TABLE 1

CARBON FORMATION DURING METHANE PYROLYSIS THERMODYNAMIC EQUILIBRIUM

Pressure = 1 bar

Molar Composition	TEMPERATURE				
	600	800	900	1200	1400
CH_4	0.41	8.4×10^{-2}	3.7×10^{-2}	5.8×10^{-3}	2.3×10^{-3}
C_2H_2	10^{-11}	10^{-8}	10^{-7}	1.4×10^{-5}	1.2×10^{-3}
C_2H_4	10^{-6}	--	--	--	--
C_3H_6	10^{-10}	--	--	--	--
C_4H_8	10^{-14}	--	--	--	--
C_6H_6	10^{-15}	--	--	--	--
$C_6H_4(CH_3)_2$	10^{-21}	--	--	--	--
C (s)	0.58	0.92	0.96	0.99	1.0
H_2	1.18	1.83	1.90	1.98	2.0

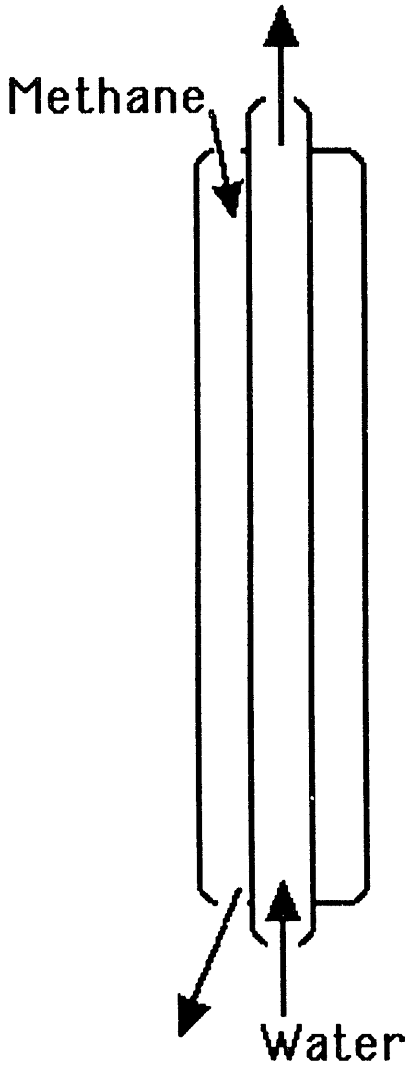


Figure 1. Concept of quench reactor.

