Table 1. Analysis of Illinois No. 6 and Black Thunder Coals

	Illinois #6, Burning Star	**Black Thunder, Wyoming**
Proximate Analyses, wt% (As Received)		
Moisture	4.2	19.3
Volatile Matter	36.9	34.9
Fixed Carbon	48.2	40.3
Ash	10.7	5.9
Ultimate Analyses, wt% (Moisture Free)		
Carbon	70.2	68.3
Hydrogen	4.8	4.8
Nitrogen	0.9	1.0
Sulfur	3.1	0.4
Oxygen	9.9	18.8
Ash	11.1	6.8
Sulfur Forms, wt%		
Sulfatic	0.03	0.02
Pyritic	1.2	0.04
Organic	1.9	0.3

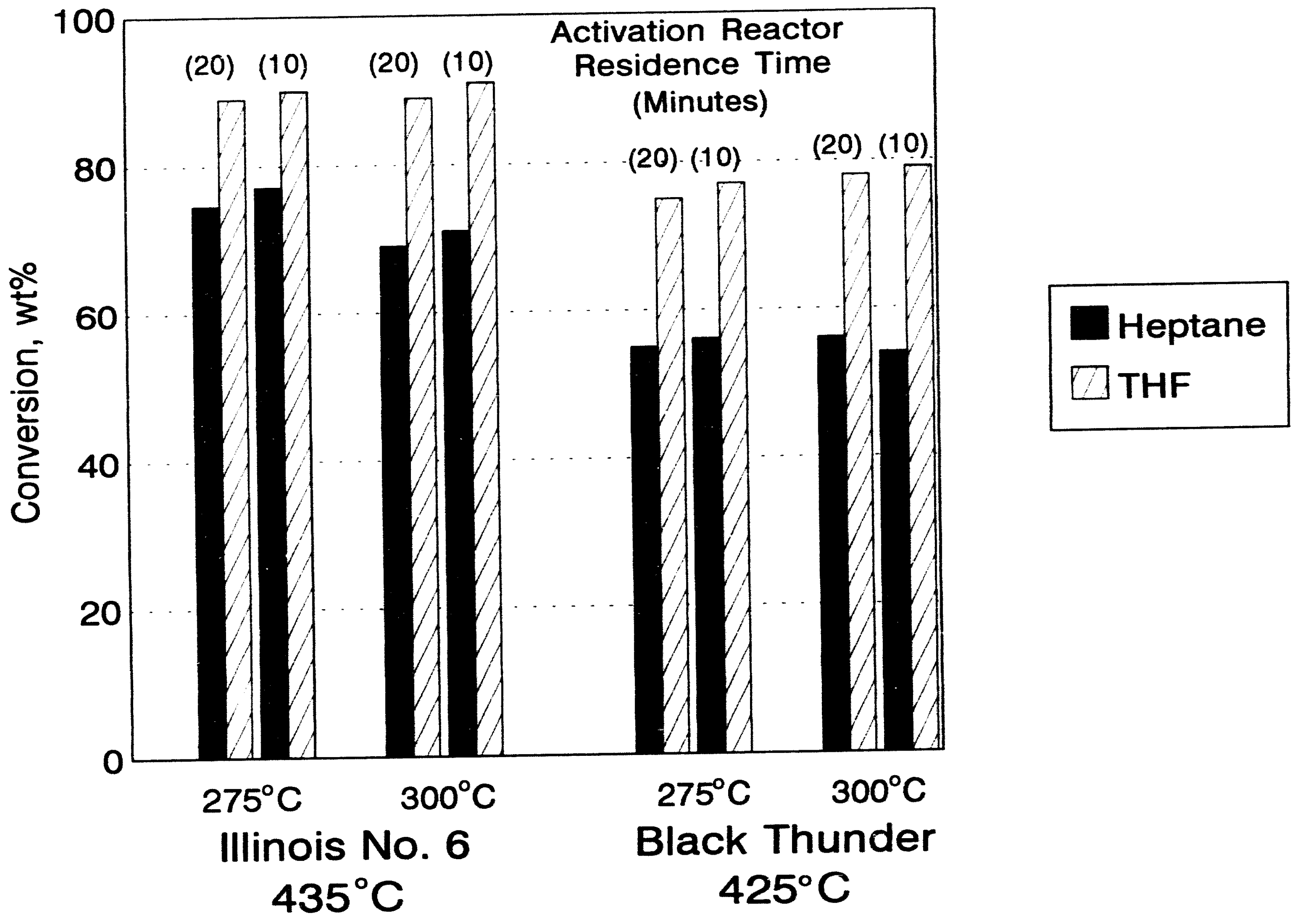
Table 2. Properties of Wilsonville Heavy Distillate Vehicle Oil

	V-1074 Run 262
Ultimate Analyses, wt% (Moisture Free)	
Carbon	87.9
Hydrogen	9.3
Nitrogen	2.5
Sulfur	0.3
Oxygen	<0.05
Ash	<0.1
850 °F- (Vol%)	78.0
Heptane Insols., (wt%)	0.5
H^*_{ar}	0.19
f_a	0.54

Table 3. Effect of Solvent to Coal Ratio on Black Tunder Coal

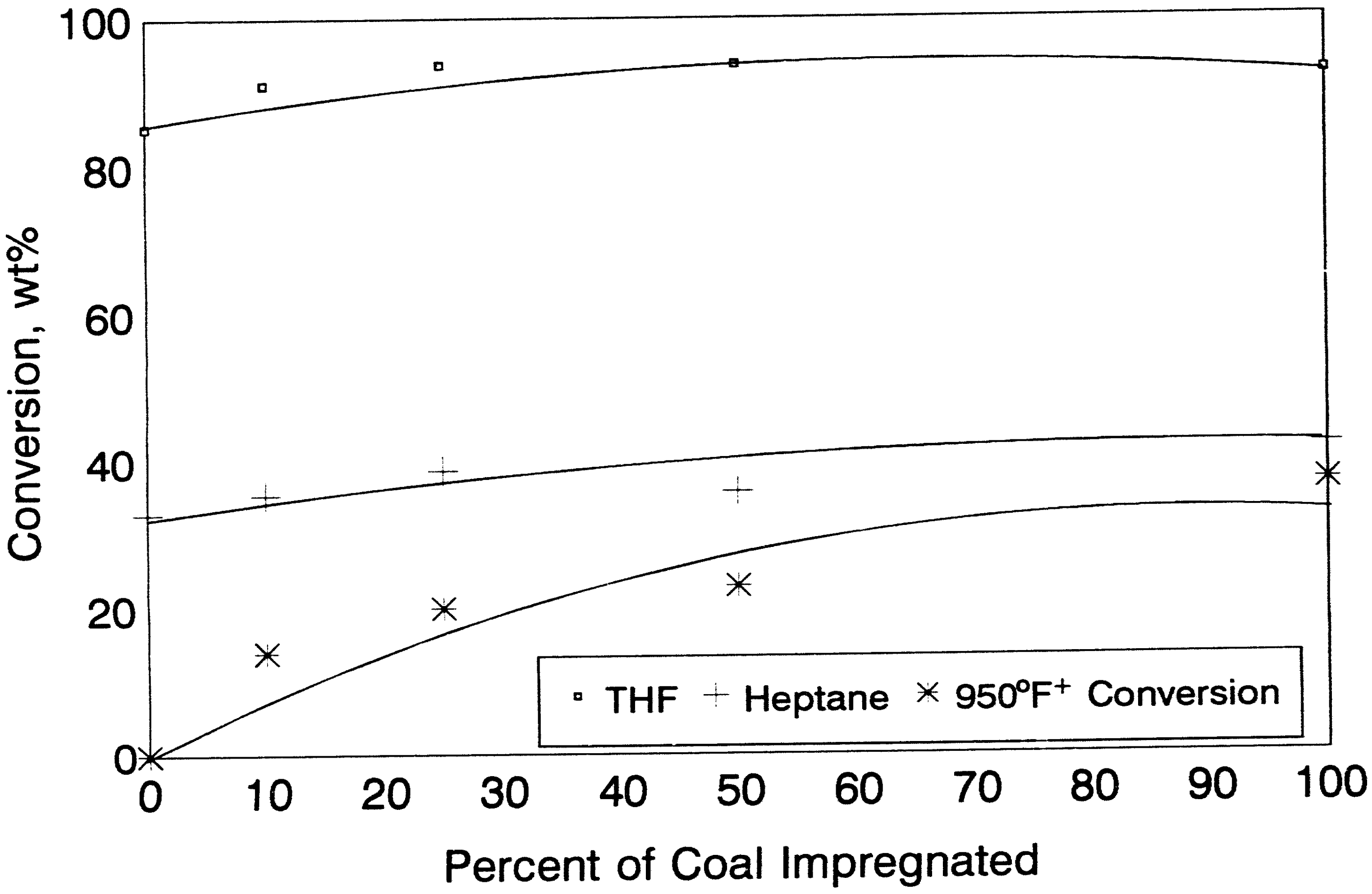
Solvent to Coal Ratio	**Catalyst**	**Coal Conversion to Heptane Solubles**	**Coal Conversion to THF Solubles**
2/1	None	22	68
2/1	Imp. FeOOH	57	90
1/1	Imp. FeOOH	60	93
2/1	AHM	74	96
1/1	AHM	79	97

Figure 1. Effect of Activation Reactor Residence Time



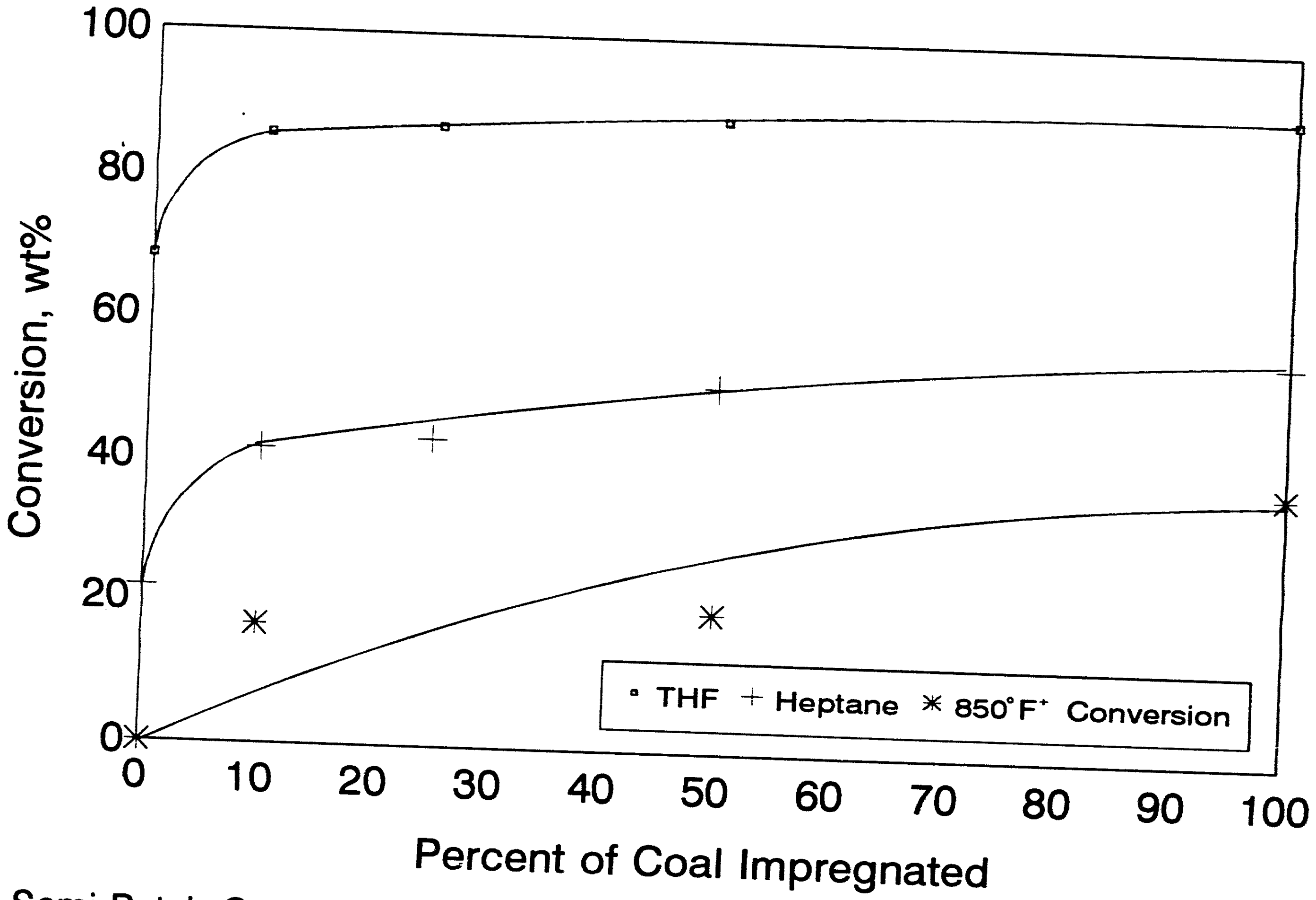
Continuous Operations, 1 h, 2:1 V-1074 to Coal, 2500 psig (H_2/H_2S)

Figure 2. Effect of Spiking - (Illinois No. 6 Bituminous)



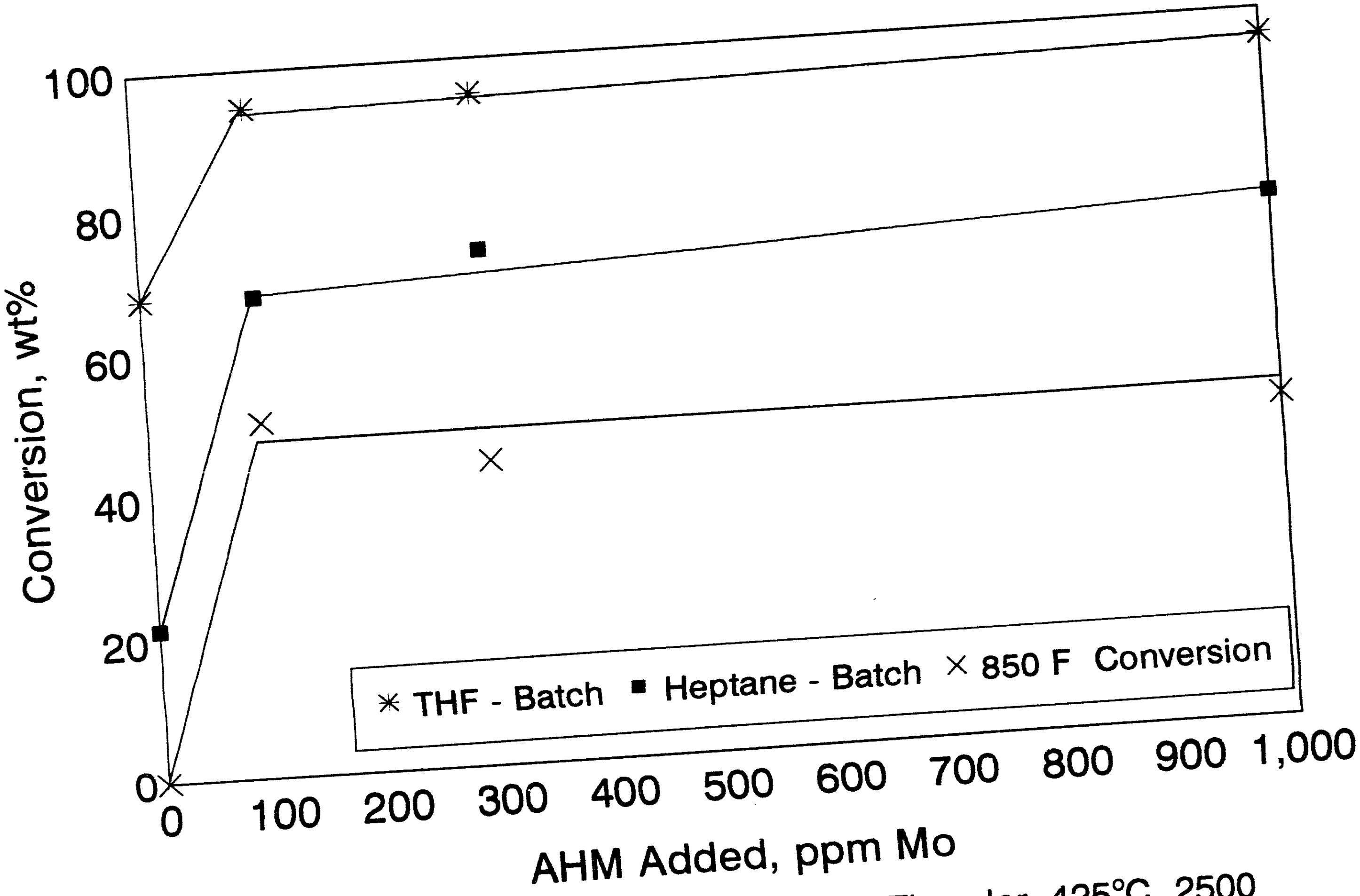
Semi-Batch Operation, 1 h, 2:1 V-1074 to Illinois No. 6, 425°C, 2500 psig (H_2/H_2S)

Figure 3. Effect of Spiking - (Black Thunder Subbituminous)



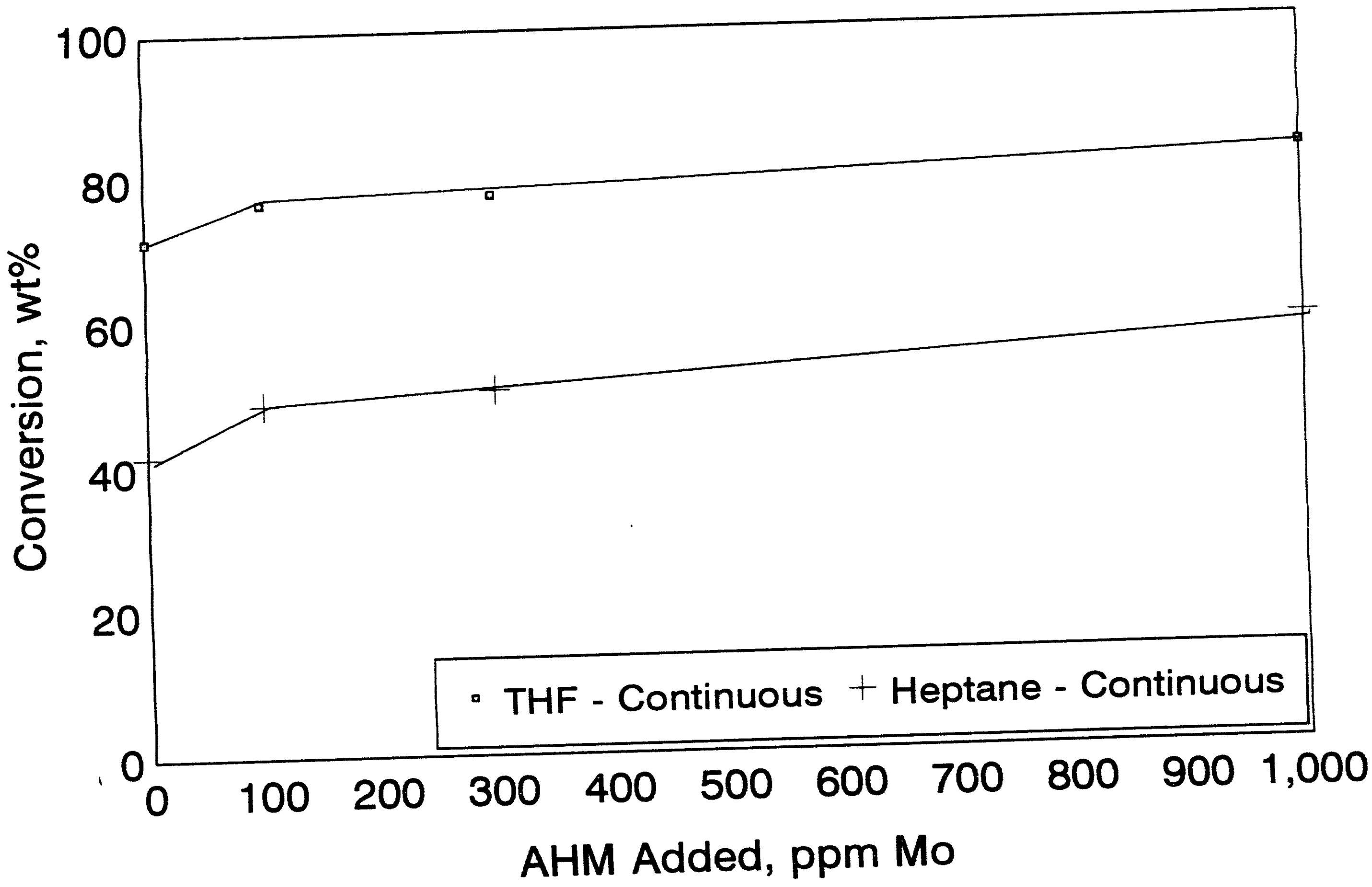
Semi-Batch Operation, 1 h, 2:1 V-1074 to Black Thunder, 425°C, 2500 psig (H_2/H_2S)

Figure 4. Effect of Mo Concentration (1-L Semi-Batch)



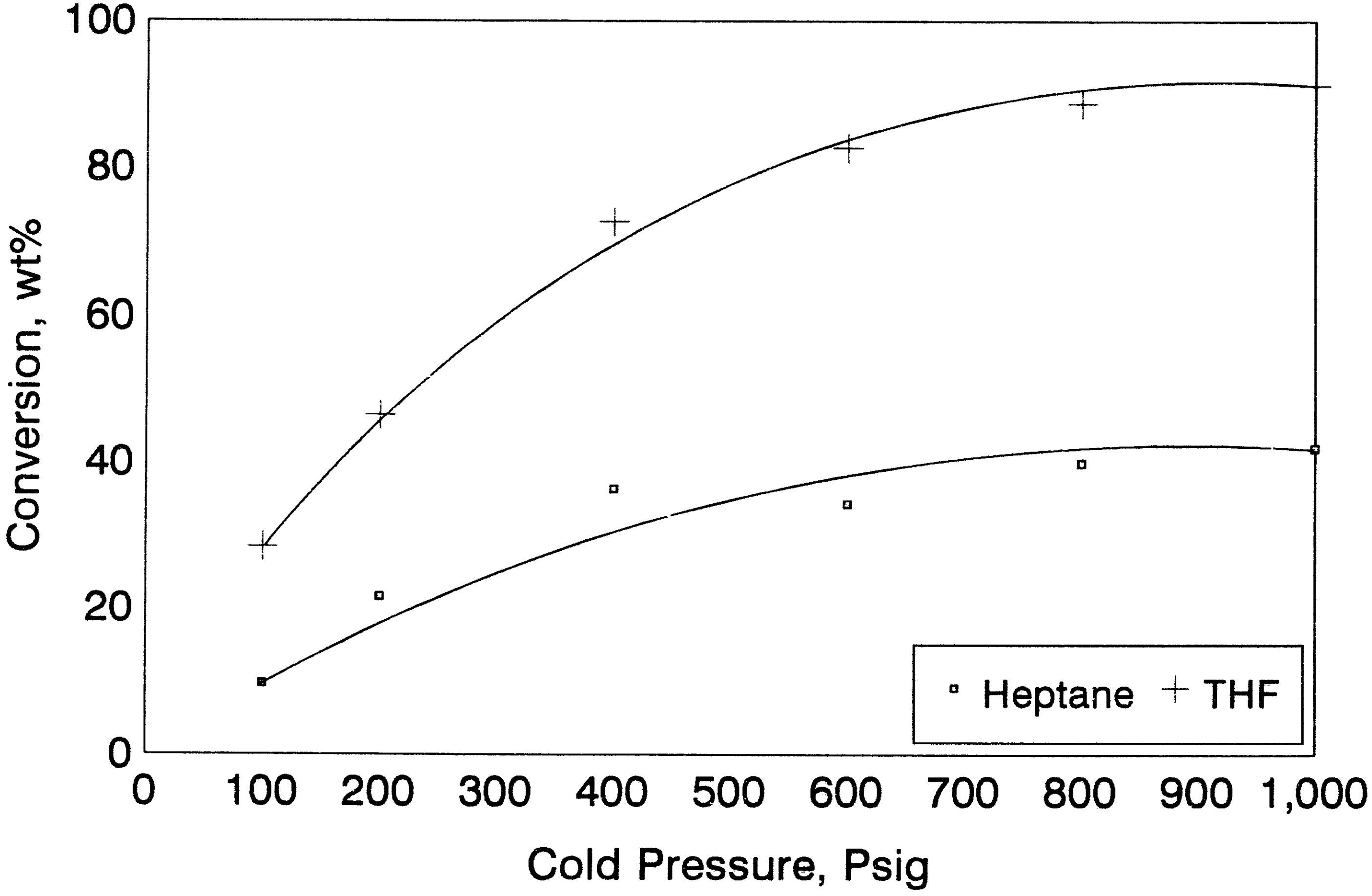
Semi-Batch Operation, 1 h, 2:1 V-1074 to Black Thunder, 425°C, 2500 psig (H_2/H_2S)

Figure 4a. Effect of Mo Concentration (Continuous)



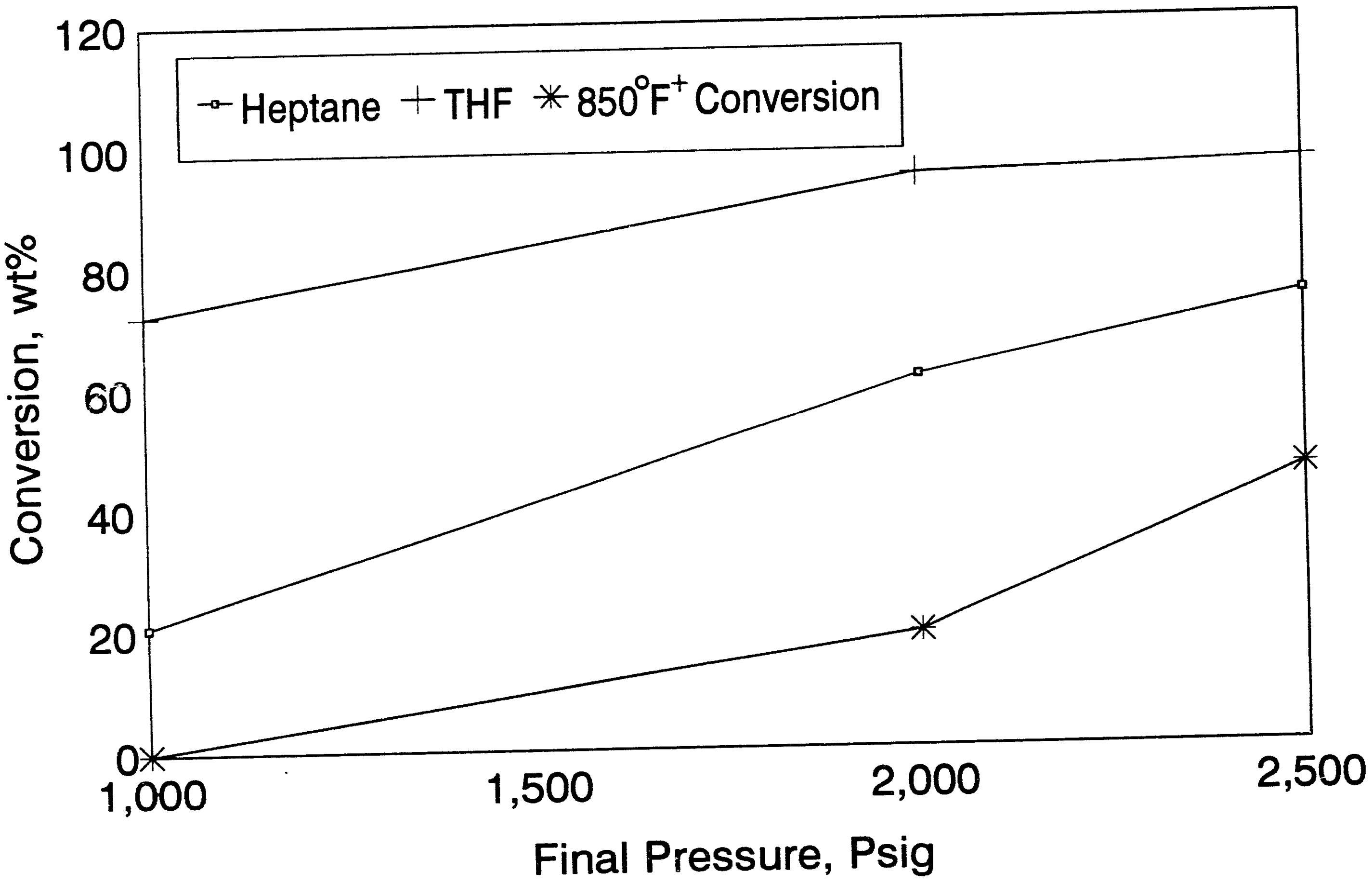
Continuous Operation, 1 h, 2:1 V-1074 to Black Thunder, 425°C, 2500 psig (H_2/H_2S)

Figure 5. Effect of Pressure (Microautoclave)



Microautoclave, 0.5 h, 2:1 1-Methylnaphthalene to Black Thunder, 425°C, Powdered MoS_2

Figure 6. Effect of Pressure (1-L Semi-Batch)



Semi-Batch Operation, 1 h, 2:1 V-1074 to Black Thunder, 425°C, H_2/H_2S

1000 ppm Mo (as AHM)

LIQUEFACTION CONTRACTOR'S REVIEW CONFERENCE
September 27-29,1993
Pittsburgh,Pennsylvania
U.S.A

Title:	CONCEPTUAL DESIGN & ECONOMIC EVALUATION Of BCL PROJECT
Authors:	S.Katsushima, T.Yoshida, H.Kitamura, S.Ueda
Organization:	New Energy and Industrial Technology Development Organization (NEDO)
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ABSTRACT

NEDO has been conducting the R&D of Brown Coal Liquefaction(BCL) process since 1981. The 50 t/d pilot plant in Victoria, Australia was closed down in 1990 after successful operation.

