgh	Tetralin	None	Curran et al. (33)
	Pittsburgh extract	None	$ZnO/ZnCl_2$	Struck et al. (34)
$C \rightarrow A{+}O$	Wyoming	None	None	Pelipetz et. al. (31)
	Utah	Tetralin	None	Hill et al. (32)
	Bituminous	Tetralin	None	Liebenberg and Potgieter (35)
	Japan	Decrystallized anthracene oil	Red mud and sulfur	Yoshida et al. (36)
	Belle Ayr	Hydrogenated phenanthrene	None	Cronauer et al. (37)

TABLE 2
(Continued)

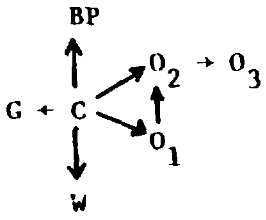
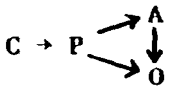
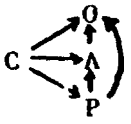
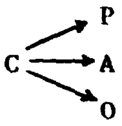
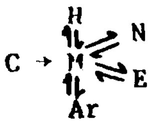
	Subbituminous	Recycle solvent and hydrogenated anthracene oil	$CoMo/Al_2O_3$	Shah et al. (38)
$C \rightarrow P \rightarrow A \rightarrow O$	Kentucky	Tetralin	None	Shalabi et al. (39)
				
				
				
	Illinois No. 6	Tetralin	None	Govindon and Silla (40)

TABLE 2
(Continued)

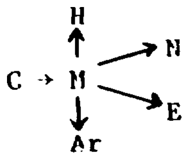
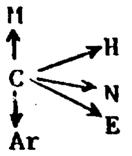
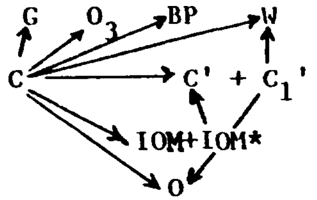
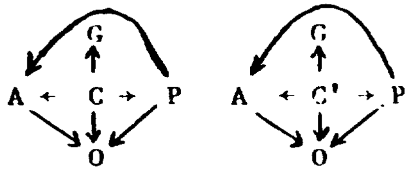
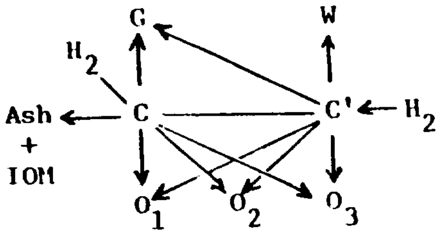
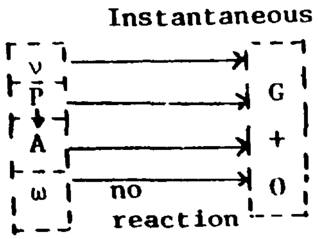
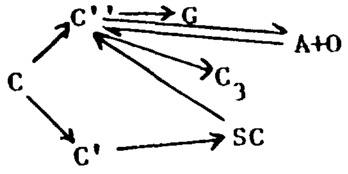
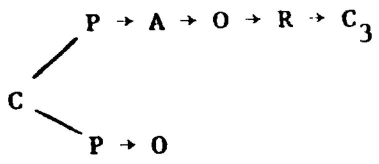
 				
	Kentucky No. 11	Recycle solvent	None	Parulekar et al. (41)
$C + O \rightarrow C'$ 	Belle Ayr Burning Star	Anthracene oil hydrogenated anthracene oil hydrogenated phenanthrene	None	Abichandani et al. (42)

TABLE 2
(Continued)

	Powhatan	SRC-recycle solvent	None	Singh et al. (43)
	Illinois No. 6	---	---	Brunson (107)
	---	---	---	Shinn et al. (108) and Shinn & Vermeulen (109)
	Japanese Australian & Indonesian	---	H_2MoO_4	Morita et al. (26)

*Legends

A - asphaltenes (benzene solubles but pentane insolubles)

Ar - aromatics

BP - by-products

C - coal, moisture and ash free

C_1, C_2 - two reactive parts of coal

C_3 - coke or char

C' - SRC

C'' - highly activated coal

C_1' - active SRC

E - ethers

G - gases (H_2O, CO, CO_2, H_2S, NH_3, light hydrocarbons)