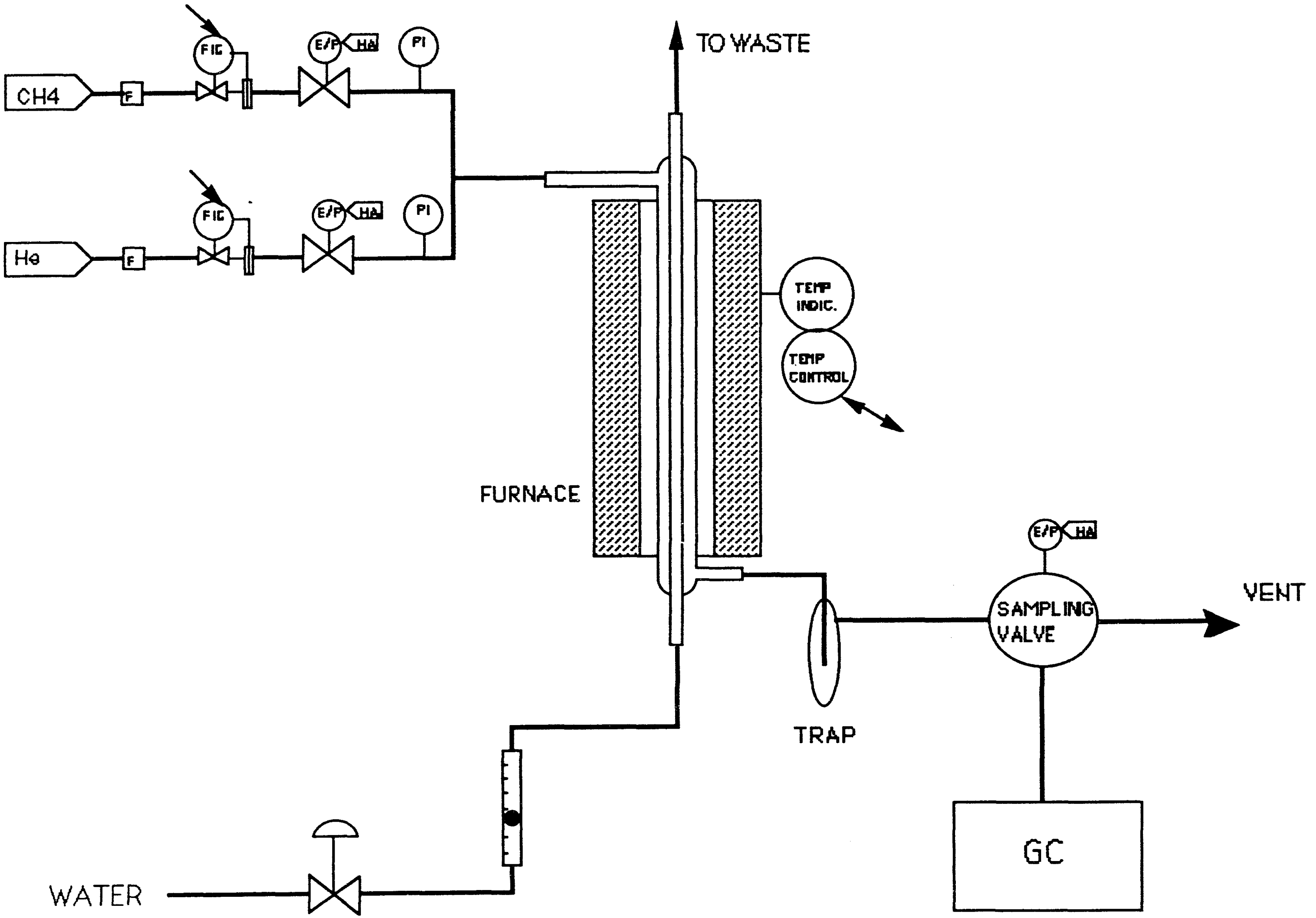


Figure 2. Schematic of reactor system.