The consolidation study has been executed based on the results of the pilot plant operation. The study consists of following items;

- Follow-up R&D
- Data analysis
- Development of process simulator
- Conceptual design for demonstration plant(6000 t/day)
- Economic evaluation of the process

Conceptual design for D.P. covers optimizatin of process flow & condition, material & heat balance, scale up techniques of major equipments, selection of equipment material, image for all required facility, and operation & maintenance procedure.

The economic evaluation shows that further R&D for process improvement is desired to realize the commercialization of the process in early 21st century.

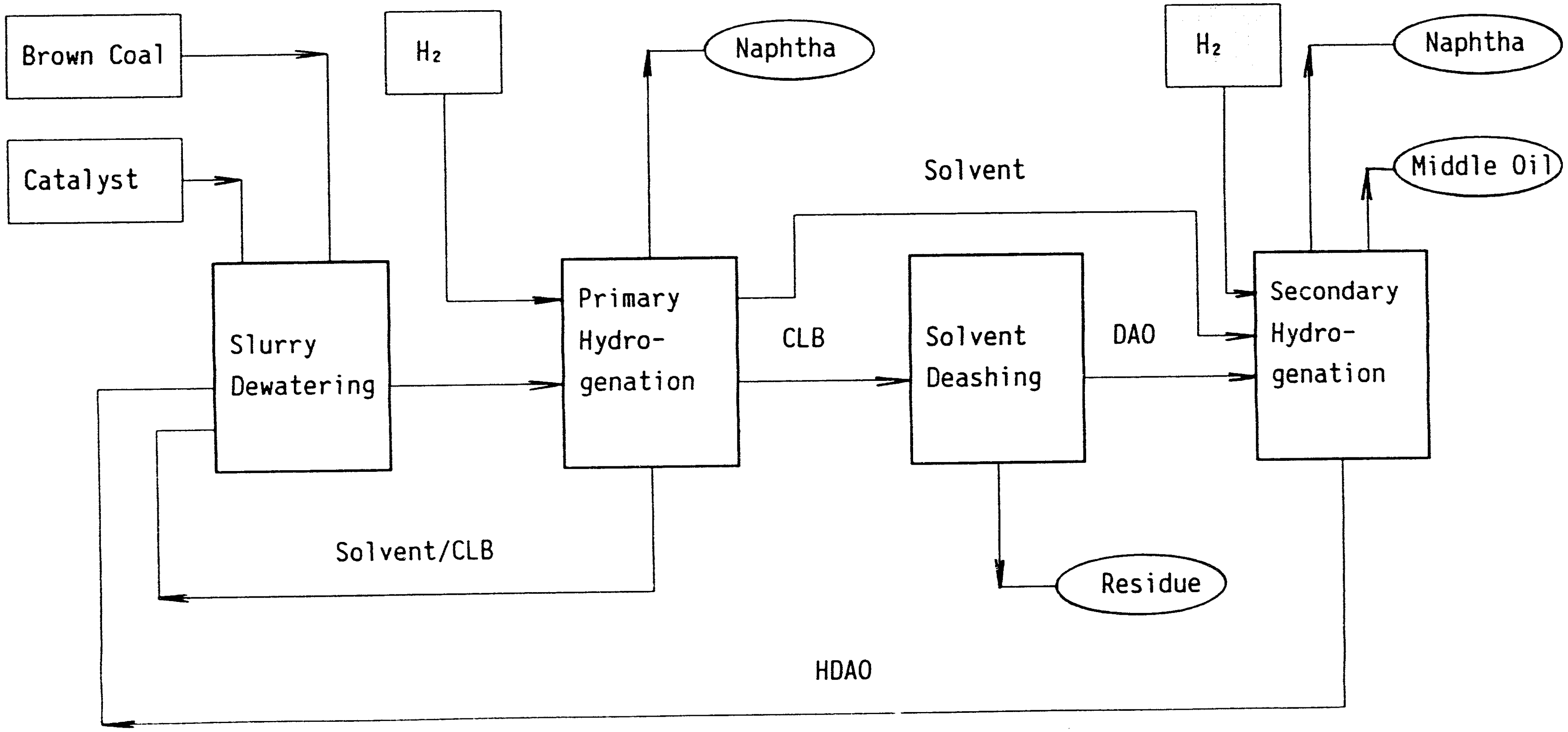
<DOE , PETC>
COAL LIQUEFACTION & GAS CONVERSION
(CONTRACTOR'S REVIEW CONFERENCE)

27-29、September, 1993

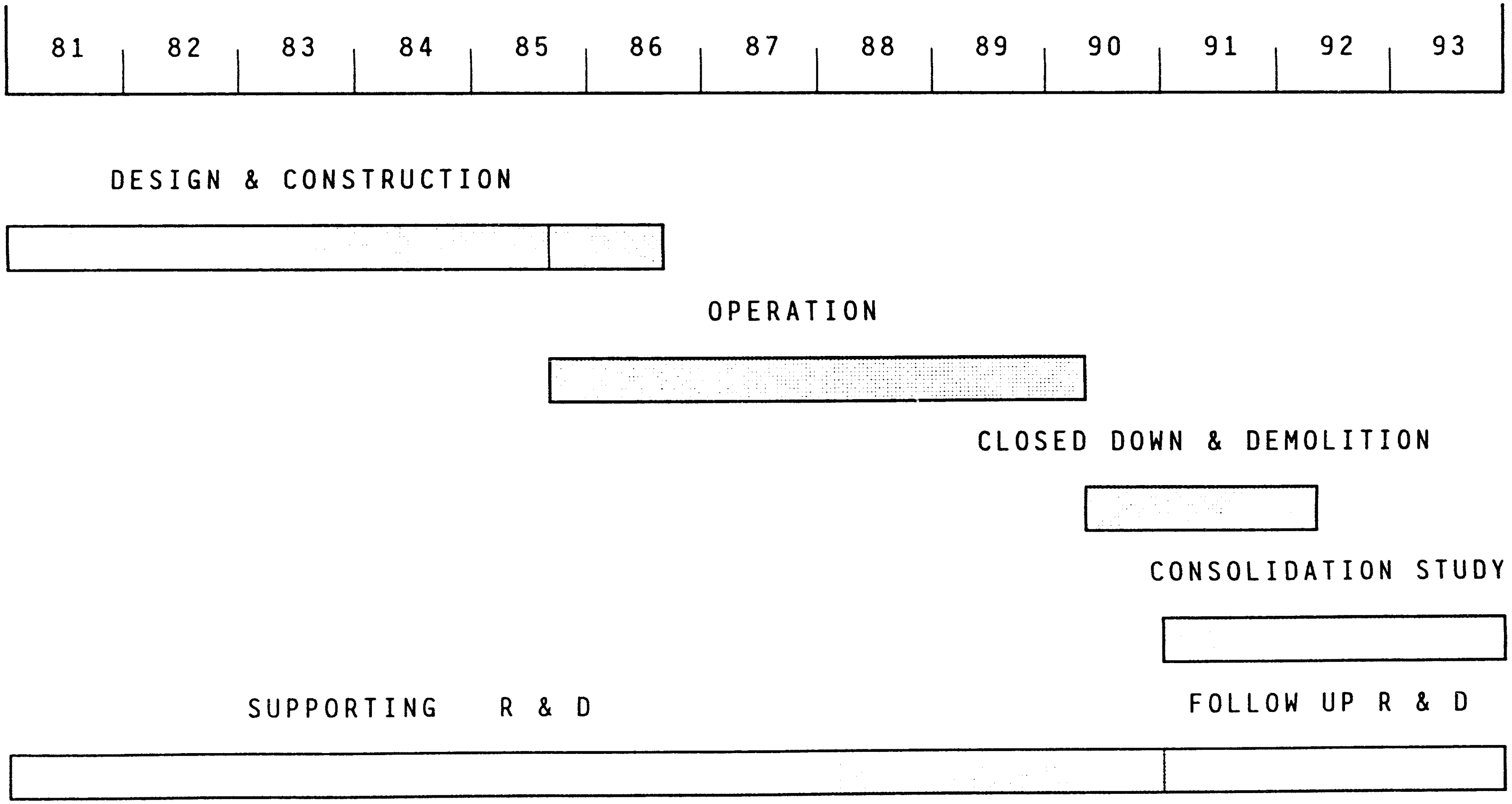
CONCEPTUAL DESIGN & ECONOMIC EVALUATION OF BCL PROCESS

S. KATSUSHIMA
New Energy and Industrial Technology
Development Organization
(NEDO)

< BCL PROCESS >


Brown Coal
Catalyst
H₂
Naphtha
Slurry Dewatering
Primary Hydro-genation
Solvent
CLB
Solvent Deashing
DAO
H₂
Naphtha
Middle Oil
Secondary Hydro-genation
Solvent/CLB
Residue
HDAO

PROJECT SCHEDULE OF BCL P.P.

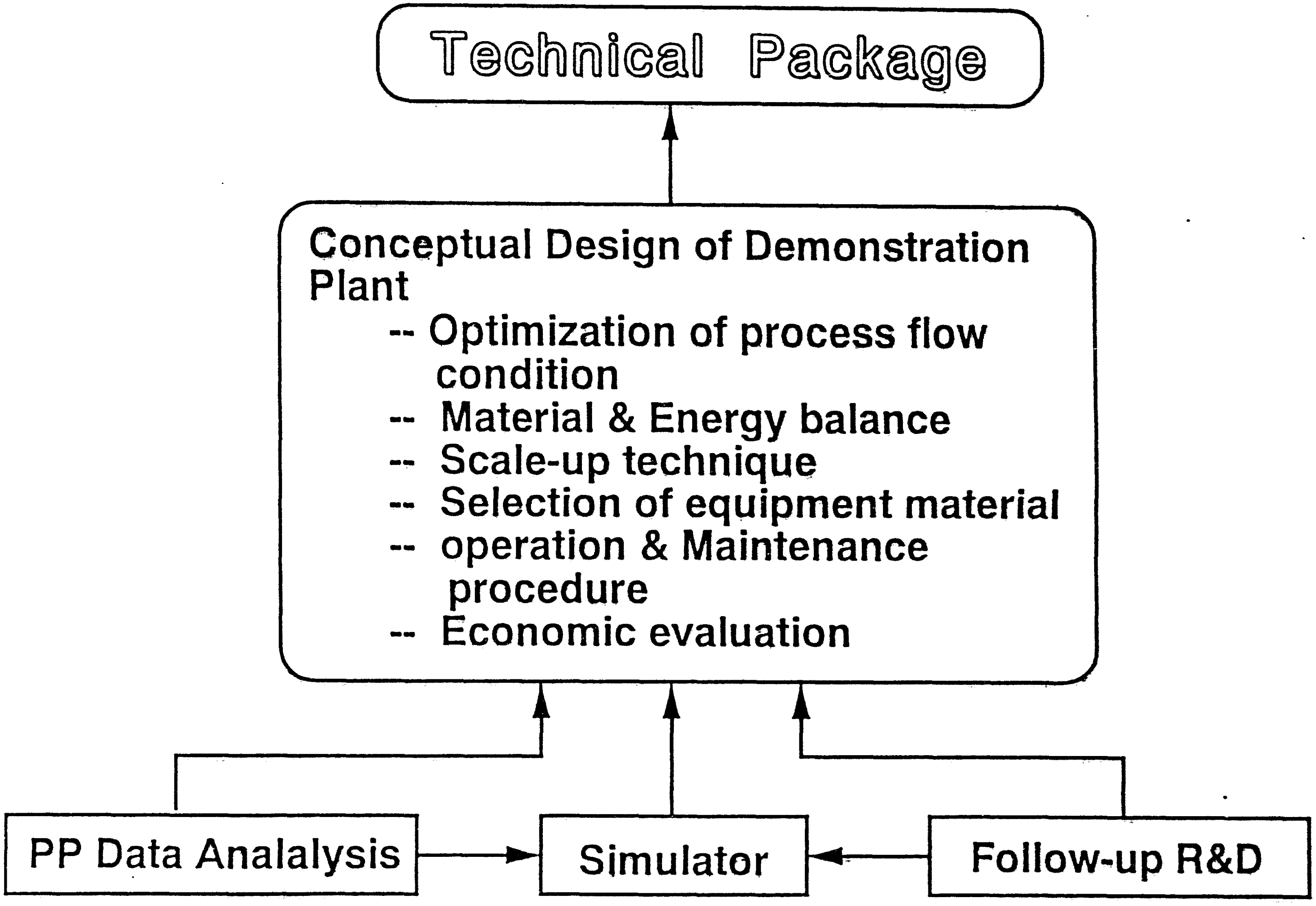


TYPICAL REACTION YIELD IN 50 T/D-BCL P.P.

(WT % Based on MAF-Coal)

	Primary Hydrogenation	Secondary Hydrogenation	Overall
H_2	- 4.6	- 1.0	- 5.6
H_2S, NH_3	1.1	Nil	1.1
CO , CO_2	13.9	Nil	13.9
Hydrocarbon Gas	10.1	0.5	10.6
H_2O	13.5	1.5	15.0
Oil (Total)	48.1	3.0	51.1
Light Oil	(16.4)	(4.0)	
Middle Oil	(16.8)		
Heavy Oil	(14.9)	(-1.0)	
CLB	17.9	- 4.0	13.9
Total	100.0	0.0	100.0

Consolidation Study for BCL Project



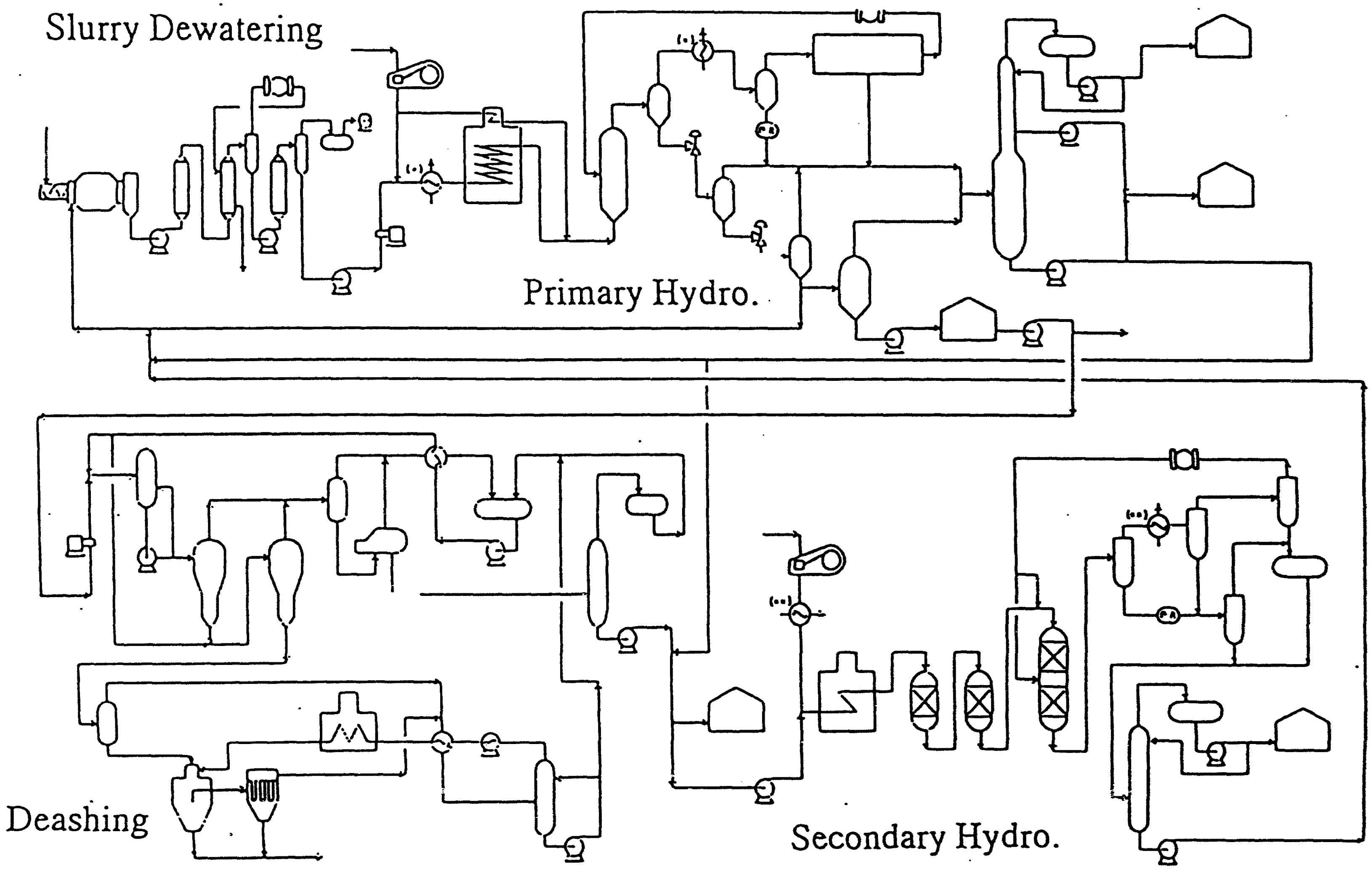
Technical Package

Conceptual Design of Demonstration Plant
- Optimization of process flow condition
- Material & Energy balance
- Scale-up technique
- Selection of equipment material
- operation & Maintenance procedure
- Economic evaluation

PP Data Analalysis

Simulator

Follow-up R&D



Process Flow of Demonstration Plant

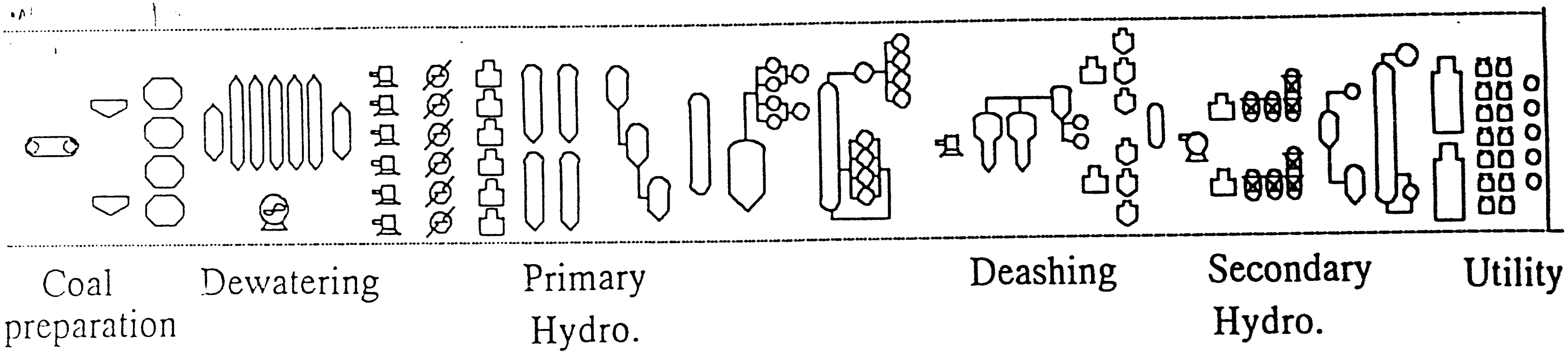


Image of 6,000 t/d Demonstration Plant

OUTLINE OF COMMERCIAL PLANT

• PROCESS	2-Stages BCL Process
• PLANT CAPACITY	30,000 t/d (maf-coal basis); 6000 × 5 Trains
• PLANT LOCATION	Latrove Valley, Victoria, Australia
• PLANT AREA	5.0×10^6 m^2
• PERSONEL	1,535 (in the Liquefaction Plant)
• UP-GRADING OF PRODUCTS	Hydrogenation mixed with petroleum fractions
• LIQUEFACTION PERFORMANCE	Case-0 Case-1 Case-2
(Oil Yield : wt% on mafc)	51.1 56.0 60.0
• HYDROGEN PRODUCTION	N.G. Reforming / Coal Gasification
• POWER GENERATION	By Conventional Coal Fired & W.H. Boiler (75 % of total power is generated)
• WASTE WATER TREATMENT	Biochemical Treatment after NH_3 & Phenols Recovered

LIQUEFACTION PERFORMANCE DATA

	CASE-0	CASE-1	CASE-2
BASE OF TECHNOLOGY	Demonstrated in P.P. Operation	Optimized through Consolidation Study	Expected to be improved by 2000
REACTION YIELD	(wt % on mafc)		
CO & CO_2	12.7	12.7	12.7
H_2O	17.0	17.0	17.0
$C_1 \sim C_4$ Gas	10.9	11.4	11.9
Oil ($C_5 \sim 420$)	51.1	56.0	60.0
Residue(420^+)	13.9	8.7	5.0
H_2 consumption	5.7	6.1	6.6

BASE LINE OF ECONOMIC EVALUATION

• FINANCIAL EVALUATION	By DCF Method	
• CONSTRUCTION PERIOD	5	Years
• PLANT LIFE	25	Years
• CONSTANT DOLLAR YEAR	1991	
• MAINTENANCE COST	3	% of Construction Cost
• OPERATION DAYS	310	Days (85% on stream)
• PRICE OF FUELS & U.T.		
Crude Oil	20	US$/bbl
Brown Coal	9.0	US$/t
Electric Power	0.04	US$/kWh
Natural Gas	0.094	US$/Nm$_{3}$
Industrial Water	0.08	US$/t
(By-Product) Sulfur	259	US$/t
Phenol	778	US$/t

CONSTRUCTION COST (FOR CASE-0)

- PLANT CAPACITY 30,000 t/d (6,000t/d × 5 Trains)
- TOTAL CONSTRUCTION COST 4.76 Billion US $

SECTION	% of TOTAL COST
COAL & CATALYST PREPARATION	6.3
SLURRY DEWATERING	9.9
PRIMARY HYDROGENATION	23.4
DEASHING	5.6
SECONDARY HYDROGENATION	7.5
HYDROGEN PRODUCTION (NG Case)	7.5
GAS PURIFICATION	4.0
BOILER & POWER GENERATION	8.8
WASTE WATER TREATMENT	5.2
OTHERS	21.8
TOTAL	100.0

<FINANCIAL PARAMETERS>

• EQUITY	25 %	of Required Capital	
• RETURN ON EQUITY	15 %	(= discounted rate)	
• INTEREST ON DEBT	10.0 %	for long term	
	8.5 %	for short term	
• INCOME TAX RATE	39.0 %		
• GENERAL INFLATION	3.5 %		
• ESCALATION		(*)	(+3.5 %)
CRUDE OIL		2.50 %	(6.0 %)
BROWN COAL		0.50 %	(4.0 %)
NATURAL GAS		2.50 %	(6.0 %)
ELECTRIC POWER		0.74 %	(4.24%)
CONSTRUCTION		1.06 %	(4.56%)
LABOR		2.50 %	(6.0 %)

(*) Escalation is defined as inflation above General Inflation.

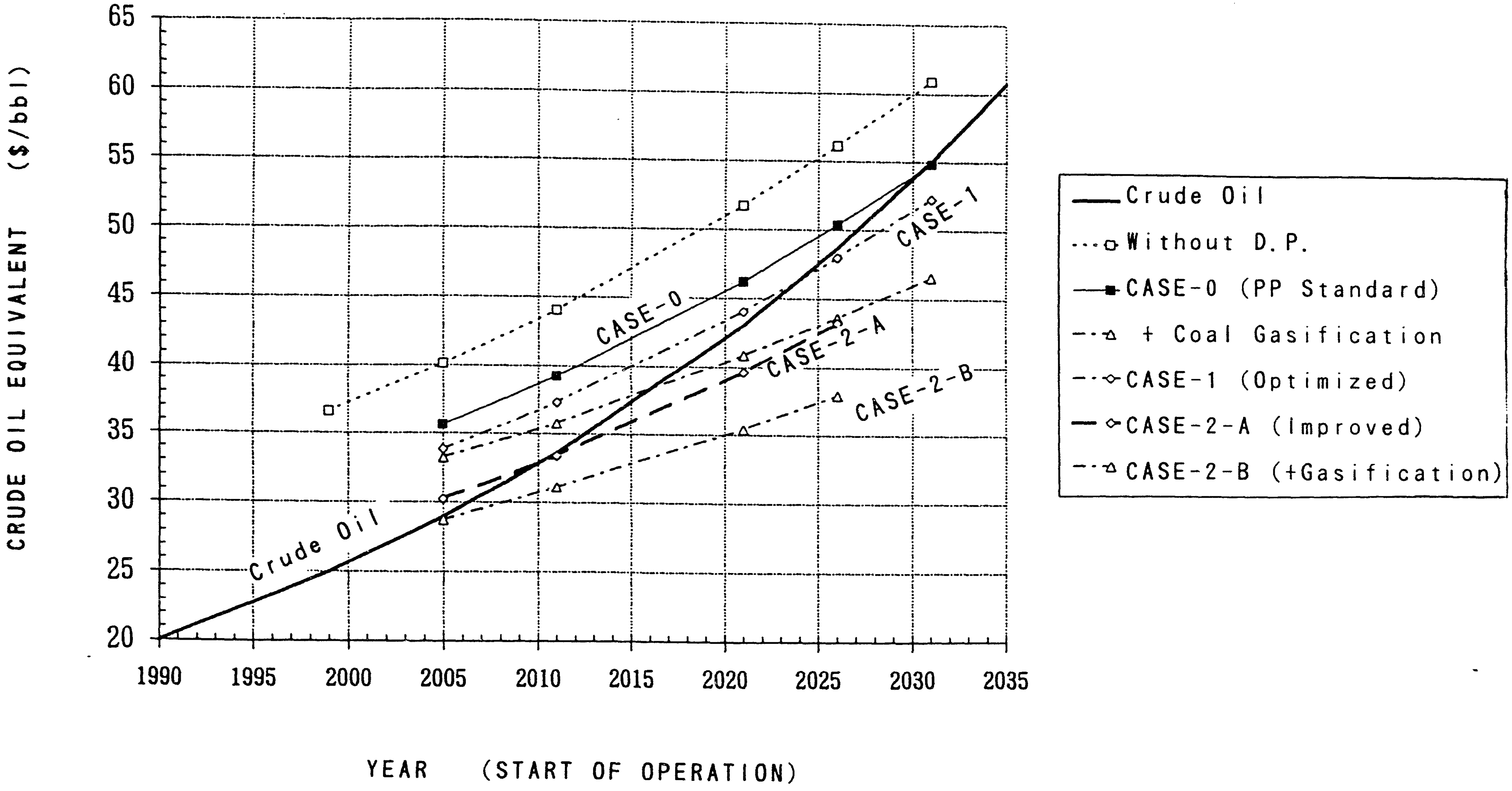
REQUIRED SELLING PRICE OF OIL

(Operation will start in 2011)

	CASE-0	CASE-1	CASE-2	
			(A)	(B)
• OIL YIELD (wt% on mafc)	51.1	56.0	60.0	60.0
• H_2 GENERATION	NG	NG	NG	Coal
• CRUDE LIQUEFIED OIL ($/bbl)	47.0	44.6	39.5	36.5
• UP GRADED OIL ($/bbl)	51.0	48.5	43.4	40.4
• CRUDE OIL EQUIVALENT ($/bbl)	39.2	37.3	33.4	31.1
• COMPONENT OF PRICE (% of Total)				
OPERATING COST	51.28	49.41	52.19	29.08
(COAL) -including for fuel-	(7.47)	(7.34)	(8.20)	(16.10)
(NATURAL GAS)	(33.31)	(32.47)	(36.56)	(—)
(OTHERS)	(10.50)	(9.60)	(7.43)	(12.98)
FIXED COST	36.63	34.04	34.29	52.90
CREDIT OF BY-PRODUCT	- 6.57	- 5.99	- 3.99	- 7.58
OTHERS (*)	18.65	22.54	17.51	25.60

OTHERS (*) : Interest on debt and general managing cost

REQUIRED SELLING PRICE OF BCL LIQUID
(CRUDE OIL EQUIVALENT $ /bbl)



Presented at the DOE Liquefaction Contractor's Review Conference
27-29 September 1993 - Pittsburgh

LIQUEFACTION STUDIES ON VICTORIAN BROWN COAL

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ABSTRACT

Victorian brown coals have been the subject of many liquefaction investigations dating back to the 1930's, the most significant being the NEDO Brown Coal Liquefaction (BCL) 50 t/day (dry coal) pilot plant in the Latrobe Valley. Victorian brown coal has many attractive characteristics which have encouraged these studies, including the large reserves, high quality and reactivity, although the high moisture content is a significant disincentive.