H - hydroxyls

IOM - insoluble organic matter

IOM* - active insoluble organic matter

M - multifunctionals

N - nitrogens

O - oils (pentane soluble)

TABLE 2
(Concluded)

O_1 - oil (heavy distillate)
O_2 - oil (middle distillate)
O_3 - oil (light distillate)
P - preasphaltenes (pyridine solubles but benzene insolubles)
R - resin
SC - soluble coal
W - water
ν - volatile portion of coal
ω - unreactive portion of coal

impregnated ammonium molybdate was used as catalyst with no added liquid as vehicle while in a second set, a proprietary catalyst was used with anthracene oil serving as vehicle. Their data indicated lower yields of oil from the lignites and subbituminous coals than from coals of higher rank. However, yields fell off again at the upper end of bituminous rank (> 90% C).

Mukherjee and Chowdhury (45) presented plots showing the catalytic effects of iron and titanium on the conversion of Assam (India) coal to oils. Their data indicated an increase in conversion with mineral matter content corresponding to an ash content of 27% and then the conversion was found to drop. This finding is corroborated by Granoff et al. (46) who also found no effect of mineral matter corresponding to ash contents beyond 20%. The reason for this drop in conversion is supposed to be due to the excessive increase in inertinites. Iron as a reduced sulfide is supposed to be active for the catalysis of the liquefaction reaction. Titanium was added in the form of a hydroxide. They found that the total iron acts as a catalyst, a finding in contrast to that of Tarrer et al. (47) who concluded that only pyritic iron acts as a catalyst for the liquefaction. It is also interesting to note that according to Given et al. (44) the organic complexes of titanium poison the catalysts for liquefaction. Kawa et al. (48) concluded that the tin catalysts were the best for conversion of coal to oil and iron catalysts were only moderately active for the same purpose.

Guin et al. (49) studied the hydrogenation of creosote oil at 683 K and 6.8 MPa initial hydrogen pressure using different catalysts. The catalytic activity was defined in terms of hydrogen consumption. They found a $CoMo/Al_2O_3$ catalyst to be the most effective while calcite, quartz, dolomite and kaolin had no effect at all. The hydrogen consumption for the demineralized coal was lower than that for untreated coal. An unexplained phenomenon observed by Guin et al. (49) was that slurrying coal with water prior to hydrogenation decreased its rate of liquefaction.

Guin et al. (50) also examined hydrogen transfer activity of tetralin under liquefaction conditions. Tetralin donates hydrogen to coal derived free radicals producing naphthalene and hydrogenated free radicals as

$$\text{tetralin} + \text{free radicals (F.R.)} \rightarrow \text{naphthalene} + \text{H}\cdot\text{(F.R.)}$$

The dehydrogenated solvent can be regenerated in the presence of a catalyst and gaseous hydrogen as

$$\text{naphthalene} + 2H_2 \xrightarrow{\text{catalyst}} \text{tetralin}$$

Using a mixture of Kentucky No. 9/14 and Illinois No. 6 coals and light recycle oil from the Wilsonville, Alabama SRC pilot plant, in place of tetralin, they also showed that the presence of mineral matter decreased benzene insolubles by about 15% and pyridine insolubles by about 24%.

Shah (28) evaluated the use of catalysts NiMoTi on Al_2O_3 and $AlPO_4 \cdot Al_2O_3$ and NiCoMo on $AlPO_4 \cdot Al_2O_3$. The study showed that Al_2O_3 support was better than $AlPO_4 \cdot Al_2O_3$ support for both catalysts. The study also showed that NiCoMo was more reactive as such than when deposited on Torvex and the catalysts supported on magnesium aluminate had low coke deposition.

Catalyst aging is one of the most important problems in catalytic coal liquefaction. The catalyst is coked very readily because of the highly aromatic nature of coal liquids. Coking causes a significant decline in the catalytic activity for hydrogenation/hydrocracking, heteroatom removal and the production of liquid fuel. Unlike the catalysts used in petroleum cracking, the regeneration of coal liquefaction catalysts is very difficult. Utmost care is, therefore, needed to protect the liquefaction catalysts from possible poisoning and coking.