This paper will briefly review the major projects on liquefaction of Victorian brown coal. Particular reference will be made to the NEDO/BCL project and the supporting studies conducted locally.

The potential to get high yields of liquid products from Victorian brown coal has been established. Further refinement of the NEDO/BCL technology is proceeding in Japan, along with feasibility studies, awaiting the economic incentive to proceed with a commercial demonstration plant. The Victorian Government continues to encourage the further development of the BCL project.

1. INTRODUCTION

Extensive deposits of brown coal (ASTM Lignite B) occur in the Gippsland Basin, Victoria, Australia. The most attractive of these for commercial utilisation are in the Latrobe Valley about 160 km East of Melbourne. The total quantities of economically winnable coal in this region are large enough to ensure Victoria's future electricity needs and to provide feedstocks for other applications such as liquefaction. This has led to many investigations over the years into the production of oil from Victorian brown coal.

This paper reviews the Victorian brown resource and the major liquefaction studies undertaken on it. Particular attention will be paid to the Japanese Brown Coal Liquefaction project, its current status and local studies in support of this project.

The attractions of Victorian brown coal which have encouraged these studies include:

- the vast reserves of Victorian brown coal and the favourable conditions for low cost mining,
- the high quality of the coal (low ash, sulphur and nitrogen contents),
- the high reactivity of the coal giving high yields of product in hydrogenation to liquid fuels,
- the extensive data base available on the resource and its characteristics, and
- the availability of a skilled workforce and extensive infrastructure in the Latrobe Region to support a major resource development project.

The advantages have been partially offset by:

- the high moisture content of the brown coal and the cost of drying, and
- the priority previously given to electricity generation in the allocation of the brown coal resource.

The pilot plant and feasibility studies reviewed in this paper cover investigations in UK, Germany, USA, Japan and South Africa. After an initial flurry of activity in the 1930's, the late 1970's witnessed a major surge in international interest in the liquefaction of Victorian brown coal, primarily as a reaction to the OPEC induced oil crises of the 1970's, coupled with the strong data base available on the quantity and quality of Victorian brown coal.

At the peak of this interest in 1982, four commercial scale brown coal liquefaction projects were being actively promoted, and several other proposals were under investigation. This led to concerns in some quarters that the Latrobe Valley would not be able to cope with the perceived development boom. However, the subsequent halving of world oil process has significantly delayed the economic viability of oil from coal and led to the indefinite deferral of most of these projects.

The Coal Corporation of Victoria (CCV) and its predecessor the Victorian Brown Coal Council (VBCC) were given as a prime responsibility, the promotion, liaison, coordination and participation in the development of alternative uses of Victorian brown coal with particular emphasis on liquefaction. The involvement in liquefaction projects has ranged from provision of coal samples, resource data and technical information to conduct of supporting R&D and participation of staff in pilot plant operations.

2. THE VICTORIAN BROWN COAL RESOURCE

2.1 Quantity and Availability

Table 1 summarises the resource and production situation with respect to Victorian brown coal. The total estimated Victorian brown coal resource in situ, is 202,000 million tonnes (Mt). Of this resource 168,000 Mt is located on shore in the Gippsland Basin, primarily the Latrobe Valley. Under Victorian law these brown coal resources are owned by the State.

TABLE 1 - VICTORIAN BROWN COAL RESERVES AND PRODUCTION

Total Geological Resource	202,000 Mt
Gippsland Basin Geological Resource	168,000 Mt
Projected Coal Reserves (after exclusion of towns, parks, etc)	65,000 Mt
Readily Recoverable Reserves by open cut mining	33,000 Mt
Brown Coal Production 1991/92	49.5 Mt
Overburden to Coal Production Ratio	0.26 M^3/t
Cumulative Production since 1924	1,200 Mt
Life-time of Reserves at present rate of consumption	660 years

The State Government's coal protection criteria are less than 2:1 overburden to coal ratio, seams greater than 3 metres thick and ash content less than 10%. Of the 98,000 Mt meeting these criteria, 33,000 Mt have been excluded from development by the Government on environmental or social grounds (beneath towns, State Parks or other sensitive areas) leaving 65,000 Mt of Protected Coal Resource. It is further estimated that about half of this Protected Brown Coal Resource (ie 33,000 Mt) is "Readily Recoverable Reserves" using existing open cut technology. Since large scale exploitation commenced in 1924, a total of about 1,200 Mt have been mined from the Latrobe Valley open cuts, about 3% of the readily recoverable reserves.

In 1991/92 49.5 Mt of brown coal was mined in Victoria, with an average overburden to coal ratio of about 0.25 m^3/t. This compares very favourably with the overburden to coal ratio for the mining of similar quality brown coal in the Rhine area of Germany which averages 4 m^3/t. At the present rate of extraction, the readily recoverable Victorian brown coal reserves will last about 660 years.

The bulk of the brown coal mined in Victoria is used to produce 85% of the State's electricity, although in 1991/92 significant quantities (2.0 Mt) were used to produce 721,000 t of briquettes, and about 60,000 t of char and other value added products such as fertilisers. From 1956-69 briquettes were also used to produce town gas for Melbourne in a Lurgi pressure gasification plant, prior to the discovery of natural gas off-shore in the Gippsland Basin.

Over 40 prospective brown coal open cut sites have been identified in Victoria, mainly in the Latrobe Valley. To provide a greater degree of planning certainty, the State Government has identified three Latrobe Valley fields, Maryvale, Driffield and Flynn 1, for possible development over the next 30 years (Figure 1). Each of these Category A fields contains more than 1,000 Mt of recoverable coal, which could be dedicated to future power station, solid fuel or liquefaction projects. Category B and C fields have also been identified, but current Government policy would delay their development for at least 30 and 60 years respectively.

2.2 Quality

Table 2 summarises the quality data for each of the existing Latrobe Valley mines and the prospective Category A fields. A common feature of these fields is their high purity, with less than 3% ash and 0.4% sulphur. However, the high moisture and oxygen contents (60+% and 25% respectively) result in a low net wet specific energy which partially offsets the purity advantage. In particular, the high moisture content necessitates upgrading the coal to higher value products before export could be considered economic.

TABLE 2 - PRESENT AND PROSPECTIVE OPEN CUTS - QUANTITY AND QUALITY

	Existing Open Cuts				Prospective (Category A) Open Cuts		
	Yallourn	Morwell	Loy Yang	Yall Nth Ext	Maryvale	Driffield	Flynn 1
Reserves Mt	430	435	1071	40	1626	1444	1151
Overburden to coal ratio m^3/t	0.25	0.27	0.29	0.91	0.50	0.45	0.33
Mining cost per tonne relative to Loy Yang	-	-	1.0	-	1.4	1.3	1.4
Moisture %	66.6	60.9	62.7	52.9	64.0	61.0	62.9
Ash %db	1.8	3.2	1.4	4.6	3.0	2.3	2.4
Volatiles %db	51.7	49.8	51.4	48.9	51.9	51.1	50.9
C %db	65.9	67.1	68.4	65.8	64.7	67.4	66.3
H %db	4.6	4.8	4.9	4.7	4.6	4.8	4.7
O (by diff) %db	27.0	24.0	24.4	23.8	26.9	24.7	25.7
S %db	0.24	0.36	0.38	0.64	0.29	0.30	0.32
N %db	0.50	0.52	0.50	0.58	0.50	0.50	0.49
Specific Energy MJ/kg							
- Net Wet	6.5	8.5	8.0	10.2	7.1	8.3	7.5
- Gross Dry	25.8	27.3	26.6	26.7	25.8	26.8	26.0

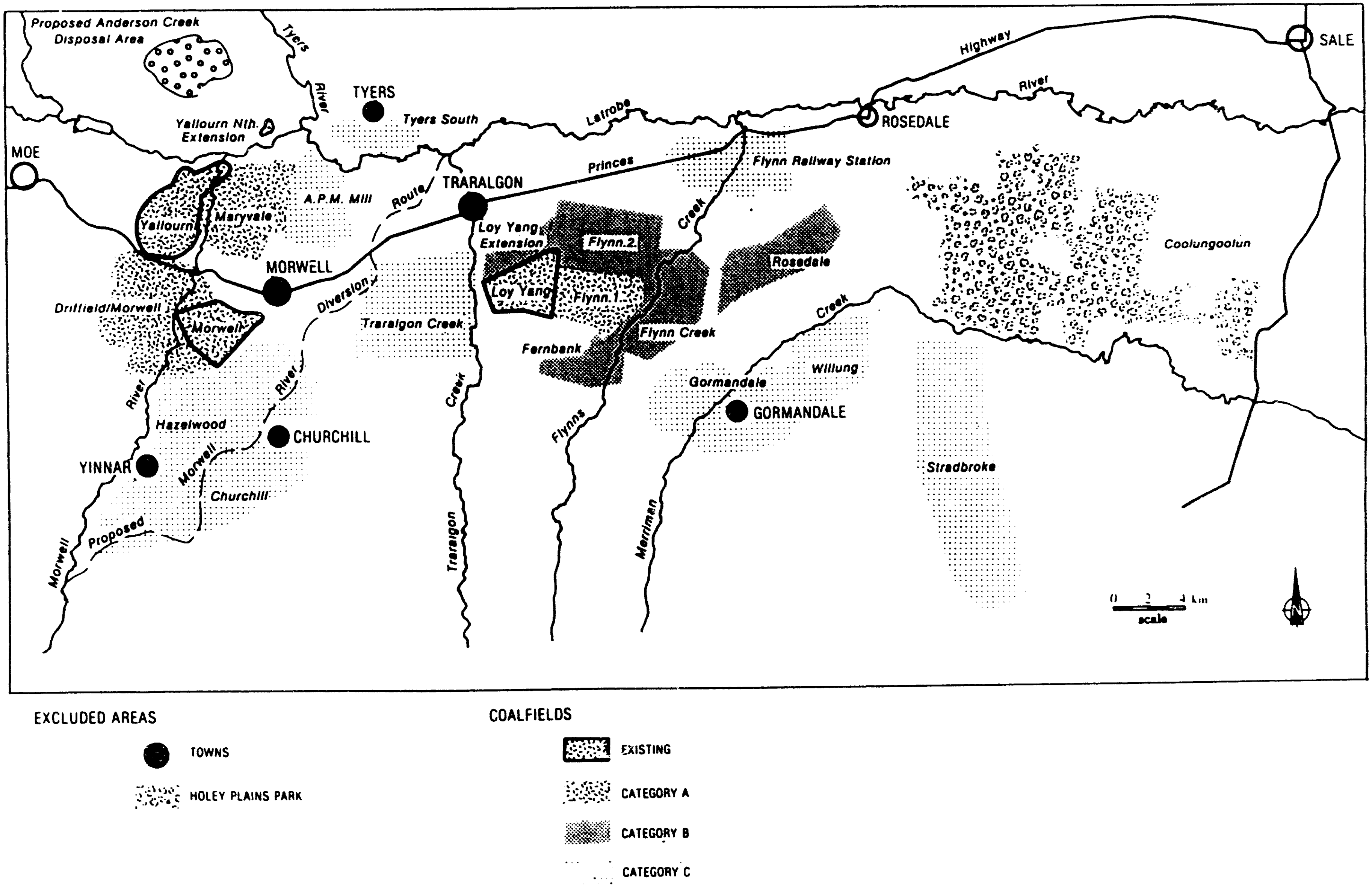

Figure 1 - Latrobe Valley Coal Fields Sequential Development Strategy

Considerable property variation occurs within and between individual coal fields. A large bore survey data base has been accumulated over several decades which enables the distribution of specific coal properties and chemical elements to be quantified. In the existing and prospective open cut areas the drilling pattern for this data base is on a 400m grid basis (or less), with samples analysed on 3 to 6m composite depths in each bore. This data base demonstrates that Latrobe Valley brown coals qualify as "clean coals" without further demineralisation.

In the late 1970's, because of the renewed interest in coal liquefaction this program of coal evaluation was extended to include a wide range of additional parameters including ones of relevance to liquefaction (Higgins et al., 1980; Perry, Allardice and Kiss, 1982).

Samples (279) selected from 3 open cuts and 26 bore cores representing 10 Victorian coal fields were analysed for a variety of chemical, physical and petrographic characteristics and utilisation parameters. These parameters included hydrogenation reactivity measures based on small tube reactor extraction tests in tetralin and batch autoclave hydrogenation with and without catalysts.

This work on coal characteristics and hydrogenation reactivity enabled comparisons to be drawn between fields as well as correlations to be established between coal properties and hydrogenation reactivity. The data is still of considerable relevance in the selection of coal fields for possible commercial liquefaction developments.

3. LABORATORY STUDIES

A wide range of laboratory investigations have been conducted on the hydrogenation of Victorian brown coals encompassing tube reactor, batch autoclave and continuous bench scale systems. These studies have been recently reviewed (Jackson and Larkins, 1991) in "The Science of Victorian Brown Coal" edited by Dr R A Durie, and will only be briefly summarised here.

Batch autoclave studies have been conducted on a range of Victorian brown coals using solvents such as tetralin, anthracene oil and hydrogenated anthracene oil; gaseous media such as hydrogen, CO/H_2 and CO/H_2O; and catalysts such as sulphided iron, molybdenum, tin and cobalt. A common feature of these studies has been the high conversions (low solid residues) obtained relative to other coals tested under comparable conditions. The coals also showed a high reactivity to CO/H_2 and CO/H_2O reductants, as illustrated in Figure 2 from the work of Candeloro et al (1985).

Continuous bench scale studies were less encouraging until BHP demonstrated the importance of retaining the hydrogen donor quality of the recycle solvent. This comprehensive work on a range of Australian coals has been reported by Smith and Cookson (1989). One frequently observed effect in continuous systems is reactor blockages caused by carbonate deposits. VBCC studies demonstrated that the carbonate deposit formation was proportional to the exchangeable calcium content of the feed coal (Perry, Gray and McKay, 1985), as shown in Figure 3.

While these laboratory studies have essentially been terminated, they provided a sound technical base which supported and encouraged the larger pilot scale developments reported below.

4. PILOT PLANT AND FEASIBILITY STUDIES

4.1 The Baragwanath Studies

The earliest reported studies on the hydrogenation of Victorian brown coals were those of Baragwanath (Sinnatt and Baragwanath, 1938, Allardice, 1973). These studies were conducted from 1934 to 1938 on Yallourn, Yallourn North and Gelliondale coal by Mr G E Baragwanath of the SECV using the coal liquefaction facilities of the Fuel Research Station UK.

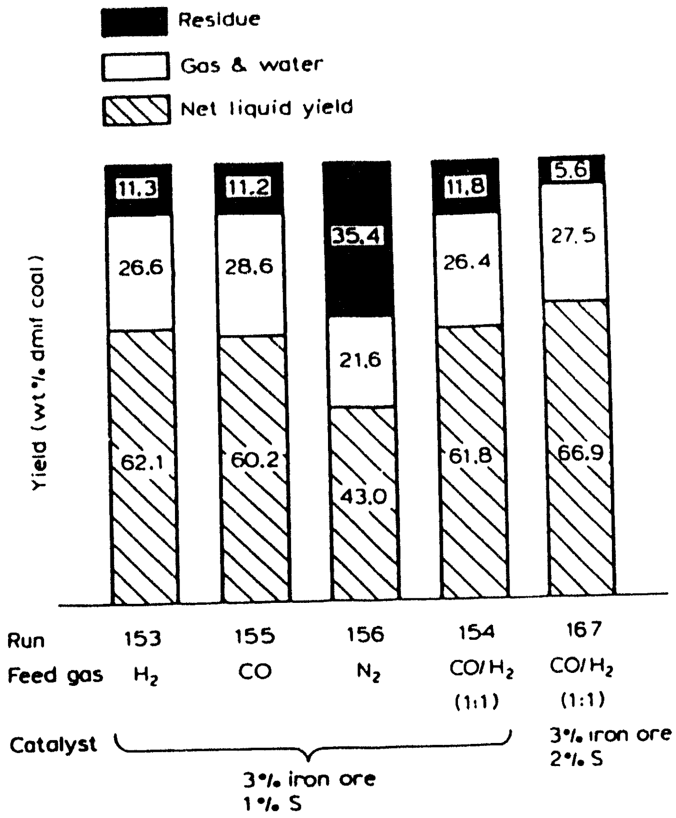

Figure 2. Effect of Feed Gas on Conversion and Oil Yields for Morwell Coal (24 MPa, 400°C, 1 hr, in Hydrogenated Anthracene Oil).

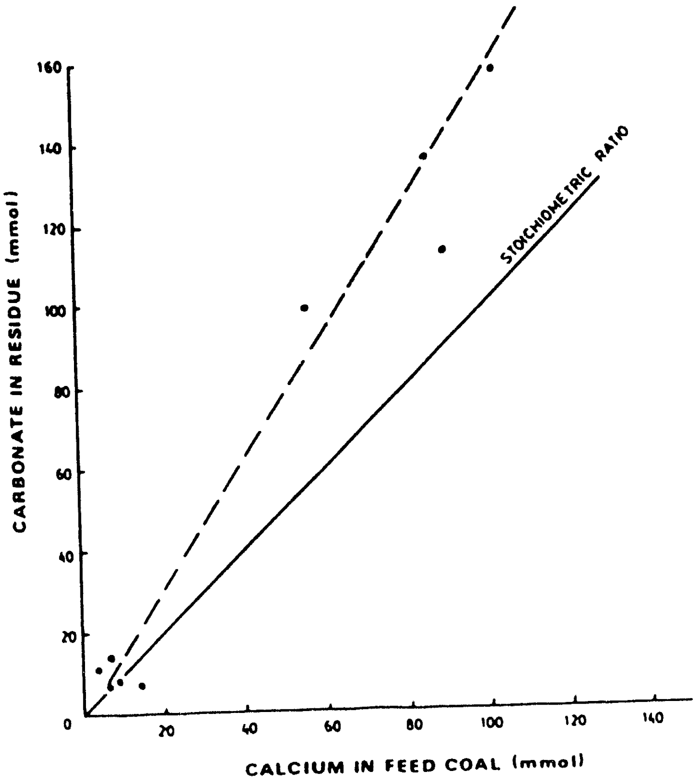

Figure 3. Correlation Between Carbonate Formation and Calcium in Coal. r=0.98

The project was initiated by the Commonwealth (of Australia) Hydrogenation Committee as a result of interest shown by ICI in establishing a commercial liquefaction plant in Australia. At that time ICI were actively involved in coal liquefaction development at Billingham in the UK, in conjunction with I G Farbenindustrie, Standard Oil (USA) and Royal Dutch Shell. ICI also held the rights to the Gelliondale brown coal deposit (Victoria) at that time and had tested samples at Billingham.

Baragwanath studied the Bergius two stage hydrogenation of Victorian brown coals in 2 litre autoclaves and continuous pilot plants for primary and secondary (vapour phase) hydrogenation, including a 2kg/hr continuous primary hydrogenation pilot plant built specifically for Victorian brown coal. This operated smoothly for up to 34 days in continuous operation. The study included detailed chemical characterisation of the various product fractions from each stage of the process.

Baragwanath found that:

- Victorian brown coals could be satisfactorily hydrogenated using the techniques developed for black coals. In fact brown coals were more readily and completely converted to a crude oil product,
- brown coal from Gelliondale was more readily hydrogenated than Yallourn,
- the yield of commercial quality motor spirit was 50% of daf coal from 2 stage hydrogenation at 420-460°C and 20 MPa (First Stage) and 300-510°C and 20 MPa (Second Stage). Heavy oil from the first stage was recycled,
- engine tests in the laboratory and on the road demonstrated that the petrol was comparable to the current commercial spirit and the diesel oil was of top quality. However, no fractions suitable for lubricants were obtained, and
- the brown coals could by hydrogenated equally well using water gas in place of hydrogen.

Although the studies were technically encouraging, the Commonwealth Hydrogenation Committee concluded in 1937 that an oil from coal plant would require heavy government subsidies to be economically viable, but that Australia should maintain awareness of developments in the oil from coal field. Essentially the same technology was applied to German brown coal to supply the bulk of the aviation fuel for Germany in World War II.

4.2 The Imhausen Study

Following the 1970's oil crises, one of the most definitive of the studies undertaken was the Joint Australia/Federal Republic of Germany Coal to Oil Feasibility Study (Imhausen, 1981) under the auspices of the FRG Ministry of Research and Technology, the Australian Federal Government and the State Governments of New South Wales, Queensland and Victoria. It involved a consortium of seven German companies: Imhausen-Chemie GmbH, Rheinisch Braunkohlenwerke AG (RBW), Lurgi Kohle und Mineraloeltechnik GmbH, Ruhrchemie AG, Ruhrkohle AG, Salzgitter Industriebau GmbH and Uhde GmbH. The study elements included conceptual design, plant and infrastructure costing and pilot plant testing on three selected Australian coals to assess the technical and economic feasibility of a commercial project. Morwell brown coal was tested by RBW in a 10 kg/h pilot plant (Figure 4) near Cologne (with Victorian participation) using an improved variant of the earlier German hydrogenation technology, at temperatures of 420-460°C and pressures up to 30 MPa (Lenz et al, 1982).

The principal finding of the Imhausen study was that specification-quality gasoline and automotive diesel could be produced from brown coal hydrogenation alone, whereas the bituminous coals tested required more expensive Fischer-tropsch synthesis to yield adequate quality diesel. The thoroughness of this study also brought to light the significance of many factors such as coal drying efficiency and maximum unit size, the hydrogen production route and compression costs, electricity cogeneration efficiency and steam

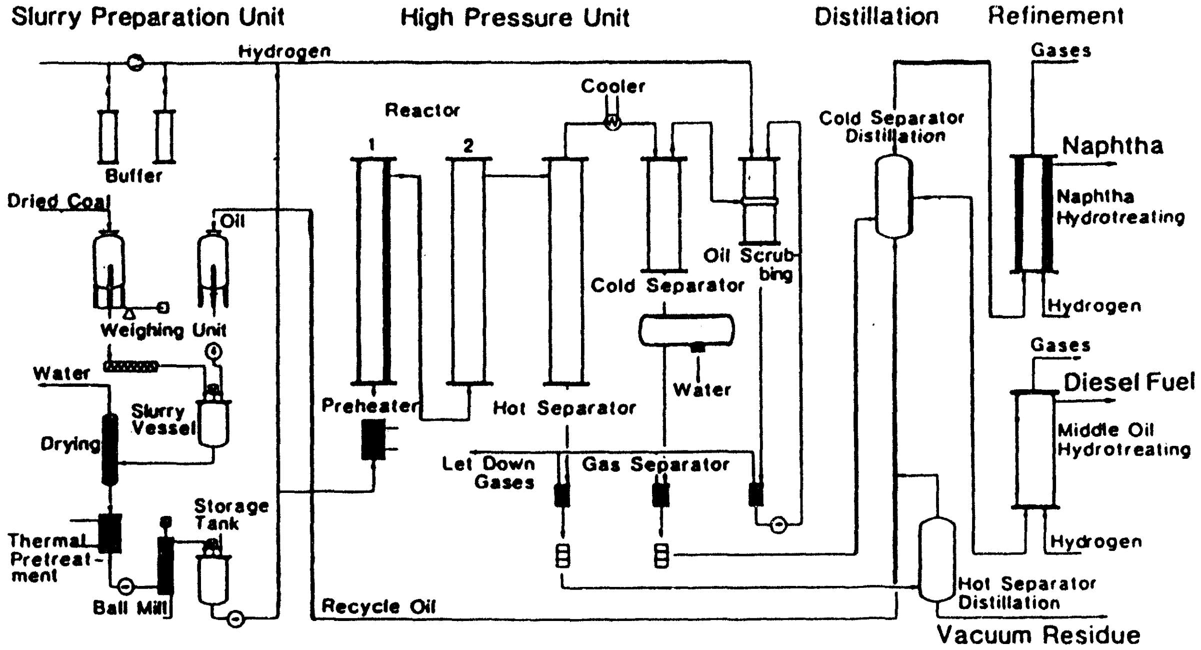

Figure 4. Rheinbraun Brown Coal Liquefaction Test Plant Flow Sheet.

utilisation optimisation, and off-gas treatment and product refining routes. Importantly, many of these findings emerged from overall plant optimisation rather than from process chemistry considerations. The economic analysis of the Victorian plant was, naturally, subject to many assumptions. However, based on the most probable pricing, taxation, financing and escalation assumptions at the time, the nominal return on investment obtained was 29% (Camier and Stevens, 1983).

One immediate consequence of the Joint Australia/FRG Study was a proposal by RBW for a 30Mt/yr (raw coal) commercial plant. A Heads of Agreement with the Victorian Government was signed in 1980, and detailed negotiations with an Australian partner, CSR Ltd, were held in 1981-82. With the subsequent fall in world oil prices the project was deferred indefinitely.

4.3 The NBCL Project

In a separate development, the Nippon Brown Coal Liquefaction Co Ltd (NBCL) consortium project has proceeded under agreement between the Japanese, Australian (Federal) and Victorian (State) Governments. This project evolved from the KOMINIC consortium proposal in the early 1970's to produce and solvent refined coal additive to promote coking in coal blends. A second hydrogenation stage was added to convert the first stage product (Coal Liquid Bottoms or CLB) to oil, and in 1980 the project was adopted as a National Project under the Japanese Sunshine Program with funding via NEDO (Nakako, Matsumura and Takematsu, 1987).

The relationship between the participating governments, their agencies and the consortium of Japanese companies entrusted to undertake the development is indicated in Figure 5. Funding for the project was provided by the Japanese Government through NEDO. The Victorian Government through the CCV has provided a package of support for the 50 t/d pilot plant development in the Latrobe Valley. This package included:

- the provision of a serviced site.
- the supply of coal to the pilot plant.
- the secondment of professional staff to the pilot plant workforce.
- technical support through the Coal Corporation of Victoria and funding of some related research projects.
- rebate of some State Government charges for services and liaison assistance with local organisations.

The Australian Government has provided:

- international liaison on the project.
- exemption from import tariffs and expedition of import and export procedures for materials and equipment from Japan.
- expediting visas for Japanese staff.
- investment approval for the pilot plant.
- funding of some parallel Australian R&D projects.

It is estimated that the value of the Australian and Victorian Government support package for the project was equivalent to about 1% of the Japanese Government expenditure on the project.

During its construction and operation, the pilot plant generated substantial economic activity in its own right. The plant was a major employer in the Latrobe Valley with 70 Japanese and 230 Australian staff and a construction and maintenance contract workforce which at times exceeded 400. The plant provided a major boost to local businesses supplying equipment and services. The project also facilitated the development of a Japanese "school within a school" in one of the Morwell government schools, which has grown to an ongoing interest in Japanese language and culture in the Latrobe Valley, with many local schools maintaining Japanese programs.

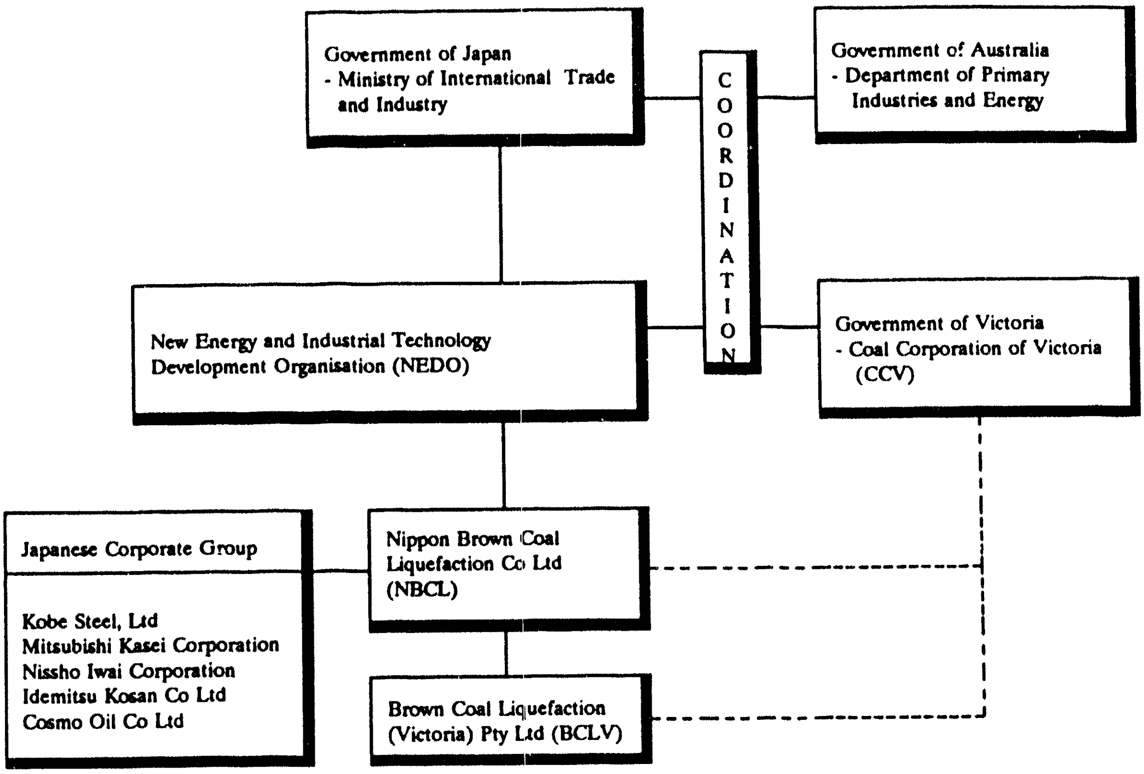

Figure 5. **Organisatonal Flow Sheet for the Brown Coal Liquefaction Project**

Technically, early investigations were conducted by KOMINIC in the mid 1970's under contract in small pilot plants in the USA (Lummus) and South Africa (Sasol). These were followed by the design and construction of a 0.5 t/d PDU (Process Development Unit) in Kobe. The successful operation of the 50 t/d (dry coal) pilot plant at Morwell (Figure 6) was based on the two stage technology developed in the PDU, using lower temperatures and pressures (15-20 MPa) than in the previous studies.

The pilot plant ceased operation in October 1990, having achieved its major objectives of high oil yields (greater than 50% dry coal basis), prolonged stable operation (1700 hours continuous), efficient deashing (less than 1000 ppm), long life second stage catalyst (one year) and demonstration of a new efficient drying process (Nasu, 1990). The pilot plant operated on both Morwell and Yallourn coals. Morwell caused substantially greater plant blockage problems, consistent with the laboratory studies on calcium carbonate formation reported earlier.

On completion of the pilot plant program the plant was partly demolished and the remainder returned to the Coal Corporation of Victoria. It has become the Principal Office of the CCV and the location of its Research and Development activities. Before handing the site back to CCV, NEDO and NBCL ensured that it was cleaned up and received a Certificate of Environmental Audit, indicating that it had achieved a standard suitable for residential use.

The project is now proceeding with a "Consolidation" study for scale up to a 30 Mt (ROM coal) commercial plant. The 0.5 t/d PDU has been redesigned and rebuilt at a new NBCL Brown Coal Liquefaction Research Centre at Takasago south west of Kobe.

Clearly this is the most advanced coal liquefaction project in Australia, and the most advanced brown coal liquefaction project in the world. The Consolidation study will enable the project to maintain its momentum and ensure its readiness for commercial development when appropriate economic conditions occur. In the interim continued refinement of the technology is expected to further improve the economics of the project.

4.4 Mitsui SRC Development Project

A third major development was proposed by the Mitsui SRC Development Co Ltd in 1976. This involved operation of a 5 t/d (dry) pilot plant at Ohmuta, Japan, on Yallourn briquettes and subsequently 3,000 t of Morwell raw coal. In 1981 a partnership Heads of Agreement was signed with CSR Ltd and a detailed Feasibility Study undertaken on an 8.3 Mt/yr (raw coal) plant to produce SRC and distillate fuels. Further development by Mitsui/CSR was officially put on hold in 1982, but with Mitsui SRC Development's subsequent involvement in the Japanese NEDOL bituminous coal liquefaction pilot plant project, reactivation of their brown coal project would appear unlikely.

4.5 International Oil Project

The fourth major development was proposed in 1980 by International Oil Proprietary Ltd (a subsidiary of Moonie Oil Co Ltd) in partnership with ARCO Australia Ltd (a subsidiary of Atlantic Richfield Co of the USA). This followed early testing of a Victorian brown coal in a H-coal pilot plant (Johnson et al, 1971) and involved an extensive geological and mining study of the Gelliondale coalfield and evaluation of a 22 Mt/yr (raw coal) liquefaction plant based on the H-coal or Exxon Donor Solvent (EDS) processes. Further testing of Morwell coal at PDU scale was arranged through Dynalectron Corp and Esso Australia Ltd for the H-coal and EDS processes respectively.

The EDS process was also nominated as part of a proposal by APM Ltd in 1981 for a 26 Mt/yr development of the Rosedale (Latrobe Valley) coalfield. However the proposal only progressed as far as pilot plant testing of the "Drikol" coal drying process.

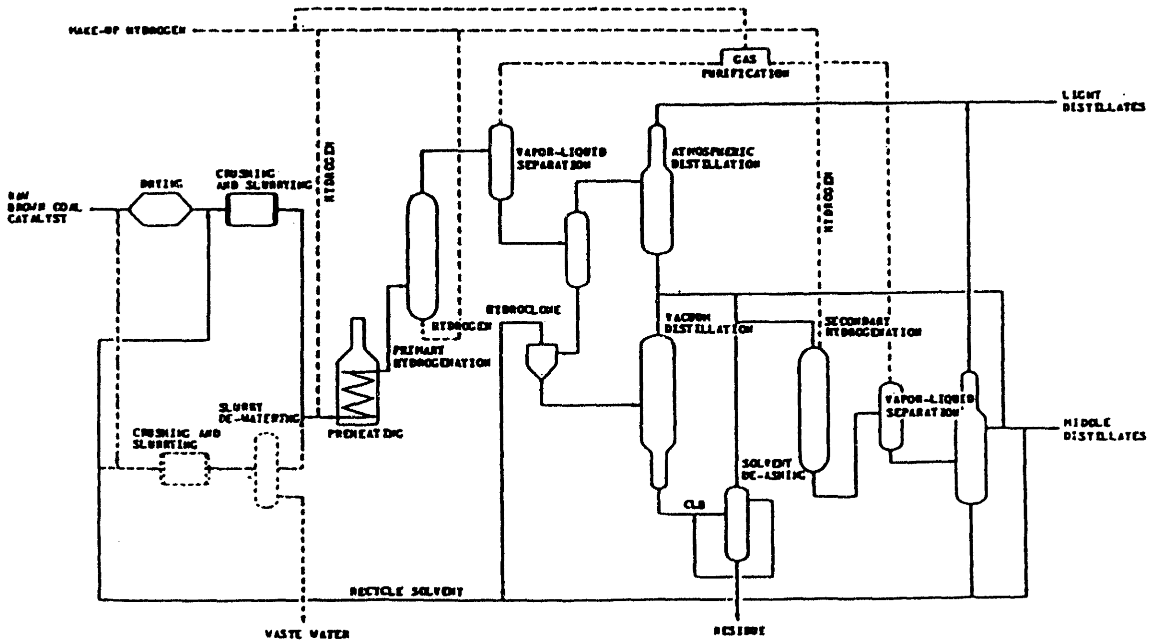

Figure 6. NEDO Brown Coal Liquefaction Process Flow Sheet - 50 t/d Pilot Plant.

4.6 BP Project

In 1981 a proposal was also put forward by BP (Australia and UK) for a 15-60 Mt/yr (raw coal) development based on either Saarberg (Germany) or CO-steam liquefaction technology. Comparative testing at the Saarbergwerke 6 t/d pilot plant indicated that Victorian brown coal had superior reactivity to Queensland bituminous coal. Subsequent experimental work concentrated on development of dewatering technology by BP Australia, and CO-steam technology by Monash University. BP were also involved in the UK National Coal Board Liquid Solvent Extraction process, in which Morwell coal was tested very successfully in 1980.

4.7 Other Pilot Scale Investigations

Such was the interest in Victorian brown coal that it also was tested in a number of other liquefaction processes as shown in Table 3.

TABLE 3 - MISCELLANEOUS PILOT PLANT STUDIES

Company	Process	Date	Coal
Dow Chemical (USA)	Hydrogenation with emulsified catalyst	1981-82	Morwell
International Coal Refining Co (USA)	SRC-1	1981	Morwell
Asahi Chemical Industries (Japan)	Flash pyrolysis	1981	Morwell
Mitsubishi Heavy Industries (Japan)	Two stage solvolysis	1981	Yallourn
Caltex (Australia)/ Chevron (USA)/ Nippon Oil (Japan)	Close coupled two stage hydrogenation	1983	Morwell
Pentanyl Technologies (USA)	CO-steam/alkali digestion	1982-83	Morwell

5. SUPPORT STUDIES RELATING TO THE NEDO/BCL PROJECT

5.1 BCL Atmospheric Monitoring - Monash University

The objective of this project which ran from 1983 to 1991 was to assess the impact of emissions from the BCL pilot plant at Morwell on the ambient atmospheric environment. Emphasis was placed on the analysis of hydrocarbons including non-methanic hydrocarbons and PNA's associated with particulate matter. Wind speed and direction, and temperature were also measured on a regular basis.

Episodes of gaseous hydrocarbon activity were found to be strongly related to wind direction but did not correlate with pilot plant operations. Evidence of non-methanic hydrocarbons was noted on most days that CLB disposal took place. Polynuclear aromatic hydrocarbons were extracted from particulate matter and monthly averages for benzo(a)pyrene, benzo(ghi) perylene and coronene have been calculated.

The general conclusions from this eight year project (Hooper, Body and Hooper, 1993) were that:

- air quality in the vicinity of the pilot plant was an order of magnitude better than air quality in Melbourne, and
- there is no evidence that air emissions from a state of the an brown coal liquefaction plant using appropriate environmental controls, would have detrimental environmental impacts.

5.2 Genotoxicity of BCLV Products and Process Materials - Latrobe University

Samples from the BCL pilot plant were tested for genotoxicity in a modified version of the Salmonella/mammalian microsome mutagenicity assay. Some samples including coal slurry, coal liquid bottoms, and process solvent were found to be mutagenic in the presence of mammalian enzymes. These materials are of course not products of the liquefaction process, but rather intermediate components which would normally be confined within the process.

The lighter final products, naphtha and light oil do not appear to constitute a greater hazard than conventional petroleum derived oils. The final report on this project is now available (MacPhee, 1992).

5.3 Refining of BCLV Liquids - Ampol

Product upgrading studies by Ampol Ltd Research and Development Department, Brisbane, were carried out with CCV support and NERDDP funding from 1987 to 1991. The project followed similar work on liquids derived rom local bench scale studies. Under an agreement with NEDO, samples of light oil, middle oil and recycle solvent were provided from BCL Run 5 ("shake-down") and Runs 6, 7 and 8. Testing was carried out in Ampol's trickle-bed continuous hydrotreater PDU.

The project objectives were to assess the range of refined product slate (gasoline/jet fuel/diesel etc) obtainable, and the hydrotreating/reforming process conditions and costs necessary to achieve this.

AMPOL (Palmer, Walker and Junk, 1992) concluded that wide range BCL syncrude containing the high boiling part of the process solvent was unresponsive to high severity hydrotreating. On the other hand lighter wide-range syncrude responded well, and the critical jet fuel smoke point specification was satisfied at 13 MPa hydrotreating pressure.

Excess quality was available in petroleum, jet and diesel fuels, and this could be exploited to reduce the cost of refining the coal synfuel. An interesting synergy between coal - and petroleum - derived diesel cetane quality was observed which also has potential for minimising refining costs. The observation that jet fuel quality is better for lighter jet fuels could also reduce refining costs. The coal-derived naphtha was very easily reformed to high octane gasoline blendstock which would be highly valued by petroleum refiners. The refined product slate was flexible and well matched to future product demands.

5.4 Reactor Hydrodynamics Studies - CSIRO

Reactor hydrodynamics studies were carried out at the NEDO/BCL pilot plant using a Neutron Attenuating Tracer (NAT) technique developed by CSIRO at North Ryde, and equipment developed originally for bore-hole logging by CSIRO at Port Melbourne. This NEDO-funded project followed from studies at BCLV by a CCV-seconded engineer into reactor hydrodynamics mathematical modelling using tracer techniques.

The NAT technique applied at BCLV measured tracer concentration-time curves detected through the wall of the reactor using a radioactive californium neutron source and back-scatter gamma ray detector. A pulse injection of neutron-opaque gadolinium was used as tracer, enabling measurements to be made without the addition of radioactive material into the process. The data obtained was applied to two mathematical models, "axially-dispersed plug flow" and "CSTR-in-series", to obtain relationships between reactor design parameters and reactant residence time distribution. The relationships obtained will greatly assist the scale-up design of the primary hydrogenation reactors.

5.5 Hydrothermal Dewatering as a Pretreatment for Brown Coal Liquefaction - CCV

The CCV has conducted a program of batch autoclave liquefaction on brown coal samples pretreated by hydrothermal dewatering (HTD) (Guy, Perry and Allardice, 1992). HTD, in addition to improving the thermal efficiency of the process through non-evaporative drying, has potential to reduce reactor blockages by prior removal of some of the troublesome cations in the expressed water. The prior decarboxylation also reduces the total liquefaction pressure by reduction in CO_2 generation during hydrogenation.

The study confirmed the HTD effects on coal properties, but unfortunately the batch autoclave liquefaction tests appeared to show that some loss of hydrogenation reactivity resulted from the HTD treatment. Work is continuing to confirm this point as well as PDU testing on larger scale HTD brown coal samples to compare the propensity to form reactor deposits.

5.6 Infrastructure Studies - CCV

As input to the BCL Consolidation Study the CCV has commissioned studies on infrastructure issues such as:

- identifying and costing heavy load transport routes to transport commercial liquefaction plant equipment from ship to the Latrobe Valley.
- estimating the cost of mining coal from a typical undeveloped Latrobe Valley coalfield at the scale required for a commercial liquefaction plant.

6. CONCLUSIONS

1. An extensive data base on brown coal properties and conversion testing has been compiled to assist in the selection of coals for future liquefaction processing.

2. Brown coal variability is considerable and must be understood in relation to a particular process or plant. Variations in coal properties can lead to unexpected plant operational difficulties eg reactor deposits. Demonstration testing at a realistic scale is therefore essential on any coal field proposed for commercial development.

3. CO-steam or CO/H_2 has potential for liquefaction of brown coals. Insufficient pilot plant testing has been conducted to date to establish the full potential of this technology.

4. Batch and continuous reactor testing has established that Victorian brown coals are particularly amenable feedstocks for most hydrogenation process routes. This has been confirmed in larger scale PDU and pilot plant studies.

5. The NEDO/BCL technology is the most advanced brown coal liquefaction technology currently available. The ongoing consolidation studies should ensure that it retains its position as the probable preferred candidate if an early commitment to a commercial coal liquefaction project was required.

6. The studies described have laid a firm foundation for the liquefaction of Victorian brown coal. Clearly, the fall in world oil prices has slowed technology development, and dramatically reduced the number of project proponents. Nevertheless the fact remains that world reserves of crude oil are limited and eventually alternatives will become competitive.

7. In Victoria, a decline in emphasis on brown coal for electricity generation has been projected on technical, economic and environmental grounds. This should improve the accessibility of the more attractive brown coal deposits for alternative applications such as liquefaction and ensure a favourable reception to such development proposals by the local community.

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LIQUEFACTION CHARACTERISTICS OF WYOMING COAL

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LIQUEFACTION CHARACTERISTICS OF WYOMING COAL

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1.INTRODUCTION

In Japan, a coal liquefaction project was launched in 1974 as one phase of the national Sunshine Project. In 1983, the NEDOL Process was developed by NEDO integrating the previous coal liquefaction technologies.

The NEDOL process 1t/d Process Supporting Unit (PSU) was constructed in fiscal 1988 to verify the NEDOL process and to support the operation of the 150 t/d pilot plant which is under construction.

In fiscal 1989, the PSU was operated successfully for 200 days with Australian Wandoan coal1) which was the design reference coal. Then the PSU has been operated under the various conditions to study the effect of reaction conditions on the product yield with two other kinds of coals, Illinois No.6 coal2) and Wyoming coal. In this paper, the result of Wyoming coal liquefaction especially about the effect of reaction conditions on the product yield is reported.

2.EXPERIMENTAL

2.1 Process flow

Fig.1 shows the process flow of the 1t/d PSU. The PSU consists of four main units; a coal storage and preparation unit, a coal liquefaction unit, a distillation unit, and a solvent hydrotreating unit.

Pulverized coal, catalyst, and recycle solvent are mixed in the slurry preparation tank and the slurry is fed into the liquefaction reactors by the slurry charge pump.

The slurry is heated up by the slurry heater and the coal is liquefied in the reactors. The liquefied slurry is separated into gas and liquid at the hot separators. The coal liquid is fractionated into each fraction at the atmospheric distillation towers and the vacuum distillation tower. The heavy distillate is hydrogenated at the hydrotreating unit and transferred to the coal preparation unit as the recycle solvent. The light distillate is discharged from the unit as a product oil.

The separated gas is washed by oil, alkali, and water for recirculation into the liquefaction unit and the hydrotreating unit.

2.2 Feed materials

The coal used in this study is Wyoming coal and the initial solvent is a 50-50 wt% mixture of creosote oil and anthracene oil. Synthetic pyrite is used as the liquefaction catalyst. These properties are given in Table 1 to 3. As a reference, the properties of Wandoan coal and Illinois No.6 coal are also given in Table 1.

2.3 Experimental conditions

Table 4 gives the operating conditions. Each experiment was conducted with only one condition factor changed at a time.

3. Results and discussion

3.1 The effect of reaction conditions on product yield

The effect of reaction temperature on product yield is shown in Fig.2. With increasing reaction temperature, the residue yield decreases sharply, the oil yield increases, and the gas yield increases.

The effect of the reaction pressure on the product yield is shown in Fig.3. As the pressure increases, the residue yield decreases and the oil yield increases without increasing the gas yield.

The effect of gas-slurry ratio (G/L) on the product yield is shown in Fig.4. With increasing G/L, the residue yield decreases and the oil yield increases. This is likely because that the increase in G/L promotes the mixing of coal, gas, and solvent to hasten the mass transfer in the slurry.

The effect of the amount of catalyst addition on product yield is shown in Fig.5. Until the catalyst addition of 2 wt%, the oil yield increases sharply. But above that catalyst addition, it increases slightly. From this results, it is considered that the amount of catalyst addition of 3 wt% is sufficient to obtain a certain product yield.

Fig.6 shows the effect of Δfa (the difference in fa between before and after the hydrotreating unit) of recycle solvent on product yield. The oil yield increases until the Δfa of 0.04, but it dose not change above that. It indicates that Δfa is sufficient at 0.04 to obtain a certain product yield.

3.2 Analysis of the product yields by the kinetic model

In order to analyze the results above and to evaluate the effect of reaction conditions on the product yield quantitatively, the new kinetic model of the Wyoming coal liquefaction was developed.

Fig.7 shows the reaction path of the model on an assumption that coal is converted to asphaltenes first and then the asphaltenes are decomposed consecutively to each oil fraction from heavy oil to light oil. Each rate constant of each reaction in the model was determined from the material balance under every operating condition.

On the basis of those results, empirical formula for each rate constant shown below was obtained by regression analysis method.

$$Ki = Ai \cdot [C_{cat}]^{x} \cdot [P_{H2}]^{y} \cdot [\varepsilon_{g}]^{z} \cdot \exp[-E/RT] \qquad \text{(Eq.1)}$$

where, Ki : reaction rate constant of unit reaction i [1/min]
C_{cat} : amount of catalyst addition ratio [wt%]
P_{H2} : partial pressure of hydrogen gas [kg/cm^2]
ε_{g} : gas hold up [-]
T : Temperature [K]
E : activation energy [cal/mol]
R : gas constant [cal/mol · K]

Using those empirical formulas, the product yields were calculated. The estimated yields, also given in Fig.2 to 5, agreed reasonably well with the experimental data.

Table 5 gives the variation of the product yields within the range of each reaction condition. The reaction temperature is the most effective factor for all product yields. The reaction pressure and the gas-slurry ratio are also useful factors for the oil yield because their increase promote the decrease in the residue yield without increasing the gas yield.

Within the range of operating conditions, the maximum oil yield from Wyoming coal was estimated to be 54.2 wt% daf coal basis and the reaction conditions which gave the maximum yield were as follows; reaction temperature 462℃, pressure 190 kg/cm^{2}G, gas-slurry ratio (G/L) 900 Nl/kg, and amount of catalyst addition 4 wt% dry coal basis. The experimental data of the oil yield under the conditions was 55.1 wt% daf coal basis and was in good agreement with the estimation, as given in Fig.8.

4. Conclusion

Wyoming coal was liquefied under various conditions with the PSU and the experimental data were analyzed by the new kinetic model.
As a result, the liquefaction characteristics of Wyoming coal were quantitatively clarified and the effect of reaction condition on the product yield was evaluated.

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Table 1 Properties of the raw coals

	Wyoming	Wandoan	Illinois No.6
Ultimate analysis			
C [wt% daf basis]	71.88	77.09	77.87
H [wt% daf basis]	6.09	6.42	5.65
N [wt% daf basis]	1.22	1.22	1.47
S [wt% daf basis]	0.62	0.26	3.29
O [wt% daf basis]	20.19	15.08	11.72
H/C [-]	1.017	0.999	0.871
O/C [-]	0.211	0.147	0.113
Proximate analysis			
Moisture [wt%]	25.9	12.7	12.8
Ash [wt% dry basis]	7.0	9.9	12.2
V. M. [wt% dry basis]	43.9	45.9	39.8
F. C. [wt% dry basis]	49.1	44.2	48.0

Table 2 Properties of the initial solvent

Ultimate analysis	
C [wt%]	91.06
H [wt%]	6.06
N [wt%]	0.78
S [wt%]	0.49
O [wt%]	1.61
Distillation test	
IBP [℃]	188
30% [℃]	256
50% [℃]	298
70% [℃]	354
Specific gravity [-]	1.077
Viscosity (at 40℃) [cP]	9.3

Table 3 Properties of the synthetic pyrite

Components	
FeS_2 [wt%]	80.9
S [wt%]	13.9
$Na_2 So_4$ [wt%]	4.8
$H_2 O$ [wt%]	0.4
Surface area [m²/g]	20
Pore volume [cm³/g]	0.025
Size distribution	
<1 μm [wt%]	19.3
1~3 [wt%]	27.8
3~8 [wt%]	25.9
8~16 [wt%]	23.7
16~24 [wt%]	3.3
24< [wt%]	0.0

Table 4 Operating conditions

Factor of condition	Range	(Basic)
・Reaction temperature [℃] :	435~465	(450)
・Reaction pressure [kg/cm²G] :	150~190	(170)
・Catalyst addition [wt% vs dry coal] :	0~4	(3)
・Gas-slurry ratio [Nℓ/kg] :	500~900	(700)
・Residence time [min] :	60	(60)
・Slurry concentration [wt%] :	40	(40)
・H_2 conc. in recycle gas [vol%] :	85	(85)
・Δfa of recycle solvent [-] :	0.25~0.75	

Table 5 Variation of the product yields within the range of each condition

	Maximum *, Minimum *, and those difference of each yield			
Range of each condition	Residue (wt% daf)	Hydrocarbon gas (wt% daf)	Oil (wt% daf)	H_2 consumed (wt% daf)
Temperature $435 < T < 465$ [℃]	32.62 − 16.40	8.67 − 20.62	44.32 − 49.66	4.13 − 5.21
	− 16.22	11.95	5.34	1.08
Pressure $150 < P < 190$ [kg／cm² G]	26.66 − 21.40	14.32 − 13.97	45.09 − 50.81	4.59 − 4.72
	− 5.26	− 0.35	5.72	0.13
Catalyst $2 < C < 4$ [wt%]	24.10 − 23.20	14.38 − 14.04	47.34 − 49.14	4.35 − 4.90
	− 0.90	− 0.34	1.80	0.55
G／L $500 < G/L < 900$ [Nℓ／kg]	29.40 − 21.38	13.86 − 14.16	42.37 − 50.74	4.17 − 4.81
	− 8.02	0.30	8.37	0.64

(*: Max. and Min. are the yields under upper and lower limits of each condition with the other conditions fixed at standard values)