Hildebrand and Tsai (51) studied the aging of a $NiTiMo/Al_2O_3$ catalyst in a Gulf-patented catalytic coal liquefaction reactor (CCL) using Big Horn coal and anthracene oil/vacuum tower overhead as solvent at 661-678 K and 28 MPa total pressure (corresponding to about 26.5 MPa hydrogen partial pressure). Their results showed that while coal conversion to pyridine soluble materials remained almost constant, the hydrocracking declined by more than 50% in one month's period. Similarly, in the syncrude mode of the H-COAL process with $CoMo/Al_2O_3$ catalyst and Illinois No. 6 and Wyodak coals required a catalyst replacement rate of 0.5-0.55 Kg/metric ton of coal. Such high catalyst consumption indicates that further research is needed to improve the catalyst age and reduce its consumption.

Table 3 presents a brief summary of some of the catalytic coal liquefaction studies.

7 HETEROATOM REMOVAL

While the organic coal matrix contains methylene bridges of the 9,10-dehydroanthracene type (54), the compounds of nitrogen, oxygen and sulfur are also constituents of coal and their presence affect the nature of the coal and the liquid fuel produced from it.

TABLE 3

CATALYSIS IN COAL LIQUEFACTION

	Type of Coal	Solvent	Catalyst	Operating Conditions	References
1.	Pittsburgh seam (hVab) and Indiana No. 5	Coal tar	Co,Mo,Ni,Sn,Fe	673 K, 13 MPa, 1800 sec	Kawa et al. (48)
2.	Vitrinite rich coals from Appalachian Province, Interior Province, North Great Plains Province, Rocky Mountain Province, Pacific Province & Gulf Province	(1) none (2) anthracene oil	(1) impregnated ammonium molybdate (2) proprietary catalyst	658-698 K 8.6 MPa 1.08×10^4 secs	Given et al. (44)
3.	North Assam (India)	None	Representative coal mineral matters	673 K, 10 MPa 1.08×10^4 secs	Mukherjee & Chowdhury (45)
4.	Kentucky No. 9/14	Creosote oil	Different coal minerals	683 K, 6.8 MPa 900-7200 secs 1000 rpm stirrer speed	Tarrer et al. (47)
5.	Kentucky No. 9/14	Creosote oil	CoMo/Al_2O_3 catalyst and almost all the coal minerals	683 K, 6.8-17 MPa 900-7200 secs	Guin et al. (49)

6. Mixture of Kentucky No. 9/14 and Illinois No. 6	Tetralin and light recycle oil
7. Brown coal	Tetralin
8. Illinois No. 6 and Wyodak	Recycle oil
9. Wyodak	Anthracene oil

TABLE 3
(Concluded)

CoMo/Al_2O_3 and representative coal minerals	673 K, 13.6 MPa 7200 secs	Guin et al. (50)
Alumina, silica gel, red haematite, heavy magnesium carbonate, calcium carbonate, anhyd. Na_2CO_3	704 K, 9.66 MPa 3600 secs	Jackson et al. (52)
CoMo/Al_2O_3	727 K, 20 MPa	U.S. DOE Report (53)
(1) NiMoTi on Al_2O_3 and $AlPO_4 \cdot Al_2O_3$ (2) NiCoMo on $AlPO_4 \cdot Al_2O_3$ and Torvex (3) NiW on Al_2O_3	683 K, 24.13 MPa	Shah (28)

Sulfur is an objectionable element due to its harmful environmental and catalytic poisoning effects. It is generally believed that mercaptan, sulfide, disulfide and thiophene are the major organic sulfur containing functional groups and minerals like pyrite and marcasite are mostly responsible for inorganic sulfur in coal. A small amount of inorganic sulfur is also present as sulfate minerals like melanterite ($FeSO_4 \cdot 7H_2O$) and jarasite ($(Na,K)Fe_3(SO_4)_2(OH)_6$) as well as gypsum.

Nitrogen compounds in coal liquids can cause storage and processing problems. During storage, they cause polymerization and hence, gum formation and deposition. Similarly, oxygen compounds will enhance the polymerization tendency of coal liquids. It is thus very important to remove S, N, and O compounds to the maximum possible extent to render coal liquids fit for end uses without causing environmental or storage problems.

An extensive study of heteroatom removal has been carried out at the Gulf Research and Development Company. This and a few other studies have been summarized by Shah and Cronauer (55) and Shah and Krishnamurthy (56) and they will not be repeated here. Instead, in the following pages, a few other reported works on hydrodesulfurization (HDS), hydrodeoxygenation (HDO), and hydrodenitrogenation (HDN) of real systems and model compounds, that may be relevant to coal liquefaction, are briefly discussed.