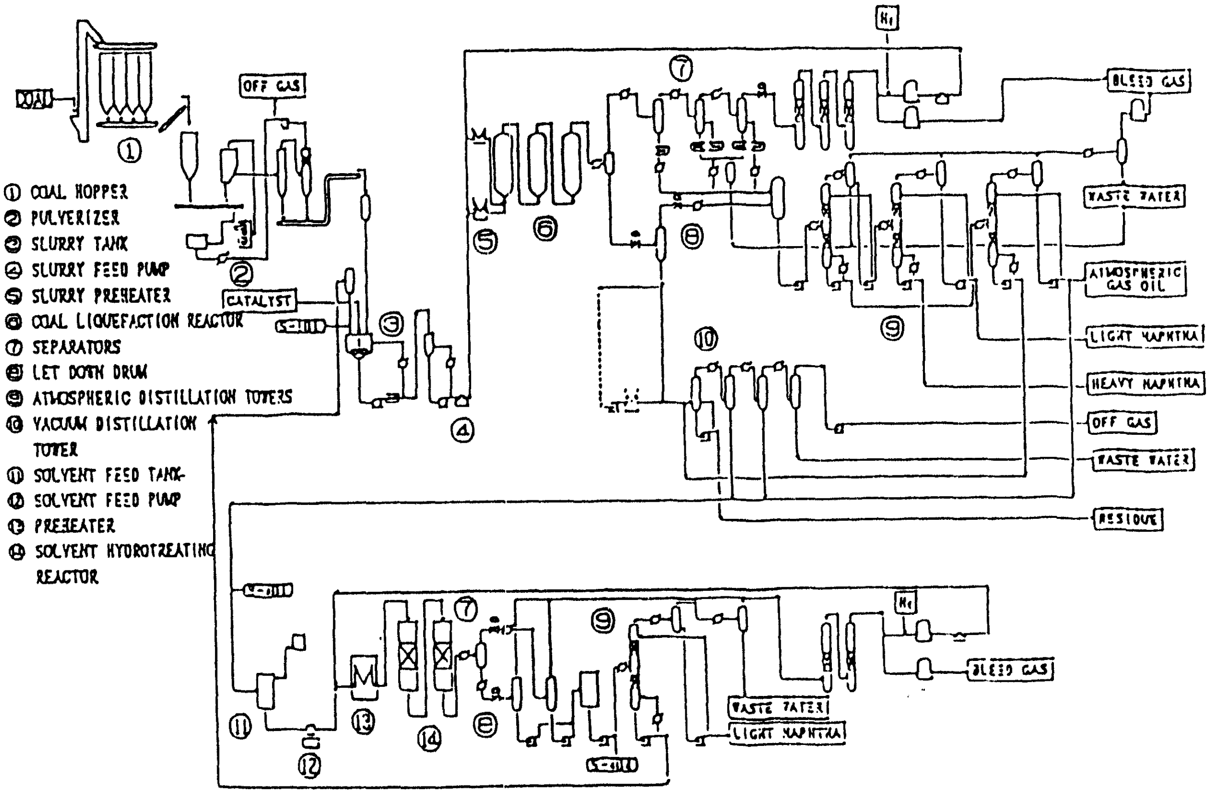

Fig. 1 NEDOL process 1t／d PSU flow sheet

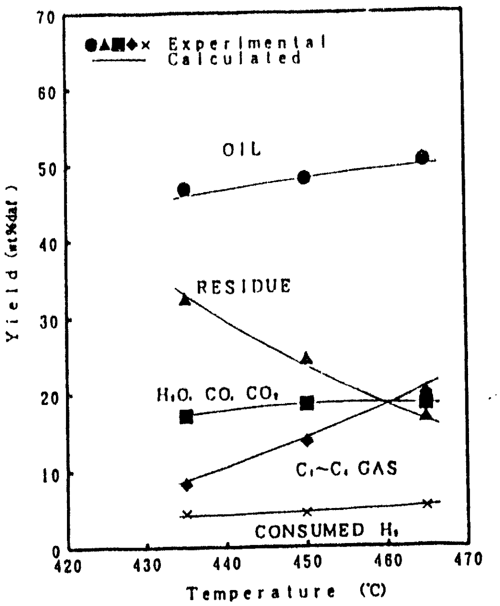

Fig. 2 Effect of reaction temperature on product yields
coal :Wyoming coal
pressure : 170 kg/cm^2 G
G/L : 700 Nl/kg
catalyst : 3 wt%

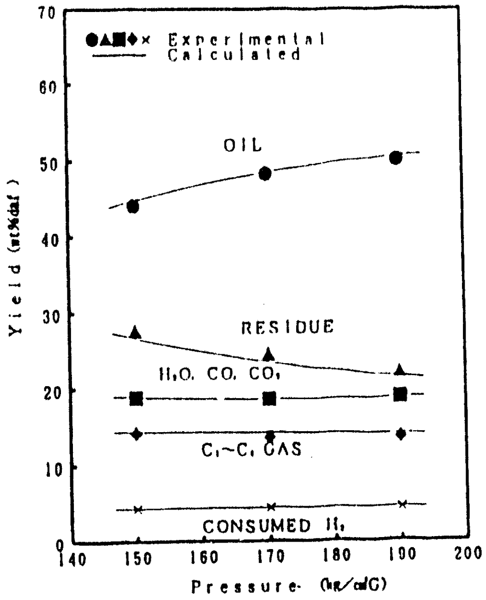

Fig. 3 Effect of reaction pressure on product yields
Coal :Wyoming coal
Temperature : 450 °C
G/L : 700 Nl/kg
Catalyst : 3 wt%

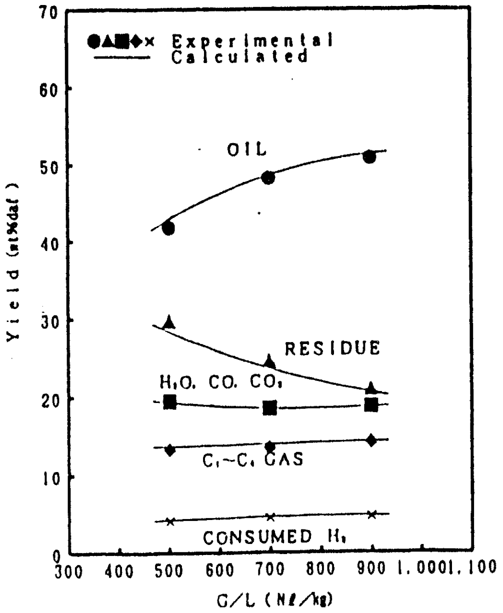

Fig. 4 Effect of gas-slurry ratio on product yields
coal :Wyoming coal
temperature : 450 °C
pressure : 170 kg/cm^2 G

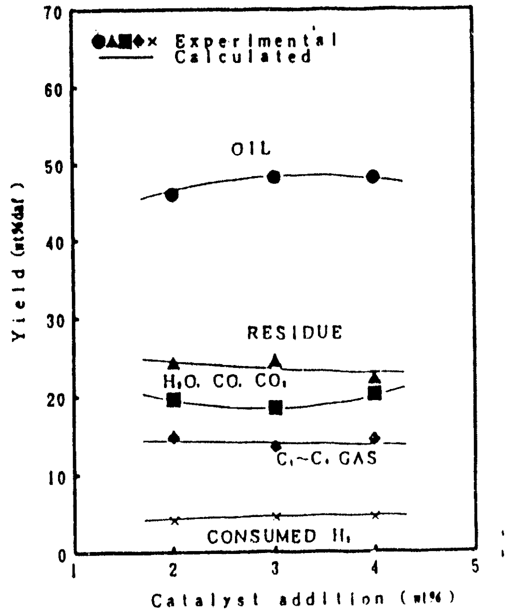

Fig. 5 Effect of catalyst addition on product yields
coal :Wyoming coal
temperature : 450°C
pressure : 170kg/cm^2 G

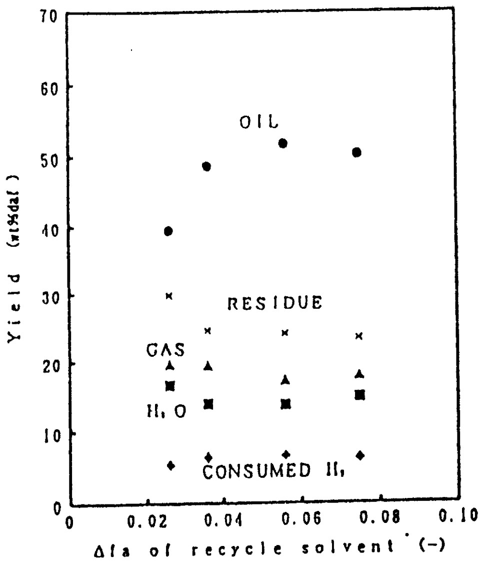

Fig. 6 Effect of Δfa of recycle solvent on product yields

coal : Wyoming coal
temperature : 450 ℃
pressure : 170 kg/cm²G
catalyst : 3 wt% dry coal
G/L : 700 Nℓ/kg

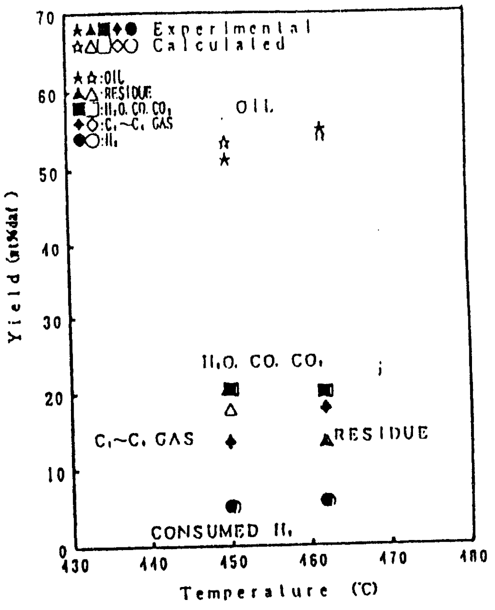

Fig. 8 Experimental and calculated maximum oil yields

coal : Wyoming coal
pressure : 190 kg/cm²G
G/L : 900 Nl/kg
catalyst : 4 wt%

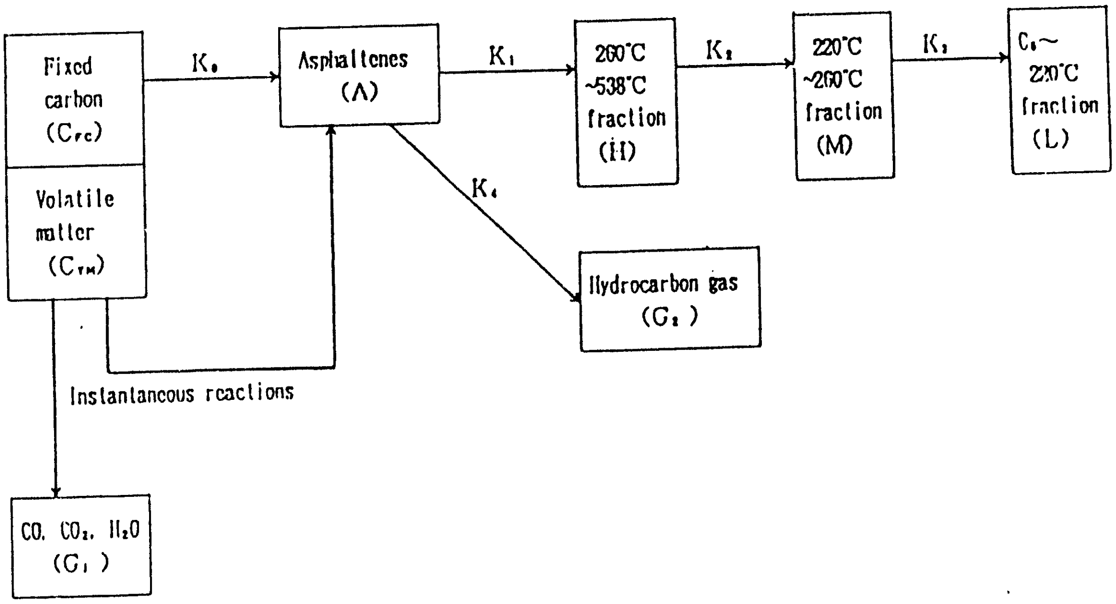

Fig. 7 The kinetic model of coal liquefaction

CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL

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COAL AND GAS CONVERSION CONTRACTORS' REVIEW CONFERENCE

WEDNESDAY, SEPTEMBER 29, 1993

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93/TL/81

INTRODUCTION

The CTSL™, Catalytic Two-Stage Liquefaction Process, has been under DOE and HRI sponsored development since 1983. The development focused on both bituminous and sub-bituminous coals using laboratory, bench and PDU scale operations. In the 1985-88 program distillate yields were improved from 4.3 bbl/maf ton of bituminous coal to 5.0 bbl/ton while reducing the cost per barrel of oil produced by more than 10%. In a recently completed program (Oct. 1988 to June 1993) further improvements were achieved through the introduction of on-line hydrotreating, addition of H_2S, the use of deashed coal, rejuvenated catalyst and chemically dispersed iron catalyst developed by PETC.

A key feature of the CTSL Process, which distinguishes it from the other two-stage processes, is the first stage low-temperature catalytic, ebullated-bed reactor. Coal is dissolved in the recycle solvent at a controlled rate allowing the catalytic hydrogenation reactions to keep pace with the free radical formation. The second stage, operating at a higher temperature, completes the coal and residual oil conversion, removes heteroatoms and produces high quality distillates at higher yields than competing technologies.

As a result of the controlled rate of liquefaction in the catalytic environment, recycle solvent quality is maintained and improved thus providing very favorable hydrogen transfer and product stabilization. Solvent quality of the heavy distillates exiting the first stage is better than that of the recycled oils entering. As a result, the reactions in the second-stage occur in an improved solvent environment completing coal and residuum conversion and heteroatom removal without approaching a severity that causes significant dehydrogenation of the first-stage products.

A 24 month program to study novel concepts using Catalytic Multi-Stage Liquefaction in a continuous bench scale units (50 lb coal/day) has been initiated since December 1992. This program consists of eight bench-scale operations supported by Laboratory Studies, Modelling, Process Simulation and Economic Assessments. This effort will fully support DOE's objective for Direct Coal Liquefaction using the Catalytic Two-Stage (CTSL) process and initial low temperature activation and prehydrogenation as a basis for experimentation and scale-up.

This paper reports results of the first three bench scale operations.

OBJECTIVES

The objective of this 24 month Bench Scale study is to produce liquid fuels from direct coal liquefaction at a cost that is competitive with conventional fuels. This objective is to be accomplished with cumulative improvements through:

- Improve the effectiveness, use and to lower the costs of catalysts.
- Investigate coal pretreatment and low temperature hydrogenation.
- Evaluate hydrogen sources and improve hydrogen management to reduce the cost of liquid fuels to less than $30/bbl.
- Improve the quality and acceptability of fuels from direct liquefaction, addressing concerns of 1990 Clean Air Amendment.
- Evaluate coals of national interest and identify coals that have a good potential for easy liquefaction at mild conditions.
- Improve process energy efficiency and reduce carbon oxide emissions during processing.
- Screen new concepts using continuous bench-scale units prior to the higher cost "Proof of Concept" demonstration.
- Provide input for the "Proof of Concept" program.

BENCH SCALE OPERATIONS

Three bench runs were completed during this reporting periods. Two of these runs were on Wyoming Black Thunder Mine coal while the other run used Illinois No. 6 coal from Burning Star #2 Mine. Results of these runs are discussed in this paper.

CMSL-01 Dispersed Iron and Molybdenum Catalysts

The use of finely dispersed molybdenum and iron catalyst precursors, evaluated separately in Bench Run CC-14 and 15, was shown to increase distillate yield, coal and residuum conversion:

Run No.	**CC-15**	**CC-14**
Additive	FeOOH	Ammonium Heptamolybdate
Loading, ppm	6100 Fe	1500 Mo
Process Improvement, W% MAF coal		
C_4-524°C	5.7	2.6
Coal Conversion	2.7	<0.5
524°C$^+$ Conversion	2.5	2.0

In CMSL-01, the impact of finely dispersed bi-metal catalysts, molybdenum and iron, on the liquefaction of Black Thunder coal was evaluated in thermal/catalytic mode of operations. A summary of the operating conditions and process performance is given in *Table 1.* The iron catalyst precursor was introduced in a hydrated oxide form impregnated on the coal matrix using a procedure developed by Pittsburgh Energy Technology Center. The iron content of the feed coal was 6100 ppm. Molybdenum was added in form of a pre-dissolved aqueous ammonium heptamolybdate solution to the slurry feed tank. The addition rate was equivalent to 300 ppm Mo.

The evaluation was performed at relatively high thermal severity conditions and high coal throughput rates with space velocity ranging from 66 to 76 lb MAF coal/h/ft^3 catalyst per stage. The first and second stage temperature was at 444°C (823°F) and 417°C (775°F), respectively. An on-line hydrotreater was in service to further remove heteroatoms from the Separator and Atmospheric Still Overhead products.

The coal conversion obtained in the presence of Fe and Mo catalysts (Conditions 1 and 2) ranged from 93.4 and 94.0 W%. These values are the highest value that had been obtained with Black Thunder coal. The distillate yield was at a reasonable high level of 63.5-64.5 W% maf coal. In the presence of 300 ppm of molybdenum only (Condition 3), coal conversion was remained high at 93.9 W% while the distillate yield was marginally lower, after taking into account of the aging effect of the second stage catalyst.

The performance of Mo/Fe catalyst is compared with previous results obtained from Run CC-1, catalytic/catalytic mode of operations, which was conducted under similar thermal severity and catalyst age. At almost 50 % higher coal throughput, the distillate yield from the Mo/Fe catalyst operations, was only 4.4 W% lower, as shown in *Table 2*. Furthermore, light Distillates (IBP-650°F) from the dispersed bi-metal operations utilizing on-line hydrotreating contained ten times less nitrogen and 17 W% more hydrogen than that of the catalytic/catalytic operations.

CMSL-02 Lowering the Solvent/Coal Ratio

Recycle solvent plays a key role in coal solubilization and hydrogen transfer. The performance of a liquefaction process is not only depend on the quality of recycle solvent, but also on the abundance of its presence in the reactors. The recycle solvent to feed coal ratio is a key parameter in the design of a liquefaction plant. This ratio has a direct impact on the size of preheated, reactor and other downstream product recovery equipment. It is anticipated that reduction in solvent/coal ratio, provided that the solvent quality can be maintained, can be translated into improvements in the utilization of reactor volume and in reaction kinetics through increasing concentration of the reactants derived from the fresh feed.

Previous CTSL studies had leaded to significant reduction in recycle solvent requirement from a solvent/coal ratio higher than 2 to 1.1. The low/high temperature sequence two-stage operations sustains high process performance even at low solvent/coal ratios through in-situ hydrogenation of the recycle solvent at favorable conditions in the first reactor. CMSL-02 further explores the lower limit of this ratio at 0.9 on the liquefaction of Illinois No. 6 coal.

Table 3 summarizes the results from CMSL-02 and compares with selected data from two previous runs (I-18 and I-27) conducted using higher solvent/coal ratios of 1.59 and 1.1 respectively. Three process conditions were achieved in CMSL-02: Condition 1 was designed to serve as a repeat for I-27 but with a less reactive higher ash coal (HRI-6107). The coal used in I-27 was a specially prepared lower ash coal (HRI-5440) with some of the less active components removed during the deashing procedure. With the exception of coal conversion, of which the higher ash coal was 3.7 W% lower, Condition 1 confirms the favorable distillate yield of 76.8 W% observed in I-27 at a solvent/coal ratio of 1.1. The poorer coal conversion in Condition 1 was compensated by low hydrocarbon gas production which was a result of lower 2nd stage temperature used in CMSL-02.

At a lower ratio of 0.9, Condition 2, both coal and residuum conversion was maintained at similar level as in Condition 1. Also, the distillates yield was only slightly lower (less than 1% lower) which was mainly due to similar magnitude of increase in C_1-C_3 yield. At a higher coal space velocity (80% increase) and thermal severity in both reactors, 26°F and 10°F increase in 1st and 2nd stage respectively, Condition 3 resulted in 4.9 W% lower in distillate yield and marginally poorer (0.5 W% less) in coal conversion. It is worthwhile to note that the difference in process performance between different Conditions would be smaller if the catalyst activities in the system can be maintained as in the case of PDU and commercial operations. In the Bench Scale operations there is no catalyst addition or withdrawal and the catalyst activities decline continuously as the run progressing.

Comparing with I-18, in which the solvent/coal was at a relatively higher level of 1.59, the distillate yield was significantly higher with less amount of solvent being recycle to the reactor. The distillate yield was 7 W% higher at lower solvent/coal ratios of 0.9 and 1.1. Moreover, distillates from runs with lower solvent/coal ratio also contained more low boiling point materials, as illustrated in Figure 1.

CMSL-03 Syngas as Reducing Gas

The potential of using synthesis gas as an alternative reducing gas for the coal solubilization step in two-stage liquefaction was explored in this bench run. A schematic process flow diagram is given in *Figure 2.* The reactor system consists of a first-stage slurry reactor and a second-stage ebullated bed charged with Shell 317 Ni/Mo supported catalysts. Reducing gas to the first-stage is either pure hydrogen or a 25/75 mixture of hydrogen and carbon monoxide. The hot vapor from the first-stage slurry reactor will be removed from the overhead of an interstage separator while the bottom from the separator will be fed to the second-stage ebullated bed reactor.

Prior to the bench-scale evaluation, two series of microautoclave tests at were conducted to screen several alkali and non-alkali based catalysts for promoting the Water Gas Shift (WGS) reaction involving syngas gas and water. The first series of test was done in the presence of coal and solvent, while the second series was carried out in the absence of coal to isolate of direct reactions between coal and syngas from that of the WGS reaction. Results of the screening tests are presented in *Table* 4. Based on microautoclave screening tests ammonium heptamolybdate plus DMDS system, a non-alkali based Water Gas Shift (WGS) catalyst which will not affect activity of the second stage supported catalyst, was selected for the bench-scale operations.

The first stage temperature in a range of 388-399°C (730-750°F) was chosen to favour the WGS reaction, while the second stage temperature was 427°C (800°F), as given in *Table 5*. This represents very mild thermal conditions in processing sub-bituminous coal. The impact of substituting hydrogen by syngas is compared in Conditions 1 and 2. Despite the higher catalyst age in Condition 2, distillate yield, coal and residuum conversion were all higher by 2.5 to 3.0 W% when syngas was used. The distillate yield of 64.6 W% is comparable with other high performance results as discussed in CMSL-01 with Mo/Fe bi-metal catalyst under much higher thermal severity conditions and with that of the catalytic/catalytic configuration in CC-1.

The effect of higher first-stage temperature was studied in Condition 3. By raising the first-stage temperature by 11°C (20°F) resulted in marginally improvement in coal conversion, but caused a 3 W% decline in distillate yield (part of this decline was due to deactivation of second-stage catalyst). The lower distillate yield was mainly due to increase in 524°C$^+$ residuum yield, as illustrated in *Figure 3*. Increasing coal throughput by 40 W%, Condition 4, resulted in marginally decrease in coal and residuum conversions, and distillate yield.

The qualities of Separator and Atmospheric Still Overheads, together these streams constituted majority of the distillable products, are compared in *Table 6*. The first-Stage Separator Overhead are of lower gravity, higher hydrogen content when hydrogen was used as reducing gas. However, it also contains more nitrogen suggesting that the bond breakage mechanisms are quite different for hydrogen and carbon monoxide.

Interstage product separation has a significant impact on the form at which oxygen is being removed. Comparing CMSL-03 Condition 1 with the two earlier test Conditions in CC-1 and CC-15, in the presence of interstage separation, a significantly higher proportion (more than five times) of the "coal oxygens" are being removed as carbon oxides, mostly in form of carbon dioxide. However, due to the difficult in performing reliable water balance around the system, a corresponding decrease in water made have not been confirmed.

CONCLUSION AND RECOMMENDATION

The use of interstage separator and on-line hydrotreater has significant implication in product quality and hydrogen efficiency. Data base on the performance of these concepts should be expanded to permit effective scale-up to PDU and commercial applications.

Reduction of the solvent/coal ratio by 20 W%,from 1.1 to 0.9, does not cause any deterioration in process performance and product quality. Potential saving in capital cost and increase in coal throughput with less solvent being recycle considerably improve the economic of the process. This observation will be further evaluated in an upcoming PDU scale test under the Proof of Concept program.

Preliminary results from the synthesis gas run are encouraging and warrant further studies to evaluate the impact of syngas composition and the effectiveness of using Ni/Mo or Co/Mo supported catalyst in the first-stage to promote the WGS reaction.

ACKNOWLEDGEMENTS

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TABLE 1

BENCH RUN CMSL-01 OPERATING SUMMARY

Coal: Wyoming Black Thunder Mine
Catalyst: FeOOH and Ammonium Heptamolybdate
2nd Stage - Shell 317 Ni/Mo (Supported)
Hydrotreater - Criterion 411 Ni/Mo (Supported)

Condition	1	2	3	4
Mo [ppm]	300	300	300	300
Fe [ppm]	6150	6150	None	None
Temperature [F]				
1st Stage	823	822	824	826
2nd Stage	775	775	775	776
Hydrotreater	659	660	661	off
Space Velocity [lb mf coal/ft3 cat. /stage]	67	76	66	69
Catalyst Age [lb mf coal/lb cat]	196	284	530	545
Process Performance [W% maf coal]				
C1-C3	9.5	9.9	11.1	
C4-975F Distillate	64.5	63.5	60.7	
Coal Conv.				
1st Stage	92.0	N/A	93.1	
Two Stage	94.0	93.4	93.9	
975F+ Conv.	91.6	90.5	89.1	
H2 Used	8.7	8.6	9.0	

TABLE 2

PERFORMANCE COMPARSION

Run No.	CMSL-01	CC-01
Configuration	Therm/Cat. Hydrotreater	Cat/Cat. —
Catalyst Age [lb coal/lb cat]	284	284
Space Velocity [lb coal/h/ft3 cat/stage]	76	44.7
Temperature [F]		
1st Stage	832	750
2nd Stage	775	824
Process Performance, [W% maf coal]		
C1-C3	9.91	8.23
C4-975F Distillate	63.5	67.9
Coal Conv.	93.4	91.4
975F+ Conv.	90.5	88.6
H2 Used	8.57	8.15
Quality of IBP-650F		
Gravity, API	33	21.4
Carbon	87.39	88.32
Hydrogen	12.79	11.1
Sulfur	43.89	10
Nitrogen	106.2	1300
H/C Ratio	1.76	1.5

TABLE 3

BENCH RUN CMSL-02 OPERATING SUMMARY

Coal: Illinois No. 6 Burning Star No. 2 Mine
Configuration: Catalytic/Catalytic Two-Stage Mode
Catalyst: Shell 317 Ni/Mo 1/32" Extrudate

Run No.	CMSL-02	CMSL-02	CMSL-02	I-18	I-27
Condition	1	2	3		
Solvent/Coal	1.1	0.9	0.9	1.59	1.14
Coal (HRI #)	6107	6107	6107	5174	5440
Ash, W% mf	12.04	12.04	12.04	10.56	5.77
Sulfur, W% mf	4.00	4.00	4.00	3.60	2.75
Temperature [F]					
1st Stage	752	751	777	750	755
2nd Stage	801	802	812	799	811
Space Velocity [lb mf coal/ft3 cat. /stage]	41	41	74	45.8	41
Catalyst Age [lb mf coal/lb cat]	124	295	422	264	298
Process Performance [W% maf coal]					
C1-C3	5.1	5.9	5.3	5.7	7.7
C4-975F Distillate	76.8	75.9	71.0	68.8	76.0
Coal Conv.	92.9	92.9	92.4	93.7	96.6
975F+ Conv.	91.3	90.6	85.8	84.4	90.9
H2 Used	8.28	8.38	7.58	7.00	7.18
H2 Efficiency	9.28	9.06	9.37	9.89	10.58

TABLE 4

WGS Catalyst Screening Test

Series I: With Coal and Solvent

	Catalyst W%	Coal Conversion, W%	
		Wet Coal	Dry Coal
K2CO3	5.0	72	76, 70
NaAlO2	4.0		77
AHM (Mo)	0.15		63
AHM+DMDS (Mo)	0.15	64	70
DMDS	3.0		69
Shell 317(Spent)	100		75

Series II: No coal

	Catalyst [gm]	CO Conversion, W%	
		With Solvent	No Solvent
K2CO3	0.12	14.0	14.7
NaAlO2	0.11	11.2	17.5
Fe2O3	0.10	3.9	5.8
AHM+DMDS	0.11	20.2	27.9
Amocat 1A	2.00	31.2	29.6

TABLE 5

CMSL-03 OPERATING SUMMARY

Coal: Black Thunder Mine Coal
Configuration: Thermal/Catalytic Two-Stage Mode
Additive: Ammonium Heptamolybdate (1500 ppm of Mo)+ DMD
2nd StageCatalyst: Shell 317 1/32 Extrudate
Interstage Separation

Condition	1	2	3	4
Solvent/Coal	1.2	1.2	1.1	1.3
Reducing Gas: CO/H2				
1st Stage	0/100	75/25	75/25	75/25
2nd Stage	0/100	0/100	0/100	0/100
Temperature [F]				
1st Stage	730	731	750	750
2nd Stage	800	801	800	800
Space Velocity [lb mf coal/ft3 cat. /stage]	42.0	43.1	42.4	59.0
Catalyst Age [lb mf coal/lb cat]	123	234	316	419
CO Conversion, W% Equilibrium	—	93.6	93.6	62.4
Process Performance [W% maf coal]				
C1-C3	6.5	6.6	6.8	5.8
CO+CO2	8.8	9.3	10.1	9.9
C4-975F Distillate	61.6	64.6	61.6	62.0
Coal Conv.	89.5	92.0	92.4	90.1
975F+ Conv.	87.2	89.9	86.9	85.8
H2 Used	7.8	7.7	7.1	7.0
HDN	75.9	84.8	90.7	72.4

TABLE 6

SYNGAS VS HYDROGEN

Inspection of Separator and Atmospheric Still Overheads

	1st Stage Separator		2nd Stage Separator		Atmospheric Still	
1st Stage Gas	H2	CO/H2	H2	CO/H2	H2	CO/H2
Separator Overheads						
IBP	185	182	141	119	266	246
API Gravity	26.9	22.9	37.0	37.2	31.0	30.3
Carbon	85.56	86.00	85.96	87.25	86.29	86.99
Hydrogen	11.74	11.37	12.52	12.84	12.10	12.21
Sulfur	0.079	0.086	0.011	0.012	0.009	0.020
Nitrogen	0.22	0.057	0.15	0.049	0.17	0.051
H/C Ratio	1.65	1.59	1.75	1.77	1.68	1.68

FIGURE 1

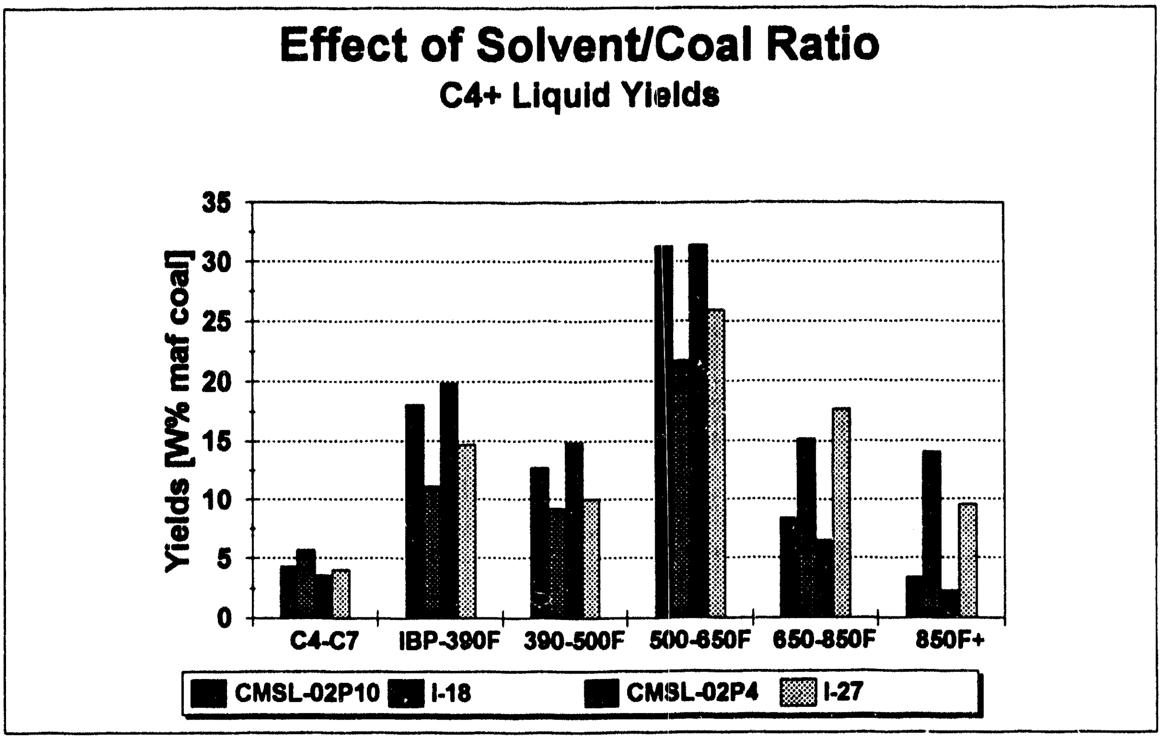
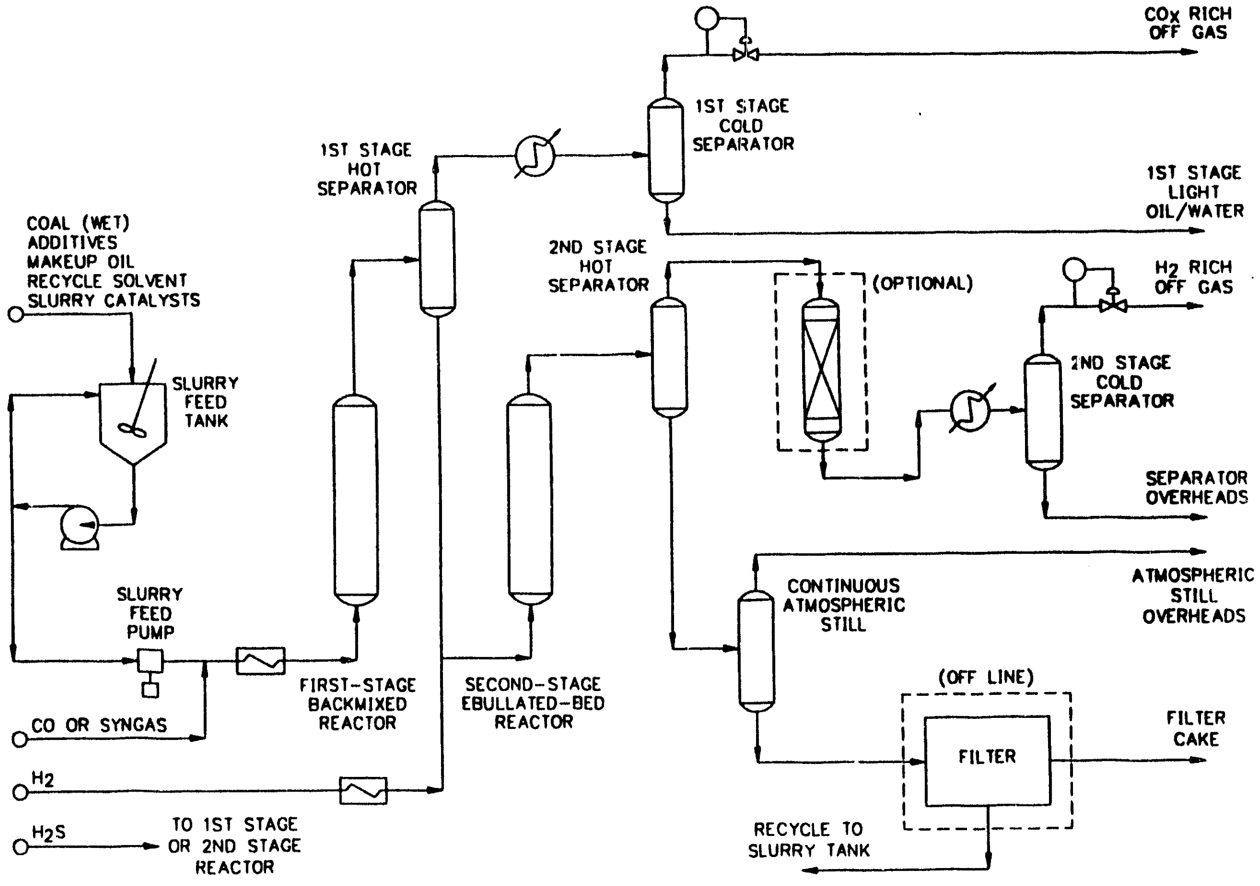
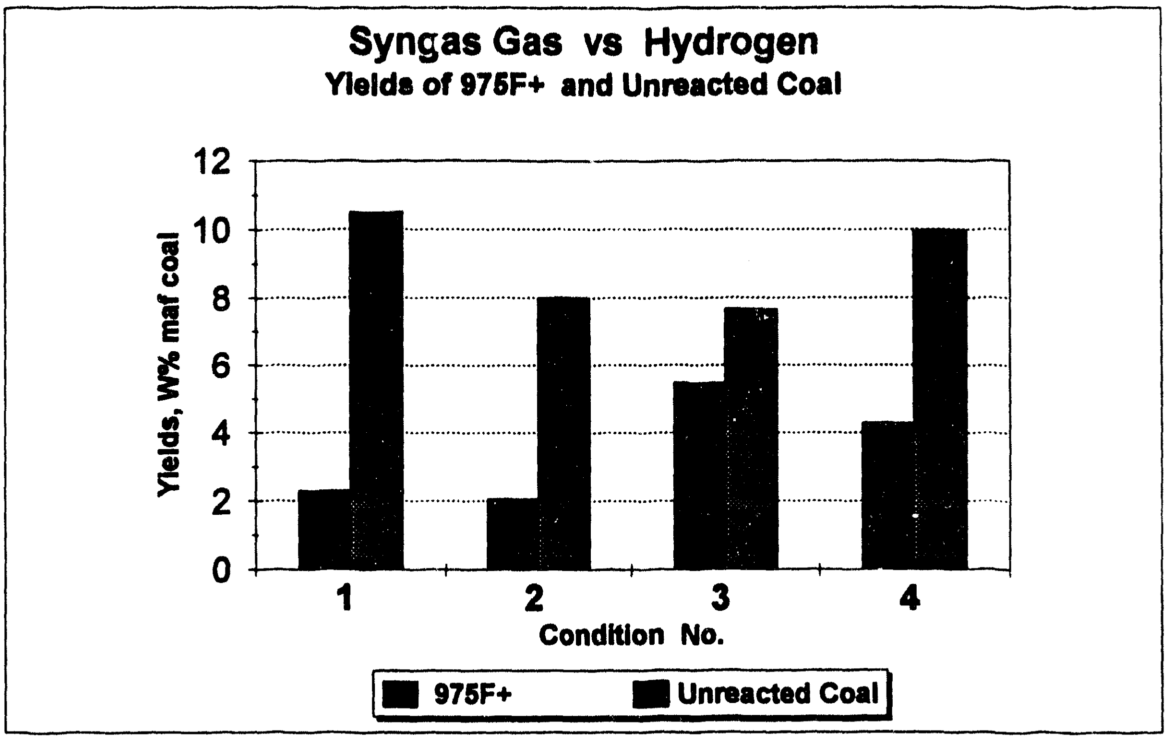


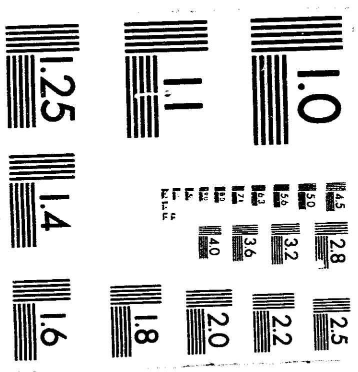
FIGURE 2



HRI SYNGAS - H_2 TWO-STAGE COAL LIQUEFACTION SCHEME

FIGURE 3


Syngas Gas vs Hydrogen
Yields of 975F+ and Unreacted Coal
Yields, W% maf coal
12
10
8
6
4
2
0
1
2
3
4
Condition No.
975F+
Unreacted Coal


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3

7 of 8

Catalytic Hydrothermal Pretreatment and Hydrogenative Pretreatment for Enhanced Coal Liquefaction over Dispersed MoS_2

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ABSTRACT

This paper describes the recent progress and development of our research project entitled "Effects of Low-Temperature Catalytic Pretreatments on Coal Structure and Reactivity in Liquefaction" in the following three aspects: 1) effects of catalyst, solvent, and reaction temperature (250-450 °C) on conversion and structural changes of a Texas subbituminous coal (DECS-1); 2) effects of predrying and mild oxidation of a Wyodak subbituminous coal (DECS-8) on its non-catalytic and catalytic pretreatments at 350 °C; and 3) the dramatic improvements in coal conversion by addition of a small amount of water in the catalytic pretreatment step at 350 °C. We found that there are dramatic synergetic effects when dispersed catalyst and a small amount of water are used together at 350 °C under H_2 pressure. Such a pretreatment may be viewed as a catalytic hydrothermal pretreatment.

INTRODUCTION

The conventional concept for high-severity conversion of coal is that coal must be heated to high temperatures (400-450°C) causing thermal cleavage of bonds in organic matrix of coal to yield free radicals, which are capped by hydrogen to form low-molecular-weight products. However, fundamental research in coal liquefaction and pyrolysis in the recent past has revealed that coal is more reactive than had been thought previously. The thermally initiated reactions of coal can take place very rapidly and, especially for low-rank coals, can occur at lower temperatures.

PROJECT OBJECTIVES

This work is a fundamental study of low-temperature catalytic pretreatment as a potential preconversion step to low-severity liquefaction. The main objectives of this project are to study the effects of low-temperature pretreatments on coal structure and their impacts on the subsequent liquefaction. The ultimate goal of this work is to provide the basis for the design of an improved liquefaction process and to facilitate our understanding of those processes that occur when coals are initially dissolved.

MAJOR ACCOMPLISHMENTS TO DATE

We have performed extensive experimental investigations to study the effects of low-temperature (250-350 °C) thermal and catalytic pretreatments on coal structure and reactivity in solvent-free and solvent-mediated liquefaction. The research work has resulted in thirteen publications including journal articles and conference papers, in addition to the quarterly technical progress reports. Our major accomplishments are in the following five areas:

1. Effects of Thermal and Catalytic Pretreatments on Coal Reactivity, and Temperature-programmed Liquefaction

Song, C.; H.H. Schobert; P.G. Hatcher, "Temperature-Programmed Liquefaction of a Low Rank Coal". Energy & Fuels, Vol. 6, No.3, pp. 326-328, **1992.**

Song, C.; Schobert, H.H., "Temperature-Programmed Liquefaction of Low-Rank Coals in H-donor and Non-donor Solvents". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 37, No.2, pp. 976-983, **1992.**

Huang, L.; Song, C.; Schobert, H.H., "Temperature-Programmed Catalytic Liquefaction of Low-Rank Coal Using Dispersed Mo Catalyst". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 37, No.1, pp. 223-227, **1992.**

2. Effects of Thermal and Catalytic Pretreatments on Coal Structure, and Spectroscopic Characterization of Liquefaction Residues

Song, C.; Schobert, H.H.; Hatcher, P.G., "Solid State ^{13}C NMR and Pyrolysis-GC-MS Studies of Coal Structure and Liquefaction Reactions". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 37, No.2, pp. 638-645, **1992.**

Saini, A. K.; Song, C.; Schobert, H.H.; Hatcher, P.G., "Characterization of Coal Structure and Low-Temperature Liquefaction Reactions by Pyrolysis-GC-MS in Combination with Solid-State NMR and FT-IR". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 37, No.3, pp.1235-1242, **1992.**

Song, C.; Hou, L.; Saini, A.K.; Hatcher, P.G.; Schobert, H.H. "CPMAS ^{13}C NMR and Pyrolysis-GC-MS Studies of Structure and Liquefaction Reactions of Montana Subbituminous Coal", Fuel Processing Technology, Vol.34, No.3, pp.249-276, **1993.**

3. Effects of Predrying and Oxidation of Wyodak Subbituminous Coal on Its Structure and Its Thermal and Catalytic Liquefaction and the Role of Water

Saini, A. K.; Song, C.; Schobert, H.H. "Influence of Drying and Oxidation of Coal on Its Catalytic and Thermal Liquefaction. 1. Conversion and Product Distribution", Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 38, No.2, pp.593-600, **1993.**

Saini, A. K.; Song, C.; Schobert, H.H. "Influence of Drying and Oxidation of Coal on Its Catalytic and Thermal Liquefaction. 2. Characterization of Dried and Oxidized Coal and Residues". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 38, No.2, pp.601-608, **1993.**

Song, C.; Saini, A.K.; Schobert, H.H. "Positive and Negative Impacts of Drying and Oxidation on Low-Severity Catalytic Liquefaction of Low-Rank Coal". Proceedings of 7th International Conference on Coal Science, Banff, Alberta, Canada, September 12-17, 1993, Vol. I, pp.291-294, **1993.**

Song, C.; Saini, A. K.; Schobert, H.H. "Effects of Drying of Wyodak Subbiyuminous Coal on Its Thermal and Catalytic Liquefaction. 1. Conversion and Products Distribution", Energy & Fuels, submitted, **1993.**

Wenzel, K.; Hatcher, P.G.; Cody, G.D.; Song, C. "The Structural Alteration of Huminite by Low Severity Liquefaction". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 38, No.2, pp.571-576, **1993.**

4. **Effects of Solvent, Catalyst, and Temperature on Liquefaction Conversion and Structural change of a Subbituminous Coal**

Huang, L.; Song, C.; Schobert, H.H. "Effects of Solvent and Catalyst on Liquefaction Conversion and Structural Changes of a Texas Subbituminous Coal". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 38, No.3, pp.1093-1099, **1993**.

5. **Dramatic Enhancement of Coal Conversion in Low-Temperature Catalytic Pretreatment by Addition of Water**

Song, C.; Saini, A. K.; Schobert, H.H. "Enhancing Low-Severity Catalytic Liquefaction of Low-Rank Coal by Adding Water". Am. Chem. Soc. Div. Fuel Chem. Prepr., Vol. 38, No.3, pp.1031-1038, **1993**.

RECENT PROGRESS - I. EFFECTS OF CATALYST, SOLVENT, AND REACTION TEMPERATURE ON COAL CONVERSION AND STRUCTURAL CHANGE

Liquefaction of a Big Brown Texas subbituminous coal (DECS-1, Table 1) was studied in the temperature range of 250°C to 450°C. Tetralin and 1-MN were used as reaction solvents to compare with the reactions without solvent. Ammonium tetrathiomolybdate (ATTM) was used as the catalyst precursor. As shown in Figure 1, in thermal (i.e, non-catalytic) experiments, tetralin, an H-donor solvent, was beneficial not only in providing high conversion but, most importantly, also in gaining a high yield of oil at temperatures higher than 350°C.

In catalytic experiments, conversions are very similar regardless of solvent used at temperatures up to 400°C, and tetralin does not provide any significant advantage, as can be seen from Figure 2. However, at 450°C, conversions with 1-MN or with no solvent dropped, while that with tetralin increased as well as did the oil yield. The gas yields appear to be independent of solvent and catalyst, but dependent on temperature. Cross polarization magic angle spinning (CPMAS) ^{13}C NMR was performed to obtain aromaticities of reaction residues. It is found that in plotting aromaticity versus conversion, the data fall into two sets: the thermal reactions and the catalytic reactions. At the same conversion, a residue from a catalytic reaction always has the lower aromaticity, as can be seen from Table 2. This is because in a catalytic reaction, more aromatic carbon has been reacted.

The study of the amount of aliphatic carbon converted from the coal to THF solubles shows that neither the catalyst nor the solvents has influence, but it is a function of temperature. This is consistent with our previous results of quantitative CPMAS ^{13}C NMR analysis of residues from Montana subbituminous (DECS-9) coal [Song et al., 1993]. In the conversion of aromatic carbon from coal to THF solubles, both the catalyst and the solvents have strong effects. For thermal reactions, tetralin gave much higher conversions of aromatic carbon than 1-MN or no solvent. For catalytic reactions, there is no significant difference among the solvents, or no solvent, at temperatures up to 400°C. At higher temperatures, tetralin again gave a much higher conversion than the other two cases, indicating that the solvent donation of hydrogen played a significant role. As for 1-MN and no solvent, compared with results at 400°C, the conversion of aromatic carbon at 450°C did not increase, but in fact decreased drastically, suggesting that retrogressive reactions occur in these situations. More details about effects of catalyst and solvents may be found elsewhere [Huang et al., 1993].

RECENT PROGRESS - II. EFFECTS OF DRYING AND OXIDATION OF WYODAK SUBBITUMINOUS COAL ON ITS THERMAL AND CATALYTIC PRETREATMENTS AT 350 °C

Influence of drying and mild oxidation on catalytic and non-catalytic pretreatment (at 350 °C for 30 min with 6.9 MPa (cold) H_2) was studied using Wyodak subbituminous coal (DECS-8, Table 1). The effects of drying and oxidation on coal structure were examined by using solid-state ^{13}C NMR (Figure 3), FT-IR (Figure 4), and pyrolysis-GC-MS (Figure 5). It appears from these spectroscopic data that vacuum-drying at 100°C for 2 h does not cause apparent chemical changes, but air-drying seems to cause oxidation (Figures 3-5). For non-catalytic runs, fresh raw coal gave higher conversion and higher oil yield than both the vacuum- and air-dried coals, regardless of the solvent. Compared to the vacuum-dried coal, the coal dried in air at 100 °C for 2 h gave a better conversion in the presence of either a hydrogen-donor tetralin or a non-donor 1-methylnaphthalene (1-MN) solvent (Figure 6).

Catalytic runs were performed using in-situ generated molybdenum sulfide catalyst from ammonium tetrathiomolybdate (ATTM) precursor impregnated on either raw coal or predried coal samples. The solvent-free runs using ATTM loaded on the raw coal gave higher conversion and higher oil yield than loading ATTM on vacuum- or air-dried coals. In the presence of either tetralin or 1-MN (Figure 7), however, the runs using ATTM loaded on air-dried coal afford better conversions and oil yields as compared to the runs using vacuum-dried coal. This may be due to the moderate increase in surface functionality contributing to decreased surface hydrophobicity, representing a case where negative effect of drying is offset by the positive effect of mild oxidation-induced increase in surface functionality contributing to better ATTM dispersion.

Upon drying coal in air at 150 °C for 20 h, the conversion significantly decreased to a lower value than that of the vacuum-dried coal in the non-catalytic runs, and the same trend was observed in the runs of the dried coals loaded with ATTM. Such a clearly negative impact of severe oxidation on coal pretreatment is considered to arise from significantly increased oxygen functionality (as also shown the solid-state NMR ^{13}C and Pyrolysis-GC-MS data) [Saini et al., 1993], which enhances the cross-link formation in the early stage of coal liquefaction.

Physical, chemical, and surface chemical aspects of effects of drying and oxidation and the role of water are discussed in detail elsewhere [Song et al., 1993]. Briefly, There are at least four physicochemical effects that drying and oxidation may have on coal. The first is the removal of water. The second is the physical changes such as those in pore structure and density that are believed to accompany drying [Vorres et al., 1992]. One way by which pore structure can be changed is the shrinkage caused by deswelling due to the removal of water, which is a good swelling solvent for low-rank coal [Suuberg et al., 1993]. If this happens, drying before the reaction could also affect the reaction with respect to diffusion of solvents, reactants, and products.

The third is the change in surface characteristics such as hydrophobicity induced by drying, as we further describe below. Finally, some chemical reactions may occur during drying. Obviously, oxidation causes chemical change in oxygen functionality. The effects of these four factors in thermal and catalytic liquefaction are not straightforward, and some of them can exert influence on coal conversion in opposite directions under the same or different conditions.

RECENT PROGRESS - III. Effect of Water Reflected by the Influence of Drying

As mentioned above, for the thermal (non-catalytic) runs, both vacuum-drying and air-drying decreased coal conversion significantly, as compared to the run of the raw coal. Original fresh raw coal contains 28.4 wt% water. To see whether the changes caused by the drying is reversible or irreversible, we added a small amount of water equivalent to the original moisture content, to the dried coal. The liquefaction results (Figures 8 and 9) showed that adding water back to the vaccum-dried and air-dried coals restored over 90% of the conversion of the fresh raw coal. The coal conversion levels always follow the order of solvent-free < 1-methylnaphthalene < tetralin; the use of the raw coal always give the highest conversion. In the absence of water, there were some differences between the vacuum-dried and air-dried coals, with the latter affording higher conversion when a solvent was used. When water is added back, the differences between the two types of dried coals become much smaller.

These trends reveal that the major effect of drying on thermal liquefaction is associated with the effect of water. Under the conditions of vacuum-drying at 100 °C for 2 h, most of the changes caused by drying are reversible, as can be seen by the over 90% restoration of coal conversion. The other effects of drying and oxidation may include the changes in pore structure [Suuberg et al., 1991, 1993; Vorres et al., 1992], surface characteristics [Song et al., 1993], and, if oxidation involved, the change in functionality [Saini et al., 1993]. These kinds of changes may be irreversible if high severity conditions were used for drying. However, when water is added back, the differences caused by using different drying methods, largely diminish. In other words, decrease in conversion caused by some undesirable changes during drying is largely compensated by the desirable effect of water addition.

The results for uncatalyzed runs demonstrate that the presence of water promotes the conversion of the coal, increases oil yields, and significantly enhances the oxygen removal as CO_2. Adding water also resulted in small but consistent decrease in the yield of CO. This is considered to be due to water gas shift reaction: $CO + H_2O = CO_2 + H_2$. However, the increase in CO_2 yield upon H_2O addition is much more than the decrease in CO on a molar basis, indicating the occurence of other reactions between water and species in or from coal, which led to substantial increase in CO_2 formation.

RECENT PROGRESS - IV. DRAMATIC IMPROVMENT OF COAL CONVERSION BY ADDITION OF WATER AT 350°C - CATALYTIC HYDROTHERMAL PRETREATMENT

In our work on the influence of drying and oxidation of coal on its catalytic liquefaction, we found that the effects of drying in vacuum and drying in air, which decrease coal conversion at 350 °C, are largely associated with the effects of water. This section describes the dramatic improvement of coal conversion upon addition of a small amount of water in low-severity solvent-free liquefaction of Wyodak subbituminous coal (DECS-8) using a dispersed molybdenum sulfide catalyst at 350 °C for 30 min with an initial (cold) H_2 pressure of 7 MPa.

In the absence of a catalyst, conversions of the raw coal containing moisture were about 23-26 dmmf wt%, while those for the vacuum-dried or air-dried coals were 11-15 wt%. Impregnating ammonium tetrathiomolybdate (ATTM) as catalyst precursor increased the conversions of the predried coals from 11-15 to 28-31 dmmf wt%, and those of the fresh raw coal from 23-26 to 43-44 dmmf wt%. Adding water back to the ATTM-impregnated and dried coals caused a dramatic increase in coal conversion (Figures 10-11). The amount of water added is selected to be equivalent to the amount of moisture in the fresh raw coal (28 wt %).

For all the catalytic runs of Wyodak coal, regardless how the coal was pre-dried or undried, all the ATTM-loaded coals were dried in vacuum at 100 °C for 2 h before use. In the runs testing the effect of water addition, we added a small amount of water (H_2O/dmmf coal = 0.46, wt ratio). It is clear from Figures 10-11 that adding water to the catalytic reactions at 350°C dramatically promoted the coal conversion from 29-30 wt% for the vacuum-dried or air-dried coals to 62-63 wt% in the solvent-free runs, and from 43 to 66 wt% for the fresh raw coal. Therefore, the present results demonstrate that dispersed MoS_2 catalyst and a small amount of water can act in concert to strongly promote coal conversion at 350 °C. In fact, the use of ATTM with added water at 350 °C without solvent or with 1-MN solvent resulted in coal conversion level (63-66 dmmf wt%) that is much higher than that (30-38 wt%) from the non-catalytic runs at much higher temperature, 400 °C.

The coal conversions in the catalytic runs with ATTM increased from 43-44 to 64-66 dmmf wt% upon water addition in the case of fresh raw coal, which represents about 50 % increase, and from 28-31 to 60-66 dmmf wt% upon water addition in the runs of air-dried or vacuum-dried coals, which represents as high as 114-135 % increase in coal conversion. These results demonstrate that adding a small amount of water can significantly enhance the conversion of low-rank coal in low-severity catalytic liquefaction at 350 °C. More details about this work may be found elsewhere [Song et al., 1993].