Guin et al. (49) studied the HDS of creosote oil and Kentucky No. 9/14 coal mixture at 683 K and 6.8 MPa and 17 MPa initial hydrogen pressures in the presence of $CoMo/Al_2O_3$ catalyst and other mineral matter. The results indicated that $CoMo/Al_2O_3$ was the best catalyst (removing almost all the sulfur) and ankerite was the worst.

Pyrite has been found to be a relatively poor catalyst for HDS. The reason for this may be due to the fact that pyrite is reduced rapidly during hydrogenation to the sulfide form and some reverse reaction by H_2S generated may occur. The H_2S formed may react with organic compounds forming more sulfur. Iron, on the other hand, acts as a sulfur scavenger, suppressing the reverse reaction and thus reducing the overall sulfur content.

Jackson et al. (52) extensively studied the catalytic effect of additives such as alumina, red haematite, magnesium carbonate, silica gel, calcium carbonate and anhydrous sodium carbonate on HDS. Surprisingly, except for haematite none of the additives increased the conversion of sulfur compounds. Haematite increased the HDS rate by 20%, almost on a par with the CoMo catalyst.

Betrolacini et al. (57) studied the liquefaction of Illinois No. 6 coal in trimethylnaphthalene at 13.79 MPa and 700 K and concluded that desulfurization increased with the addition of MoO_3 and CoO. After an addition of about 10% of MoO_3, the desulfurization attained a constant value and it dropped suddenly from its peak value after addition of 2% of CoO. They also found that the desulfurization increased steeply with the surface area of the catalyst; but the conversion dropped after a surface area of about 80 m^2/gm was attained. No explanation is presently available for this peculiar trend.

Garg et al. (58) studied the effects of haematite on HDS of Western Kentucky No. 9/14 coal at 658-693 K for 15-20 min at hydrogen partial pressures varying from 7.0 to 20.8 MPa. They found that after 15 minutes of reaction time in the presence of haematite, the same amount of sulfur was removed as is removed in 120 mins without haematite. Haematite was found to be very active during short reaction times; however, it was not very effective at the large reaction times. They also concluded that the desulfurization rate was independent of catalyst particle size but it depended upon the surface area.

Significant hydrodenitrogenation (HDN) does not take place during liquefaction unless externally added good denitrogenation catalysts are used. The denitrogenation is usually achieved by the separate refining of coal liquids. Both denitrogenation and deoxygenation increase with increase in temperature, hydrogen partial pressure and a decrease in feed coal concentration. Hydrodeoxygenation (HDO) also depends upon the nature and rank of coal. Both HDN and HDO studies have been extensively reviewed by Shah (28) and Shah and Cronauer (55). Hildebrand and Tsai (51) also showed that HDS, HDO and HDN all decline rapidly with catalyst aging, the effect being most pronounced for HDN. A brief summary of the reported heteroatom removal studies with real systems is given in Table 4.

7.1 Model Compound Studies

7.1.1 Hydrodesulfurization. Several model compound studies have been undertaken to understand the mechanism of sulfur removal during coal liquefaction. Hydrodesulfurization of thiophene has been reported by Amberg and his co-workers (86-91), Schuit and Gates (92), Lipsch and Schuit (67) and Shah and Cronauer (55). The last authors indicated that the hydrodesulfurization of thiophene proceeds through butadiene and not through a hydrogenation-hydrogenolysis sequence. Further, they claimed that the reactivity of the thiophene ring is decreased by an addition of a benzene ring, as in benzothiophene, resulting in a hydrogenation-hydrogenolysis route for the sulfur removal.

The HDS of thiophenes and their derivatives have been investigated by Schuit and Gates (92), Guin et al. (50), Houalla et al. (93), and Givens and Venuto (94). They concluded that for these reactions CoMo/Al_2O_3 was a better catalyst than Fe, pyrite, SRC residue, SRC ash and reduced pyrites. Besides thiophenes and their derivatives, Schuit and Gates (92) examined hydrodesulfurization of phenyl sulfide and Cronauer et al. (95) investigated the reaction of dibenzyl sulfide in solvents like tetralin or mesitylene. Shah and Cronauer (55) studied reactions between a variety of sulfur compounds and cyclohexane. Their study indicates the order of reactivity of different sulfur compounds to be disulfide (aliphatic or aromatic) > diarylsulfide > aliphatic sulfide > thiophene. Further studies in the area is warranted with other donor solvents like tetralin and hydrophenanthrene.