For the solvent-free runs, the increased coal conversion upon water addition is mainly manifested by the significant gain in asphaltene and preasphaltene yields (Figure 10). In the presence of either a H-donor tetralin solvent or a non-donor 1-MN solvent (Figure 11), the enhanced conversions are largely due to the increase in the yields of preasphaltene and oil, and this trend was most apparent with 1-MN solvent.

With respects to the effect of water associated with influence of drying, it also appears that dispersing ATTM on vacuum-dried coal gives higher conversion upon water addition, as compared to loading ATTM on air-dried coal. The extents of increase in conversion due to water addition are also higher with the former than with the latter. These results show that for water-aided catalytic liquefaction at 350 °C, less oxidation of the coal sample can lead to higher conversion.

The use of catalyst generally decreased the yield of CO_2 in the runs of the dried coals without added water. Similar to the thermal runs, adding water to the catalytic runs also decreased the CO yield and significantly enhanced the formation of CO_2. The increasing extent in CO_2 yield is much higher than the decrease in CO yield, as can be seen from Figure 12, indicating the contribution of the reactions between water and coal species, other than water gas shift reaction, to the increased CO_2 formation.

Negative Effect of Added Water in Catalytic Liquefaction at 400°C

In order to examine the effect of added water in relation to the influence of reaction temperature, we also carried out the liquefaction experiments at 400°C. In uncatalyzed runs, adding water resulted in moderate increase in oil yields and coal conversion (5-7 wt%) with 1-MN solvent and without solvent, and small increase in coal conversion with tetralin solvent. The changes in coal conversion with solvents are much larger at 400 °C than at 350 °C, but conversion always increases in the consistent order of none < 1-MN < tetralin.

As can be seen by comparing Figure 13 with Figure 10, the trends for the water effect in catalytic runs at 400 °C are different from those in non-catalytic runs. In the absence of added water, the solvent-free run of the vacuum-dried and ATTM-impregnated coal afforded highest conversion, 85 wt%, and highest oil yield, 46 wt%. The run with 1-MN solvent gave the lowest conversion, 71 wt%. Relative to the solvent-free run, the use of H-donor tetralin solvent at 400 °C did not display any advantage in terms of coal conversion and oil yields. Given the fact that water acts as a very good promotor for coal conversion at 350 °C (Figure 10), it is surprising to note from Figure 13 that adding water to the catalytic runs at 400 °C decreased coal conversion substantially in the runs with 1-MN and without solvent. We conducted duplicated runs under the three different conditions at 400 °C, and confirmed a reproducible trend for the negative impact of water on the catalytic reactions at 400 °C. The solvent-free run suffered large decrease in coal conversion from 85 to 62 wt%. The run with tetralin displayed less sensitivity to the water, with slight but consistent decrease in conversion in duplicated runs from about 84 to 80 wt%.

These results show that the catalytic activity is significantly lower in the presence of water at 400 °C, indicating that water is detrimental for liquefaction at higher temperature. The action of water at 400 °C may be inferred through the following comparative examination. The highest oil yield and the highest conversion in the solvent-free run with no added water indicate that dispersed molybdenum catalyst exhibited maximum activity in activating molecular H_2, namely dissociation of H_2 on catalyst surface, and in transfer of the active H atom to the coal-derived free radicals and other coal species when there is no externally added solvent.

Relative to the solvent-free catalytic run, the decrease in conversion and H_2 consumption upon addition of 1-MN may be attributed to the decrease in partial H_2 pressure, additional difficulty in mass transport of H_2 to the catalyst surface in the presence of solvent, and competitive adsorption of aromatic 1-MN molecules on catalyst surface. The same trends also applies to the run using tetralin, but the negative impact of tetralin to mass transport of H_2 gas is largely compensated by hydrogen donation from benzylic hydrogens in tetralin. As a result, oil yield decreased but conversion did not decrease as much as oil yield. Relative to the runs with added 1-MN, the added water initially occupied less space and therefore the partial H_2 pressure should be higher during the water-added but solvent-free run. Such a inference indicates that the presence of water deactivated the catalyst.

The conversion decrease due to water addition was also accompanied by significant reduction in gas-phase H_2 consumption, from 2.8 to 1.4 in solvent-free runs, and from 1.8 to 0.7-0.9 in the runs with a solvent. It should also be noted that the enhanced formation of CO_2 upon water addition seems to be unaffected at higher temperature, suggesting the enhanced CO_2 formation is caused by thermal reaction between added water and coal species.

Desirable Effect of Water at 350 °C and Undesirable Function of Water at 400 °C

Little is reported in literature about the effects of water on the catalytic coal liquefaction using dispersed catalyst. However, for non-catalytic coal conversion such as pyrolysis, liquefaction and coprocessing, hydrothermal pretreatments of coal has been reported to be beneficial in terms of increased conversion, or oil yield [Graff and Brandes, 1987; Bienkowski et al., 1987; Ross and Hirschon, 1990; Pollack et al., 1991; Serio et al., 1991; Tse et al., 1991]. Siskin et al. [1991] have suggested that the presence of water during coal pretreatment will facilitate depolymerization of the macromolecular structure to give an increased proportion of liquids by cleaving important thermally stable covalent cross-links in the coal structure. On the other hand, Tse et al. [1991] suggested that the pretreatments of low rank coals in the presence of water should minimize retrogressive reactions such as crosslink formation by phenollic compounds such as catechol and lead to higher conversion or a better quality product.

The present results for thermal runs are consistent with those in literature. However, there is no comparable literature data for the desirable and undesirable effects of water addition in catalytic liquefaction. Ruether et al. [1987] reported that in uncatalyzed systems, a substantial water partial pressure at fixed H_2 partial pressure increases the conversion of Illinois #6 bituminous coal, but in the runs using 0.1% dispersed Mo catalyst at 427 °C for 60 min, highest conversions are obtained without added water. How water affects the catalytic reaction is not clear. The present results suggest that water promotes coal liquefaction with dispersed MoS_2 catalyst at 350 °C, but has less promoting effect to thermal reaction at 400 °C and can deactivate or passivate the catalyst at 400 °C.

CONCLUSIONS

In summary, water can be excellent promoter or undesirable inhibitor for coal conversion in catalytic pretreatment/liquefaction, depending on the reaction systems and conditions. For catalytic reaction at 350°C, adding a small amount of water has a dramatic promoting effect on coal conversion, but a significant inhibiting effect of water is observed for catalytic runs at 400 °C. It appears that water and dispersed molybdenum sulfide catalyst can act in concert to promote coal conversion and oil production at 350 °C, but water can passivate the catalyst at 400°C. The remarkably high conversion level at low-temperature (350 °C) achieved with the co-use of ATTM and added water (catalytic hydrothermal pretreatment) may give rise to new opportunities for developing novel low-severity catalytic liquefaction processes with significantly reduced oprational costs.

FUTURE PLANS

Most of our work to date has addressed detailed studies with selected coals and ATTM catalyst precursor. As the project proceeds toward completion, we will extend the work to incorporate additional low-rank coals and bituminous coals, and additional catalyst precursors, such as Molyvan and molybdenum hexacarbonyl. We will also try to clarify the effects of water in catalytic reactions, particularly the origin of synergetic effects between dispersed Mo catalyst and water, and their impacts on progressive and retrogressive reactions.

Furthermore, the coal conversion data in combination with detailed characterization of soluble products and residues will allow us to elucidate the following: 1) the "reactive" structures in raw and pretreated coals; 2) the structures responsible for retrogressive reactions; 3) the effect of various pretreatment on coal conversion & product quality; 4) the structure-reactivity relationship for effects of temperature, catalyst, coal rank, and solvent on coal preconversion and liquefaction.

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Table 1. Properties of Department of Energy Coal Samples (DECS) from DOE/Penn State Coal Sample Bank

	DECS-1	DECS-8	DECS-9
Proximate (wt%)			
Moisture	29.9	28.4	24.7
Fixed Carbon	25.8	29.4	37.1
Volatile Matter	33.2	32.3	33.5
Ash	11.1	9.9	4.8
Ultimate (wt%, dmmf)			
Carbon	76.1	75.8	76.1
Hydrogen	5.5	5.2	5.1
Nitrogen	1.5	1.0	0.9
Organic Sulfur	1.1	0.5	0.3
Oxygen (by diff)	15.8	17.5	17.5
Source & Rank			
State	Texas	Wyoming	Montana
County	Freestone	Campbell	Bighorn
Seam	Bottom	Wyodak	Dietz
ASTM Rank	Sub C	Sub C	Sub B
Sampling Date	12/11/89	6/11/90	6/12/90
Storage Method	Ar/Multi-layer Bag	Ar/Multi-layer Bag	Ar/Multi-layer Bag

Table 2. Aromaticity of Liquefaction Residues of DECS-1 Coal by CPMAS ^{13}C NMR

ATTM Solvent	No No	Yes No	No Tetralin	Yes Tetralin	No 1-MN	Yes 1-MN
Temp, °C						
250	0.52	0.50	0.50	0.52	0.53	0.52
300	0.55	0.45	0.63	0.57	0.60	0.58
350	0.64	0.59	0.69	0.62	0.74	0.66
400	0.80	0.78	0.85	0.76	0.86	0.72
450	0.89	0.85	0.91	0.94	0.94	0.93

Figure 1.

Conversion of Non-Catalytic Experiments

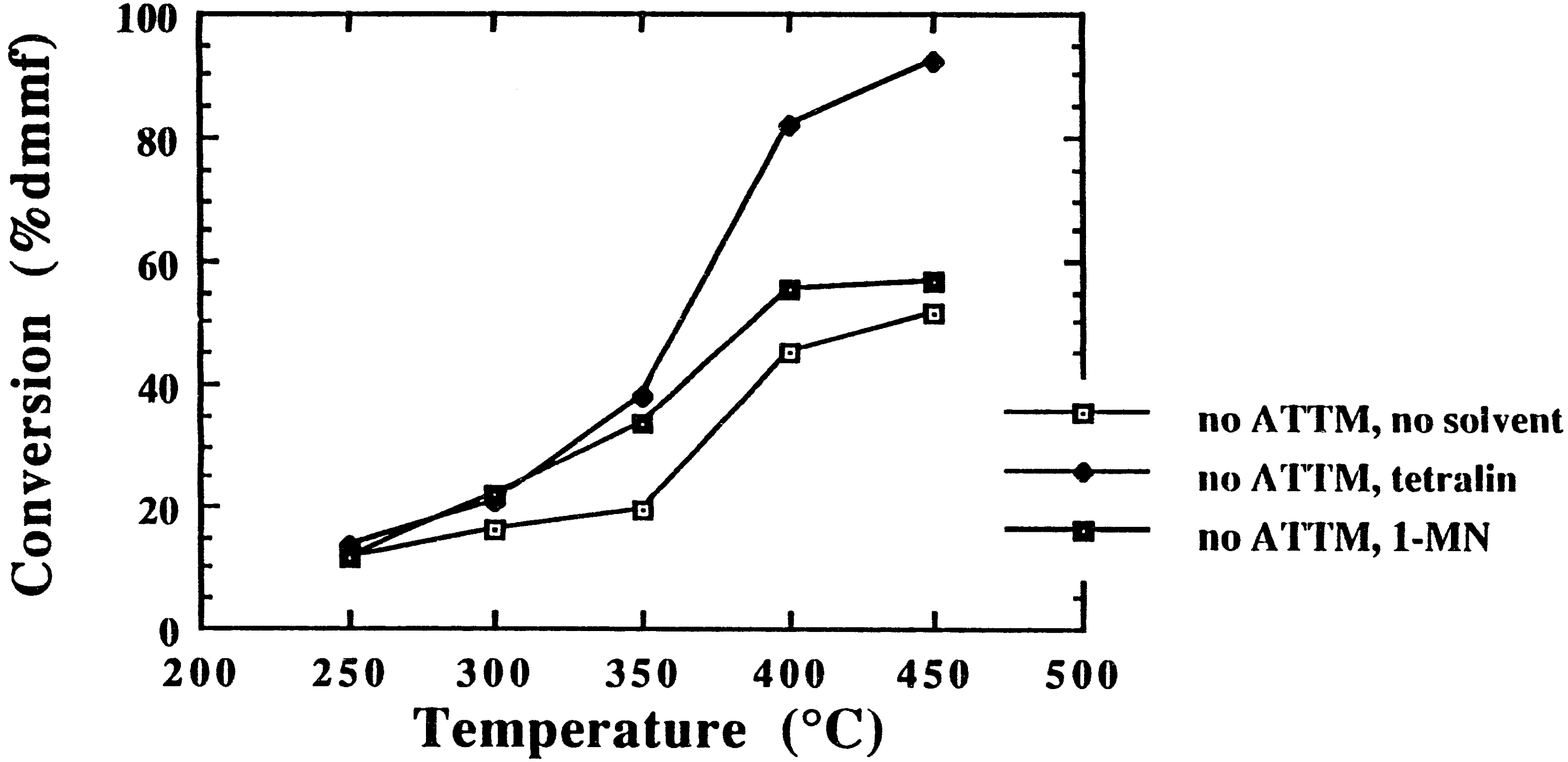


Figure 2.

Conversion of Catalytic Experiments

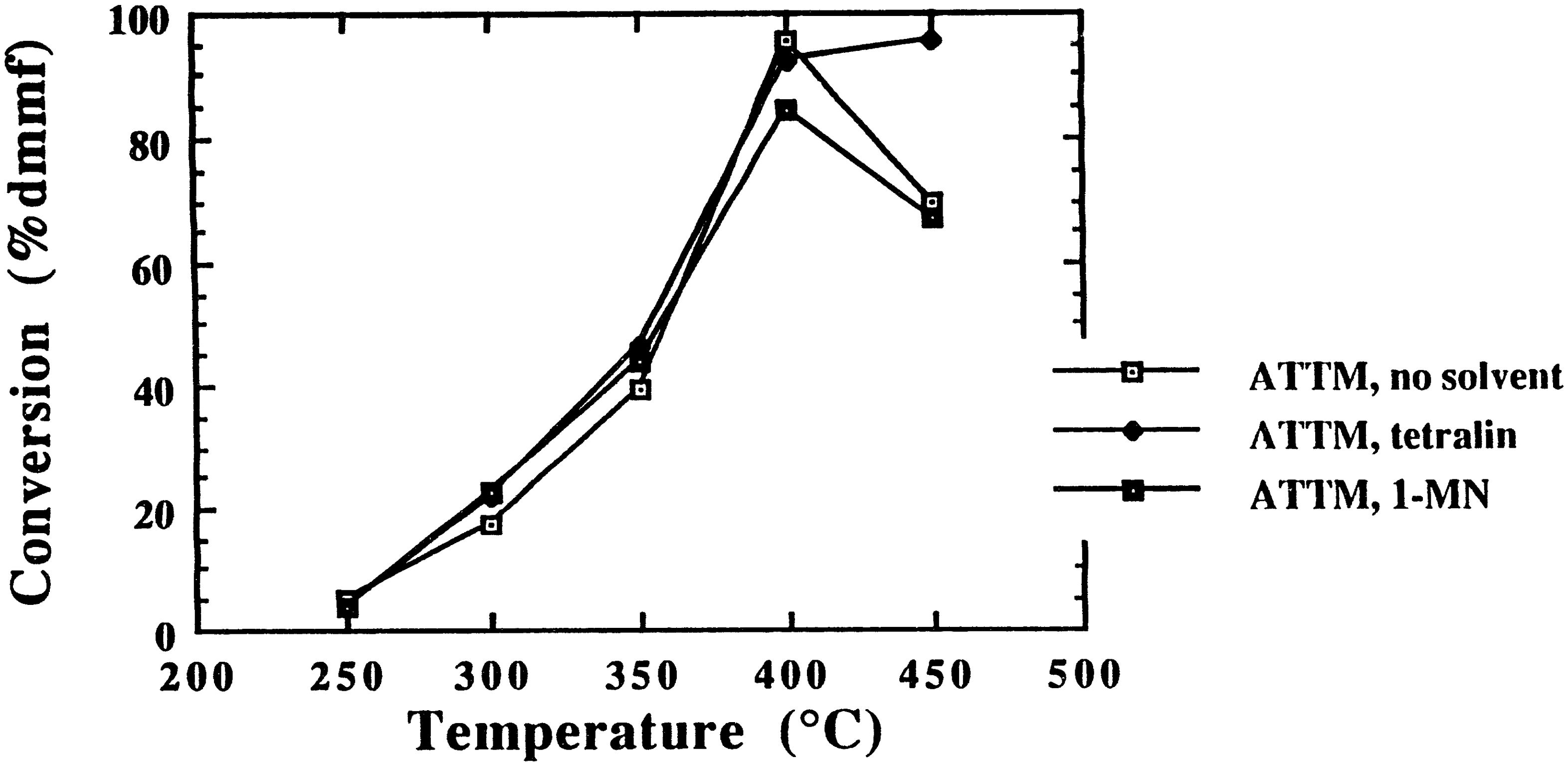


Figure 3.

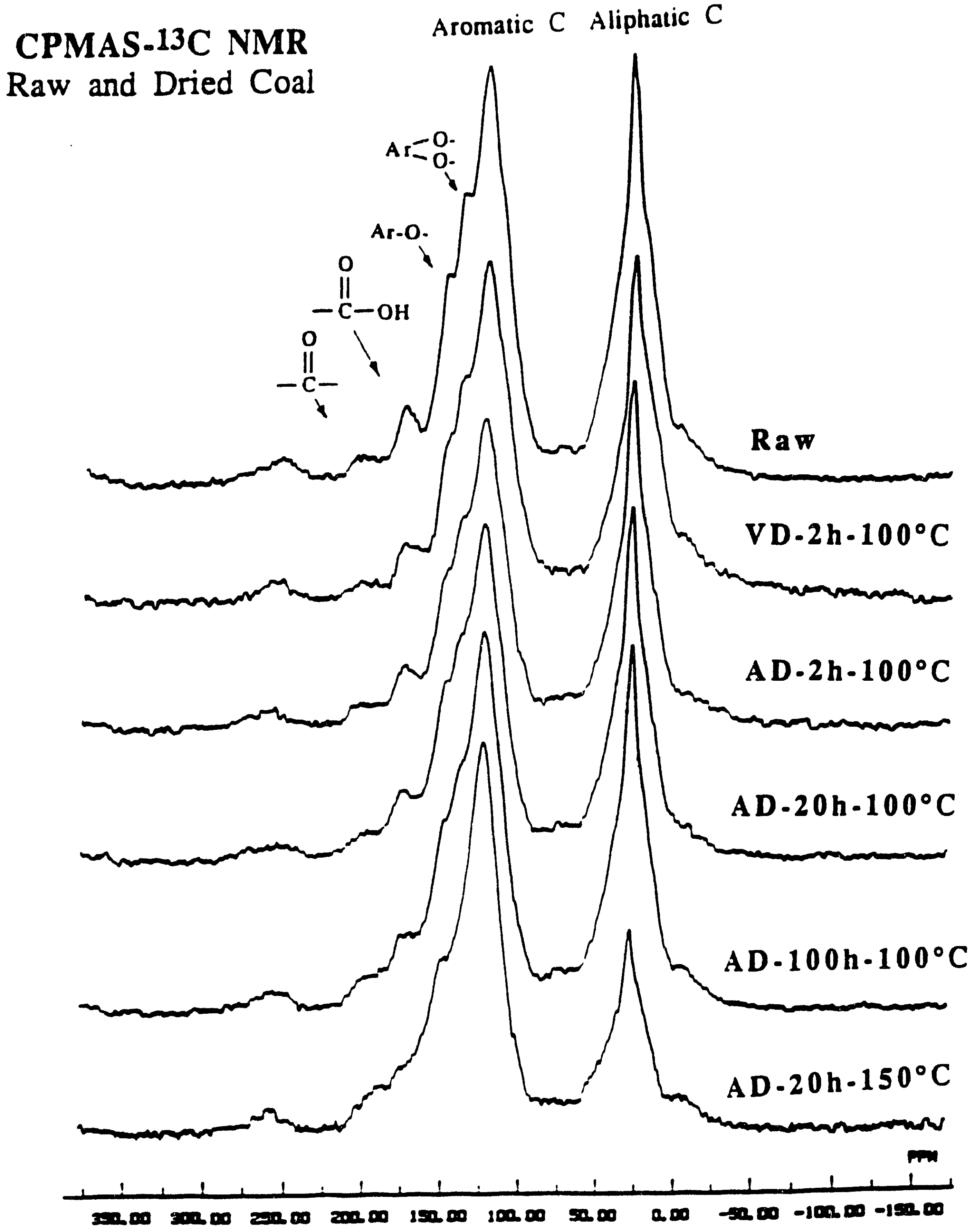

CPMAS-^{13}C NMR
Raw and Dried Coal
Aromatic C
Aliphatic C
Ar<O- O-
Ar-O-
—C(=O)—OH
—C(=O)—
Raw
VD-2h-100°C
AD-2h-100°C
AD-20h-100°C
AD-100h-100°C
AD-20h-150°C
PPM
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
-100.00
-150.00

Figure 4.

FTIR-difference spectra between the Air-dried and Vacuum-dried coal.

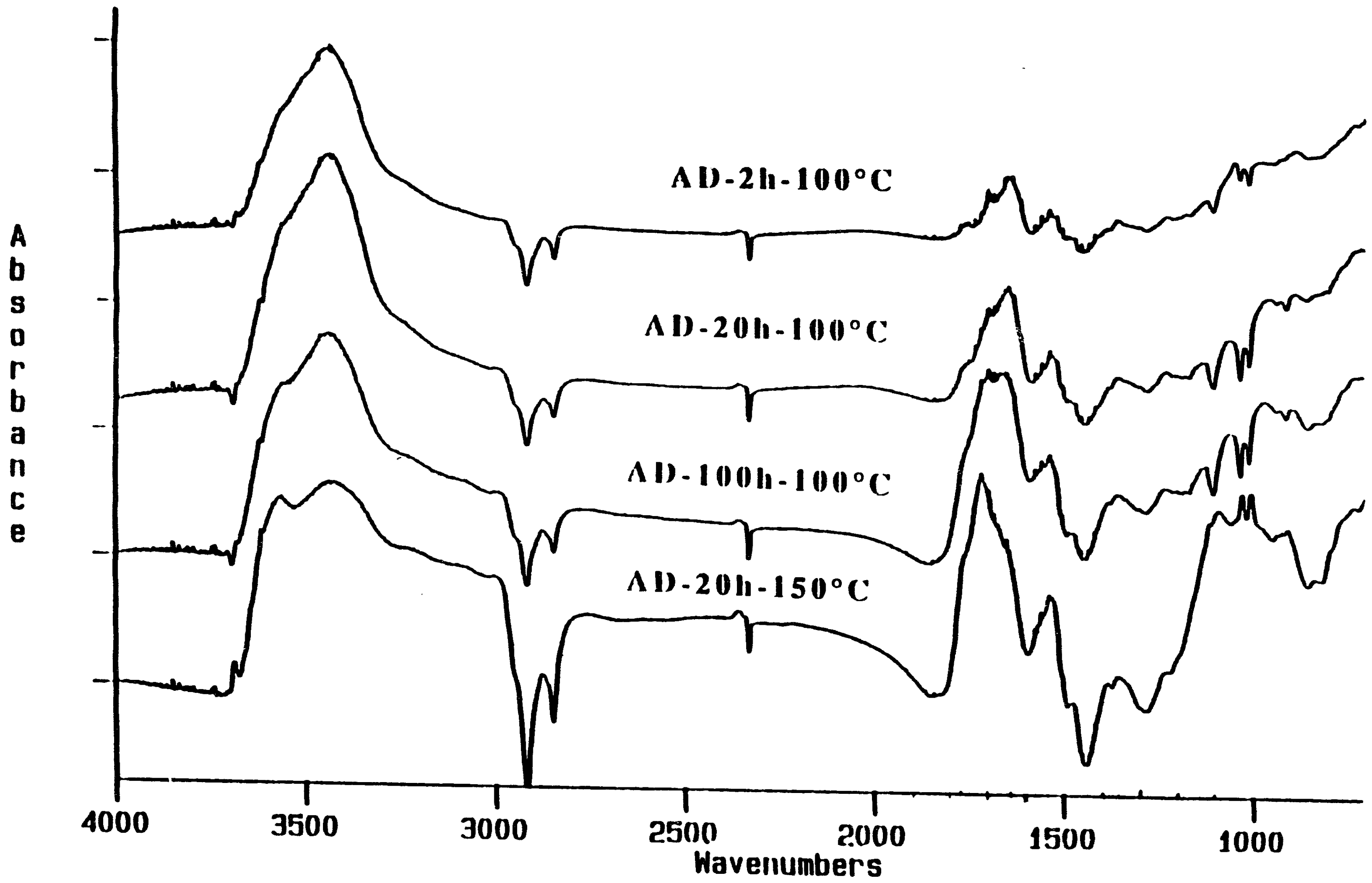
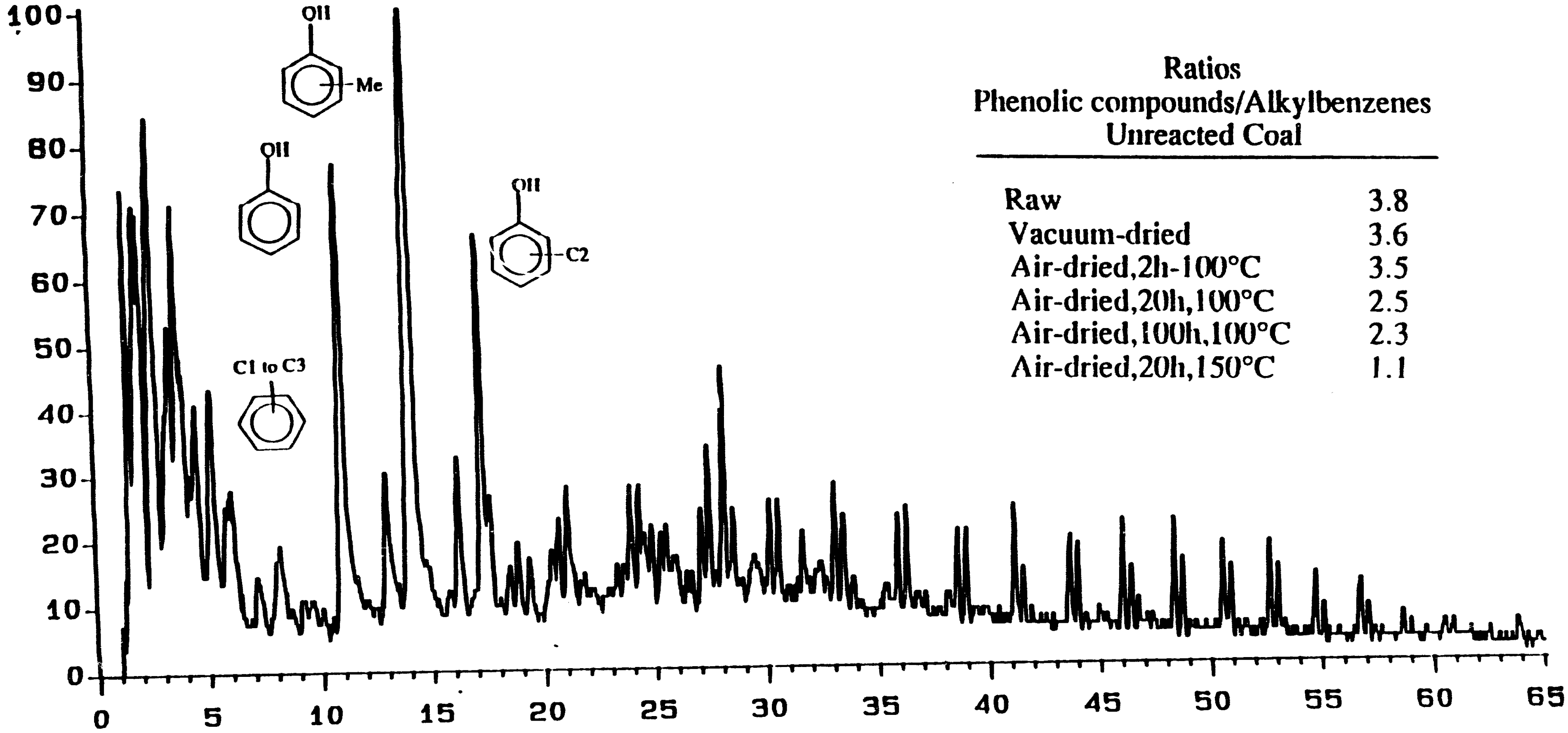


Figure 5.