Burow et al. (96) recently explored the utility of liquid SO_2 for the removal of organic sulfur from Eastern bituminous coals. Liquid SO_2 is supposed to be an excellent solvent for aromatic heterocyclic and alkyl sulfides derived from coal. They have considered the mild Lewis acid characteristics of SO_2 and presented the following scheme for reaction

$$-\underset{..}{S} : + SO_2 \rightarrow -\underset{..}{S} : SO_2$$

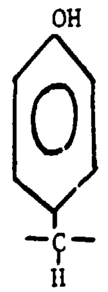
Products from this reaction are usually highly colored and highly soluble in liquid SO_2.

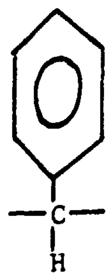
7.1.2 Hydrodenitrogenation. Heterocyclic compounds containing nitrogen in coal liquids are either basic (pyridines, quinolines and acridines) or non-basic (pyrroles, indoles and carbazoles). Attempts have been made to study these model compounds to highlight the mechanism involved in hydrodenitrogenation process. The important reported studies are those of Sonnemans et al. (84,97), Goudriaan et al. (77), Satterfield et al. (79,82,83), McIlvried (75) and Cox and Berg (81) for the denitrogenation of pyridine and its derivatives, Doelman and Vlugter (72), Madkour et al. (74), Larson (98), Shih et al. (78), and Satterfield et al. (79,82,83) for the denitrogenation of quinolines, Hartung et al. (99) for the indole denitrogenation, Flinn et al. (73) for the hydrogenation of aniline, n-butylamine, indole and quinoline, and Aboul-Gheit and Abdou (76) for the denitrification of pyridine, quinoline, aniline, pyrrole and indole. In many cases, the overall nitrogen removal reaction was found to be of first order with respect to the nitrogen containing species. Some of these studies are briefly described below.

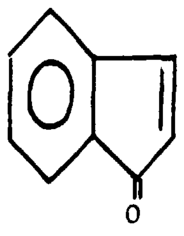
Gourdiaan et al. (77) studied CoMo/Al_2O_3 catalyst for pyridine hydrodenitrogenation at about 8 MPa pressure and 523-673 K temperature. They concluded that the conversion was 25-45% higher on the presulfided catalyst than on the oxide catalyst and the hydrogen sulfide pressure was found to have little effect on conversion. Satterfield and Cocheto (83) studied NiMo/Al_2O_3 catalyst for pyridine hydrodenitrogenation at 1.1 MPa pressure and 673 K temperature. Their conclusion was that NiMo/Al_2O_3 catalyst has greater activity for hydrogenation-dehydrogenation than CoMo/Al_2O_3 but the latter appears to have greater hydrogenolysis activity than NiMo/Al_2O_3 at the temperatures below 573 K. Satterfield et al. (79,82) also studied intermediate reactions in the HDN of quinoline at pressures of 3.4 MPa and 6.8 MPa and at temperatures ranging from 503 K to 693 K. The catalyst was American Cyanamid Aero HDS-3A NiMo/Al_2O_3 extrudates (3.1 wt% NiO, 15.0 wt% MoO_3). Its performance was compared with those of CoMo/Al_2O_3 used by Doelman and Vlugter (72) and NiMo/Al_2O_3 used by Shih et al. (78). They concluded that CoMo catalyst was less active for the first step of hydrogenation of quinoline to pytetrahydroquinoline than the NiMo catalyst. Similarly for the HDN of pyridine, the first step of hydrogenation to piperidine was more rapid on a NiMo/Al_2O_3 catalyst than on a CoMo/Al_2O_3 catalyst. Madkour et al. (74) found that the presence of HCl accelerated HDN on a CoMo/Al_2O_3 catalyst suggesting the possibility of a catalyst with stronger acid sites to be more active for the overall rate of HDN.