Pyrolysis-GC-MS profile of the Raw coal.



Ratios Phenolic compounds/Alkylbenzenes Unreacted Coal	
Raw	3.8
Vacuum-dried	3.6
Air-dried,2h-100°C	3.5
Air-dried,20h,100°C	2.5
Air-dried,100h,100°C	2.3
Air-dried,20h,150°C	1.1

Figure 6.

Products Distributions for Thermal Runs at 350 °C with 1-MN

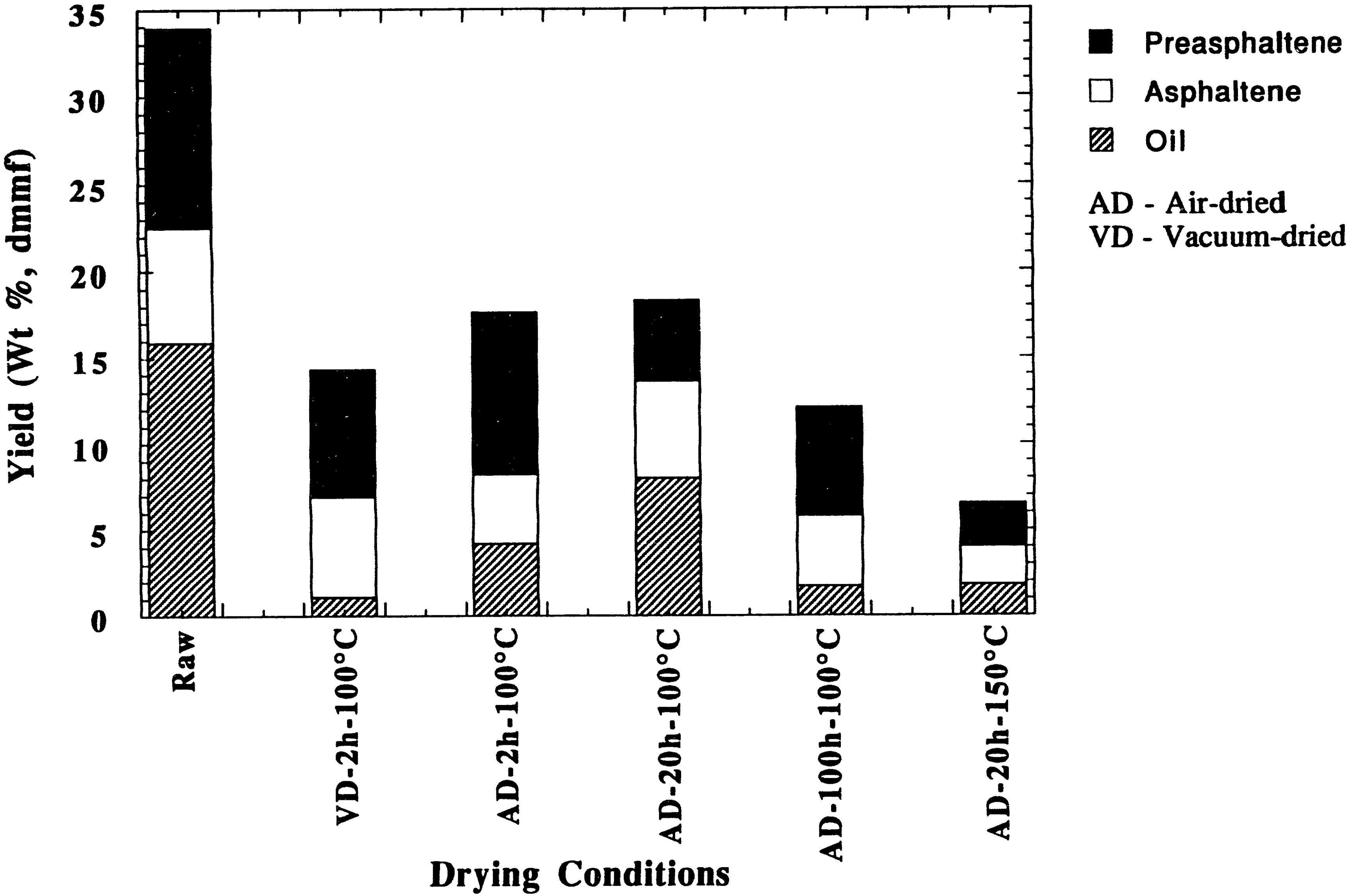


Figure 7.

Products Distributions for Catalytic Runs at 350 °C with 1-MN.

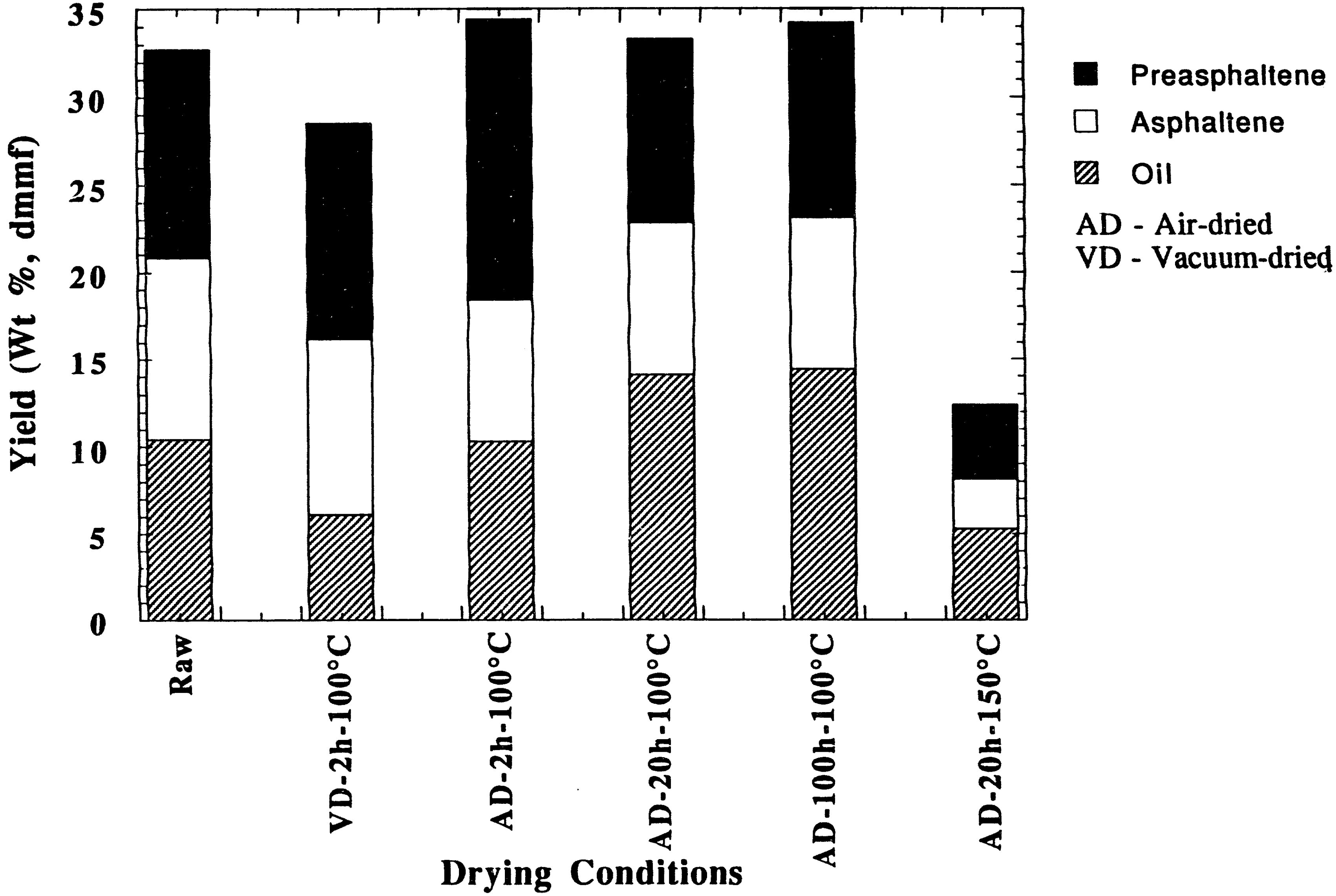


Figure 8.

Role of Water Reflected by Drying Effect // Solvent-Free

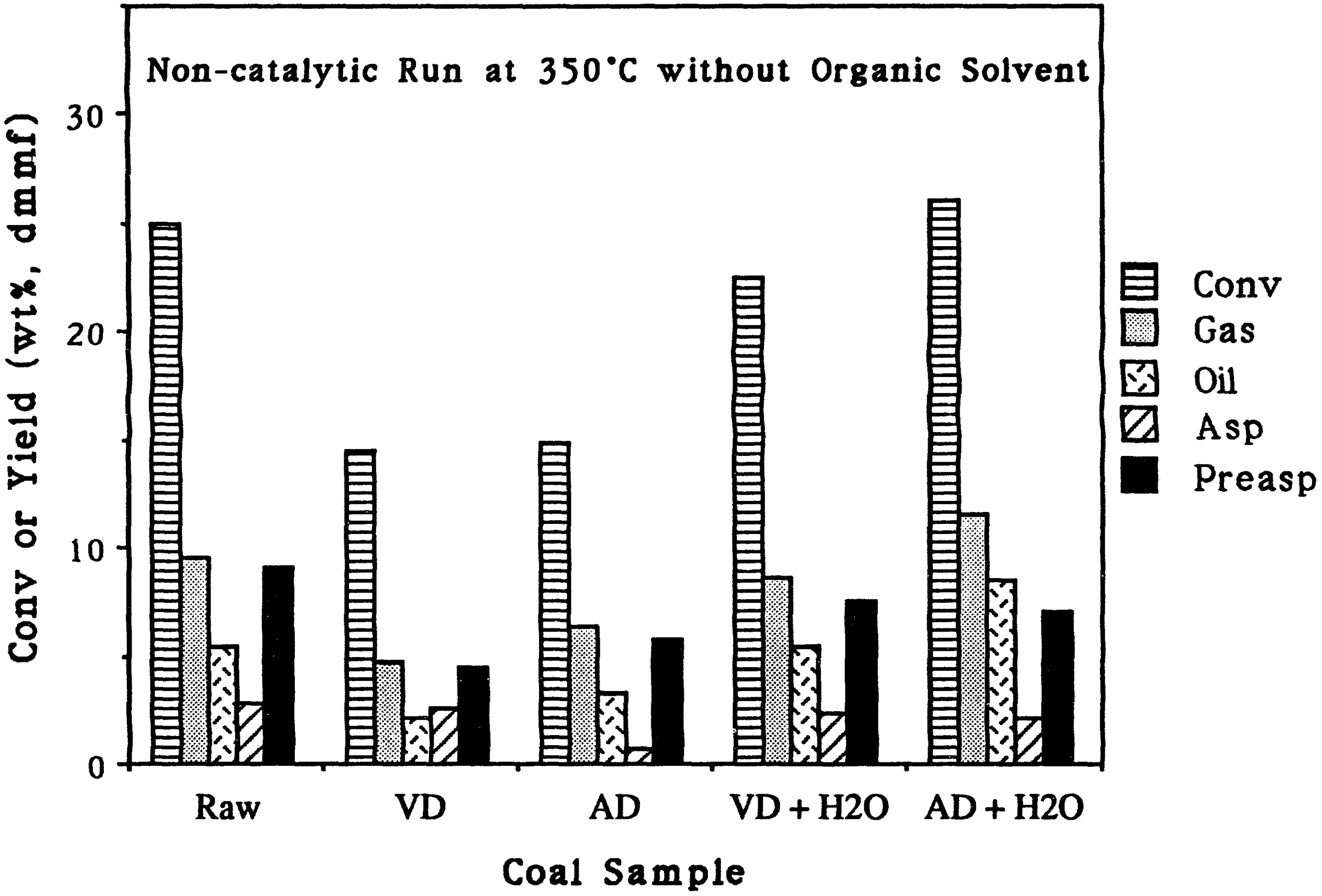


Figure 9.

Role of Water Reflected by the Drying Effect // with 1-MN

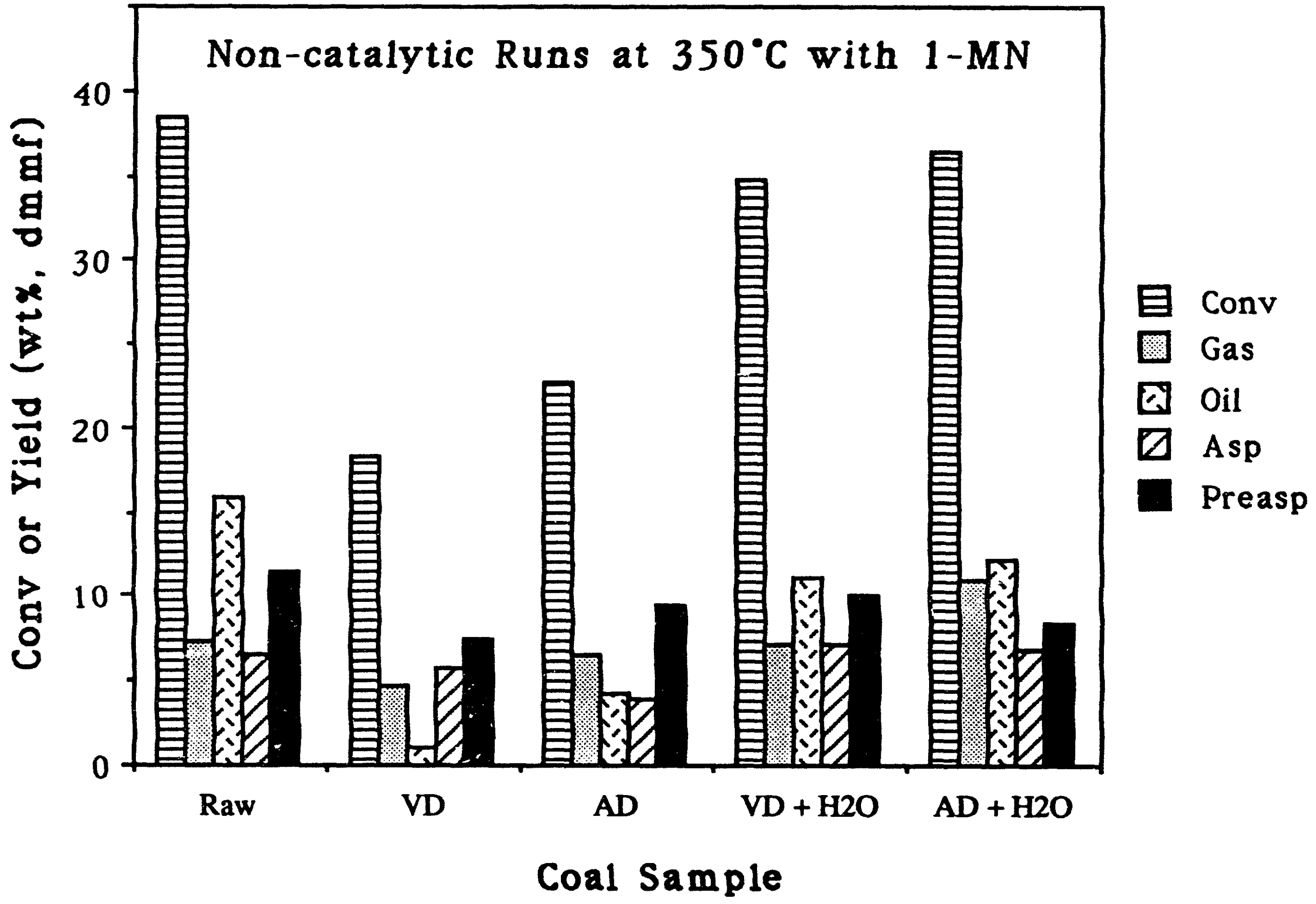
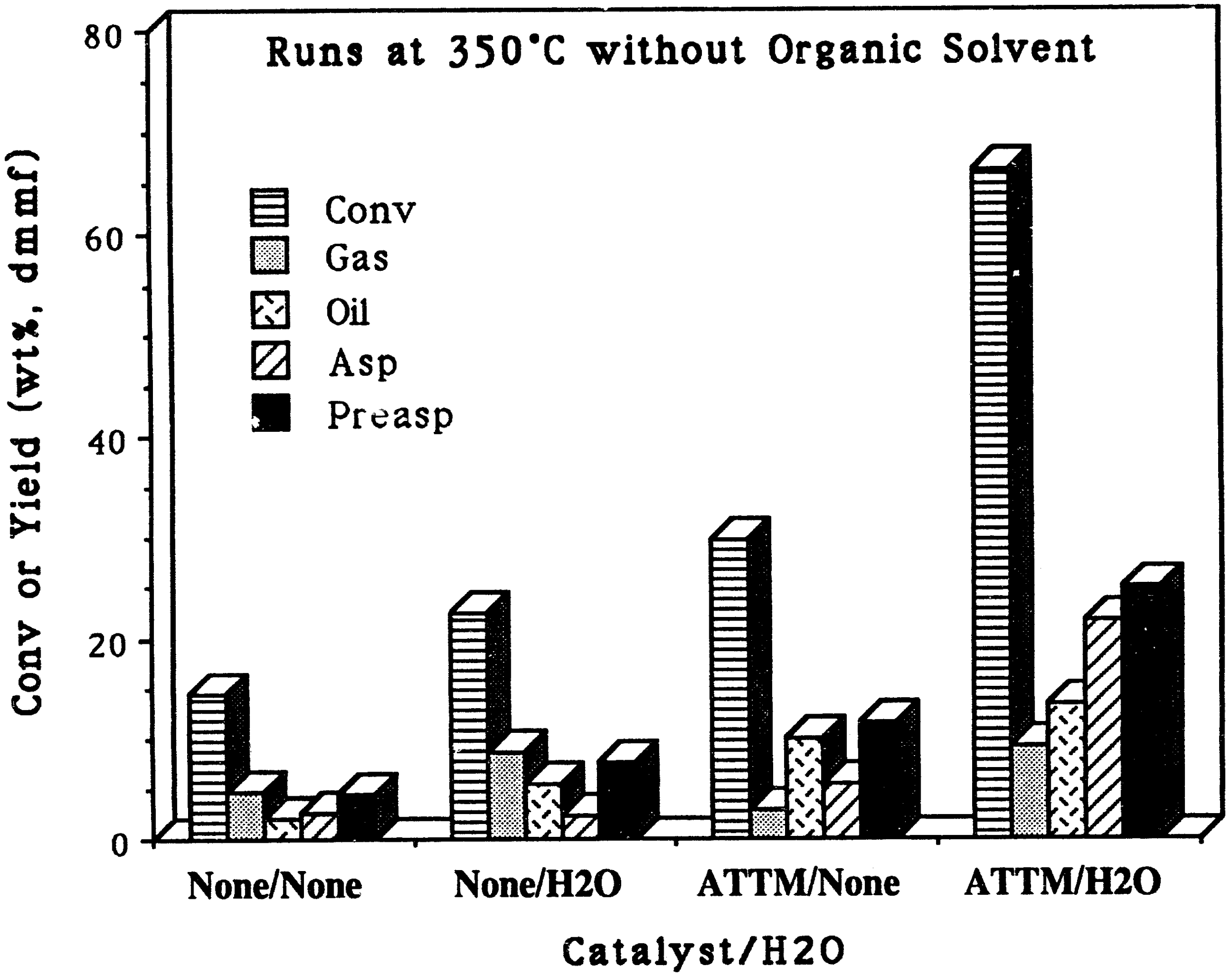


Figure 10.

** Effect of Water Addition on Coal Conversion ** in Catalytic Liquefaction Using In-Situ Generated MoS_2 at 350 °C



Runs at 350°C without Organic Solvent

** C. Song, A. Saini and H. Schobert, ACS Fuel Chem. Prepr. 1993, 38 (3), 1031.

Figure 11.

Effect of Water Addition on Coal Conversion in Catalytic Liquefaction Using In-Situ Generated MoS_2 at 350 °C

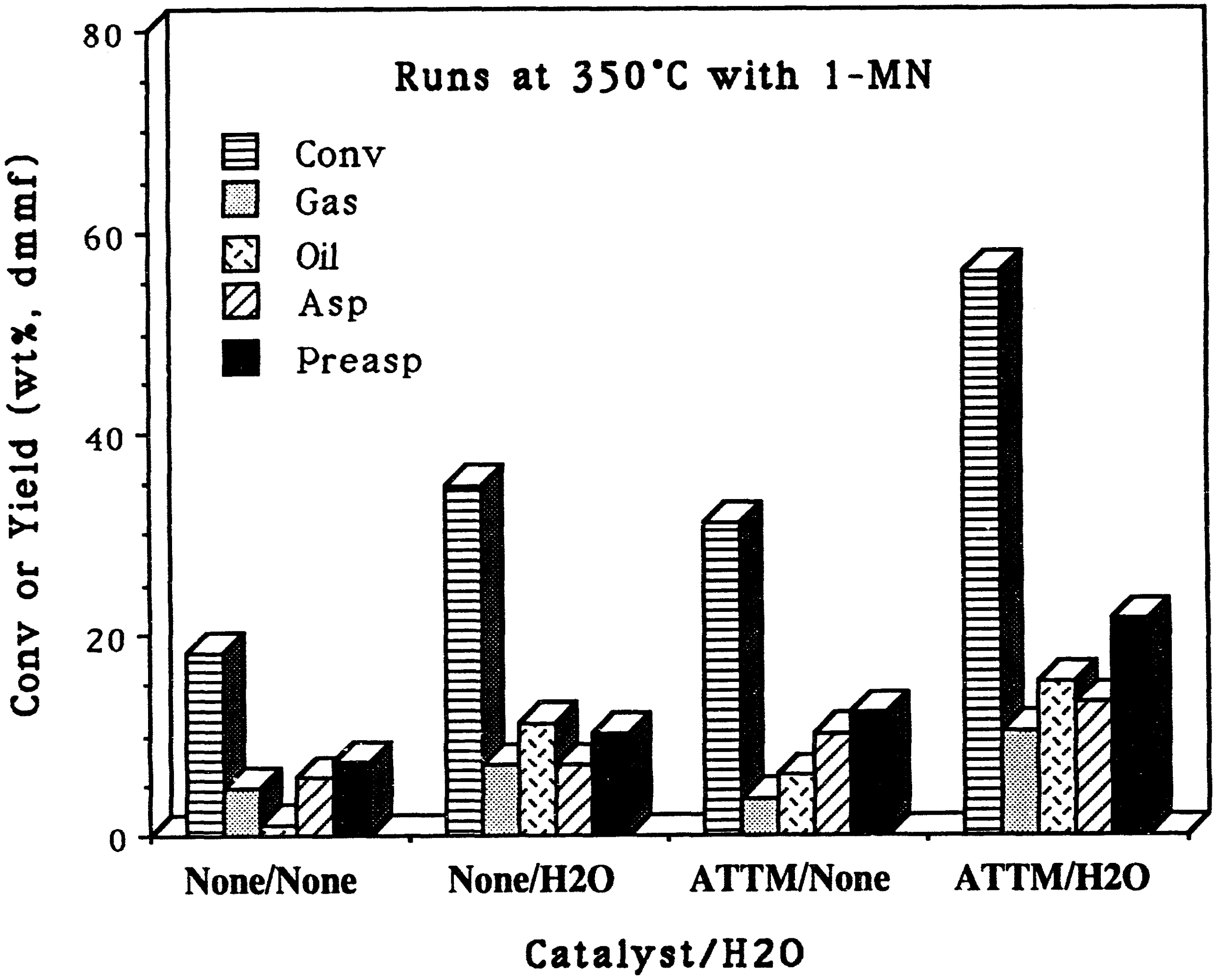


Figure 12.

Effect of Water on Gas Formation at 350 °C

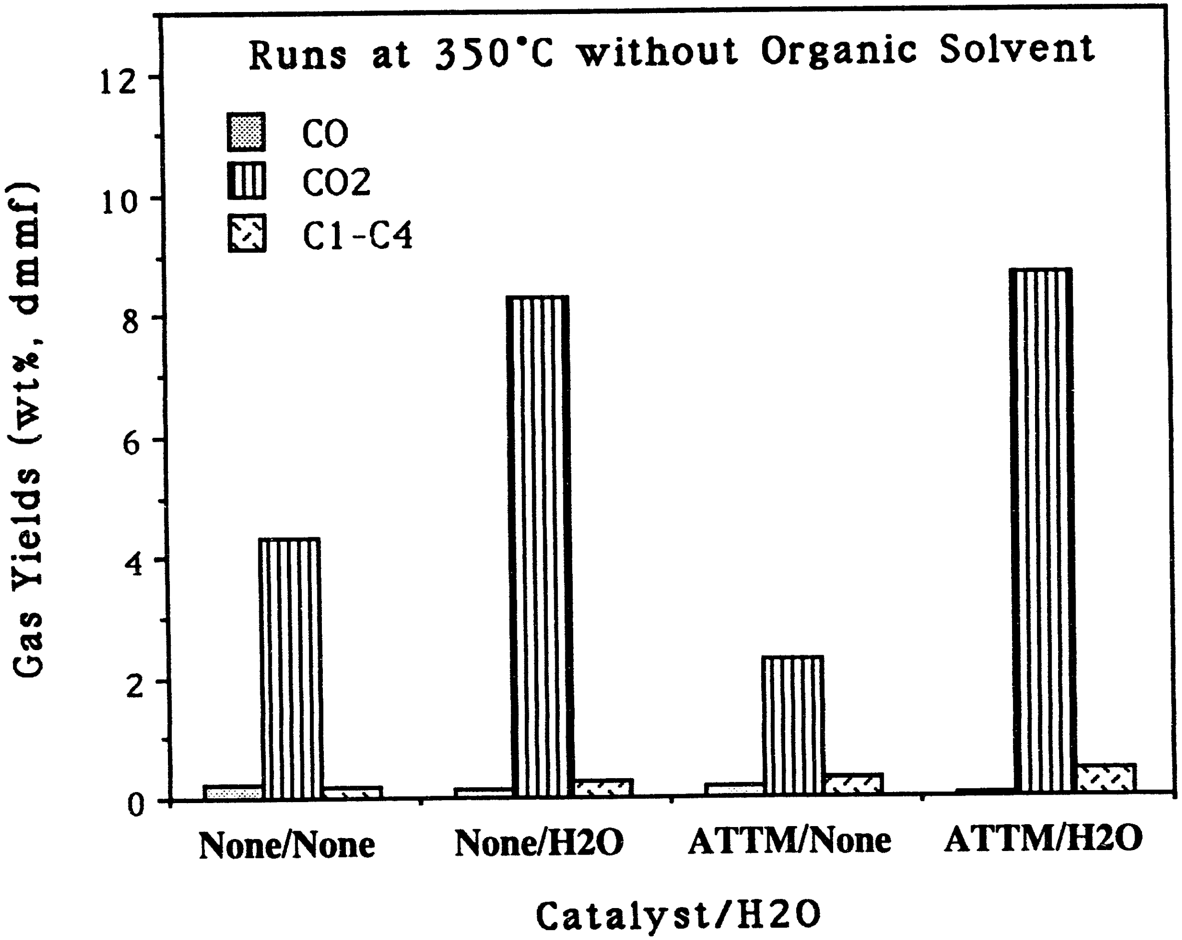


Figure 13.

Effect of Water Addition in Catalytic Liquefaction at 400 °C