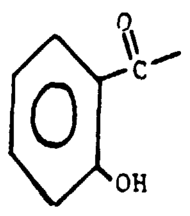
Zawadski et al. (100) studied the denitrogenation of acridine whereas Stern (101) studied the hydrodenitrogenation of pyrroles, indole and carbazole using commercially available CoMo/Al_2O_3 catalyst containing 3% CoO, 15% MoO_3 on alumina containing 5% SiO_2; NiMo/Al_2O_3 containing 3.8% NiO, 16.8% MoO_3 and some novel catalysts such as: Re/Al_2O_3 containing 5% Re as Re_2S_7 on alumina and CoRe/Al_2O_3 containing 0.79% CO, 5% Re as $Co(ReO_4)_2$ on alumina. Conversion over each of the catalysts decreased as the five membered ring of pyrrole was increasingly substituted. The Re catalysts, which were somewhat more reactive for the conversion of pyrrole than CoMo and NiMo catalysts, were less reactive for indole conversion and had the same activity as the commercial catalysts for the conversion of carbazole.

7.1.3 Hydrodeoxygenation. Davies and Lawson (102) demonstrated the presence of oxygen compounds such as









and even more complex compounds in coal liquids. Almost half of the oxygen in coal liquids is present as ethers and all the carboxylic acids are probably esters in the original coal. The largest unknown and indeterminate parameter of solid coals is oxygen incorporated in water of hydration which is erroneously assumed to be "organic" in nature.

The severity requirement of a liquefaction process can very well be known before hand due to the fact that removal of an (OH) group requires two hydrogen atoms whereas removal of (-C=O) and (C-O-C) groups require 4 atoms. Some of the relevant model compound studies are briefly described below.

Cronauer et al. (95) presented a scheme for deoxygenation of dibenzyl ether and concluded overall reaction to be a second order. They also gave a mechanism for thermal dehydration of a tetralone and Eisenbraum et al. (103) determined that this reaction would normally take place above 673 K without a catalyst but in the presence of an alkali or noble metal catalyst it may proceed at lower temperatures.

Roberti (68,69) and Polozov (70) studied the catalytic activity of commercial catalysts: CoS, MoS_2 for the hydrodeoxygenation (HDO) of phenol to cyclohexane. Their conclusion was that the reaction followed a path via cyclohexanol while Moldavskii and Livshits (104) found the direct dehydration rate to dominate at least at low pressures. Hall and Cawley (71) studied the HDO of dibenzofuran on a MoS_2 catalyst and presented two different possible schemes. Benjamin et al. (105) have presented a summary of reactions of oxygen compounds (phenols and ethers) in tetralin at 673 K for 18 hour reaction time. A brief summary of some of the reported model compound studies is given in Table 4.

8 REACTOR DESIGN

Reactor design considerations for coal liquefaction are discussed in another paper presented at this NATO School (106) and hence they will not be repeated here.

9 SUMMARY

It is obvious that in spite of vast efforts being put forth on the development of various processes, the basic understanding needs further work. The areas of most importance are (a) analytical chemistry for the product distribution, (b) hydrogen transfer mechanism and (c) sophisticated lumped kinetic model. Future work needed for the reactor design is discussed by Shah and Gopal (106).

TABLE 4

SUMMARY OF HETEROATOM REMOVAL STUDIES

Part A - Study Related to Real Systems

Feedstock	Pressure (MPa)	Temperature (K)	Catalyst	References
Illinois No. 6 coal/ creosote solvent	6.8	678	FeS, Montmorillonite Fe_2S_3, pyrite, ZnS SRC-residue	Granoff et al. (46)
Illinois No. 6 coal/ trimethylnaphthalene solvent	13.79	700	MoO_3, CoO	Betrolacini et al. (57)
Western Kentucky No. 9/14 coal	7-20.8	658-693	Fe_2O_3	Garg et al. (58)
Petroleum fractions ranging from naphthas to residues	2-41	478-700	$Ni-W/Al_2O_3$	Cited in (55)
Raw anthracene oil, COED filtered oil, synthoil liquid	3.4-10	589-700	$CoMo/Al_2O_3$ (presulfided)	Ahmed and Crynes (59)
Raw anthracene oil	3.4-13.6	589-700	$CoMo/Al_2O_3$ (presulfided)	Wan and Crynes (60)
SRC liquids	19	705	$NiMo/Al_2O_3$ (presulfided)	Kang and Gendler (61)
Athabasca bitumen	13.9	713	$CoMo/Al_2O_3$	Hardin et al. (62)

Low temperature tar	10
Heavy gas oil	13.9
Athabasca bitumen	7.0-13.9
Athabasca bitumen distillates	13.9
Benzothiophene, thiophene, phenyl sulfide, dibenzothiophene	13.6
Thiophene	atmospheric pressure
Phenol	----
Dibenzofuran	----
Quinoline isoquinoline	8.1
Aniline, indole n-butylamine and quinoline	6.8

TABLE 4
(Continued)

573-773	WS_2	Qader et al. (63)
673-723	$NiMo/Al_2O_3$ (presulfided)	Ternan and Whaley (64)
713-743	$CoMo/Al_2O_3$ (presulfided)	Aarts et al. (65)
593-693	CoO, NiO and MoO_3, on several Al_2O_3 supports (presulfided)	Furimsky et al. (66)
Part B - Model Compound Studies		
683	$CoMo/Al_2O_3$, 10% iron, pyrite, SRC residue, SRC ash	Guin et al. (50)
773	$CoOMoO_3/Al_2O_3$	Lipsch and Schuit (67)
---	CoS, MoS_2	Roberti and Polzov (68-70)
---	MoS_2	Hall and Cawley (71)
423-673	$CoMo/Al_2O_3$	Doelman and Vlugter (72)
873	$Ni\text{-}W/Al_2O_3$	Flinn et al. (73)

Quinoline	8.1
Pyridine, piperidine and a hexylamine in mixed xylenes	5.1-6.8
Pyridine, quinoline, aniline, pyrrole and indole in high purity paraffin oil	20
Pyridine in p-xylene	8
Quinoline, acridine in a highly paraffinic white oil	3.4-13.6
Quinoline	3.4-6.8
5,6 benzoquinoline 7,8 benzoquinoline	19.5
Twenty-nine heterocyclic nitrogen compounds	1.7
Thiophene, pyridine	0.4-1.1

TABLE 4
(Continued)

473-723	CoMo/Al_2O_3	Madkour et al. (74)
583	CoNiMo/Al_2O_3 (presulfided)	McIlvried (75)
623-673	CoMo/Al_2O_3	Aboul-Gheit & Abdou (76)
523-673	CoMo/Al_2O_3 (presulfided, H_2S)	Goudriaan et al. (77)
615-640	NiOMo, CoMo, Ni-W/Al_2O_3 (unsulfided and presulfided)	Shih et al. (78)
503-693	NiMo/Al_2O_3 (presulfided)	Satterfield et al. (79)
473-653	Ni-W/Al_2O_3 (presulfided)	Shabtai et al. (80)
643		Cox and Berg (81)
373-773	CoMo, NiMo, Ni-W/Al_2O_3 and Ni-W/SiO_2-Al_2O_3	Satterfield et al. (82)

TABLE 4
(Concluded)

Pyridine, piperidine	1.1	473-698	NiMo, CoMo/Al_2O_3	Satterfield and Cocchetto (83)
Pyridine	15.75-75.31	523-648	Mo, CoMo/Al_2O_3	Sonnemans et al. (84)
Mixture of fused ring thiophenes furans, quinolines indole and alkylphenols	2-10	573-723	CoMo (presulfided)	Rollmann (85)

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TABLE 4

SUMMARY OF HETEROATOM REMOVAL STUDIES

Part A - Study Related to Real Systems

Feedstock	Pressure (MPa)	Temperature (K)	Catalyst	References
Illinois No. 6 coal/ creosote solvent	6.8	678	FeS, Montmorillonite Fe_2S_3, pyrite, ZnS SRC-residue	Granoff et al. (46)
Illinois No. 6 coal/ trimethylnaphthalene solvent	13.79	700	MoO_3, CoO	Betrolacini et al. (57)
Western Kentucky No. 9/14 coal	7-20.8	658-693	Fe_2O_3	Garg et al. (58)
Petroleum fractions ranging from naphthas to residues	2-41	478-700	$Ni\text{-}W/Al_2O_3$	Cited in (55)
Raw anthracene oil, COED filtered oil, synthoil liquid	3.4-10	589-700	$CoMo/Al_2O_3$ (presulfided)	Ahmed and Crynes (59)
Raw anthracene oil	3.4-13.6	589-700	$CoMo/Al_2O_3$ (presulfided)	Wan and Crynes (60)
SRC liquids	19	705	$NiMo/Al_2O_3$ (presulfided)	Kang and Gendler (61)
Athabasca bitumen	13.9	713	$CoMo/Al_2O_3$	Hardin et al. (62)