Figure 3.
EQUILIBRIUM METHANE CONVERSION

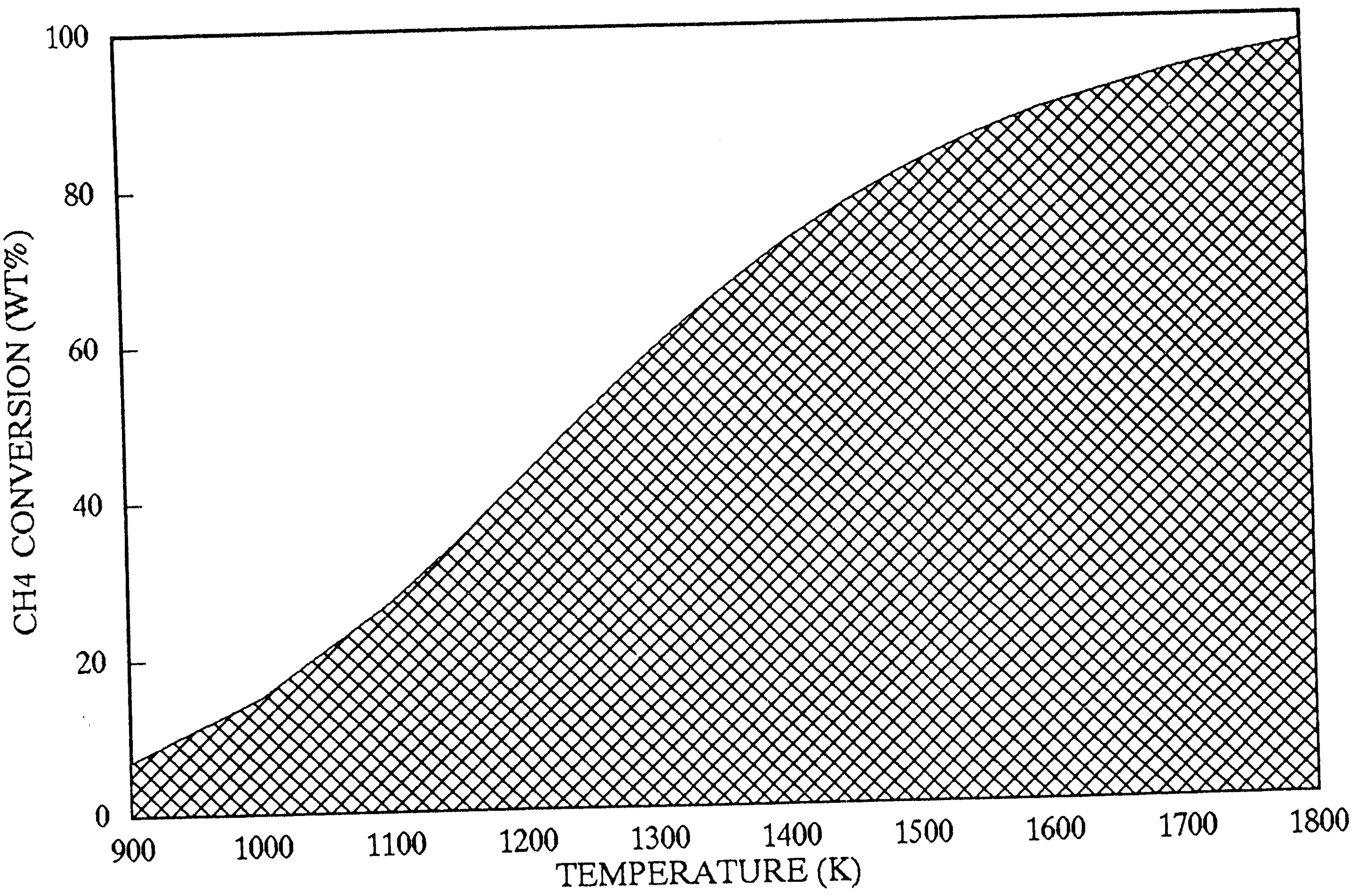


Figure 4.

EQUILIBRIUM PRODUCT DISTRIBUTION

(INCLUDING HYDROGEN)

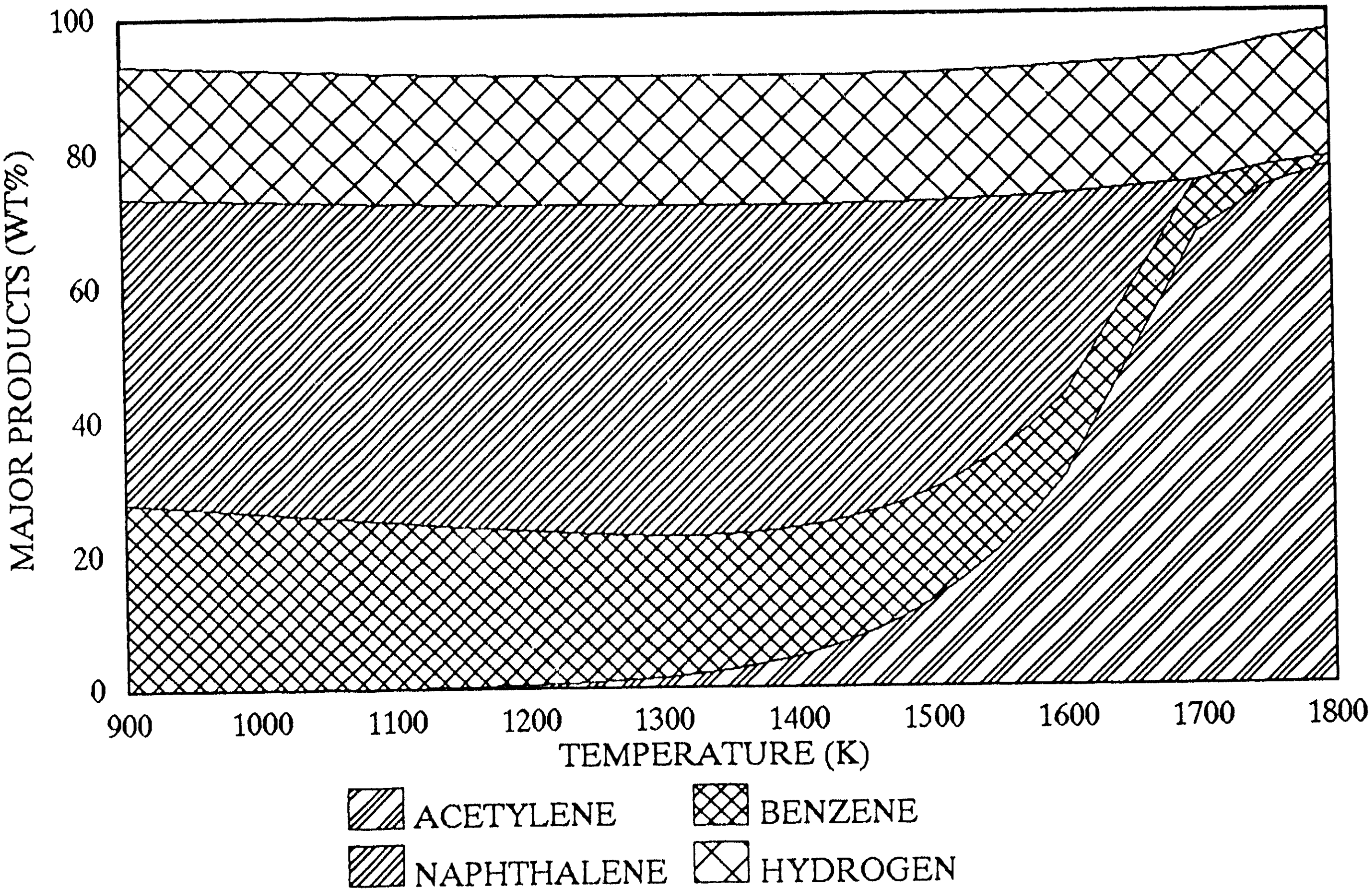
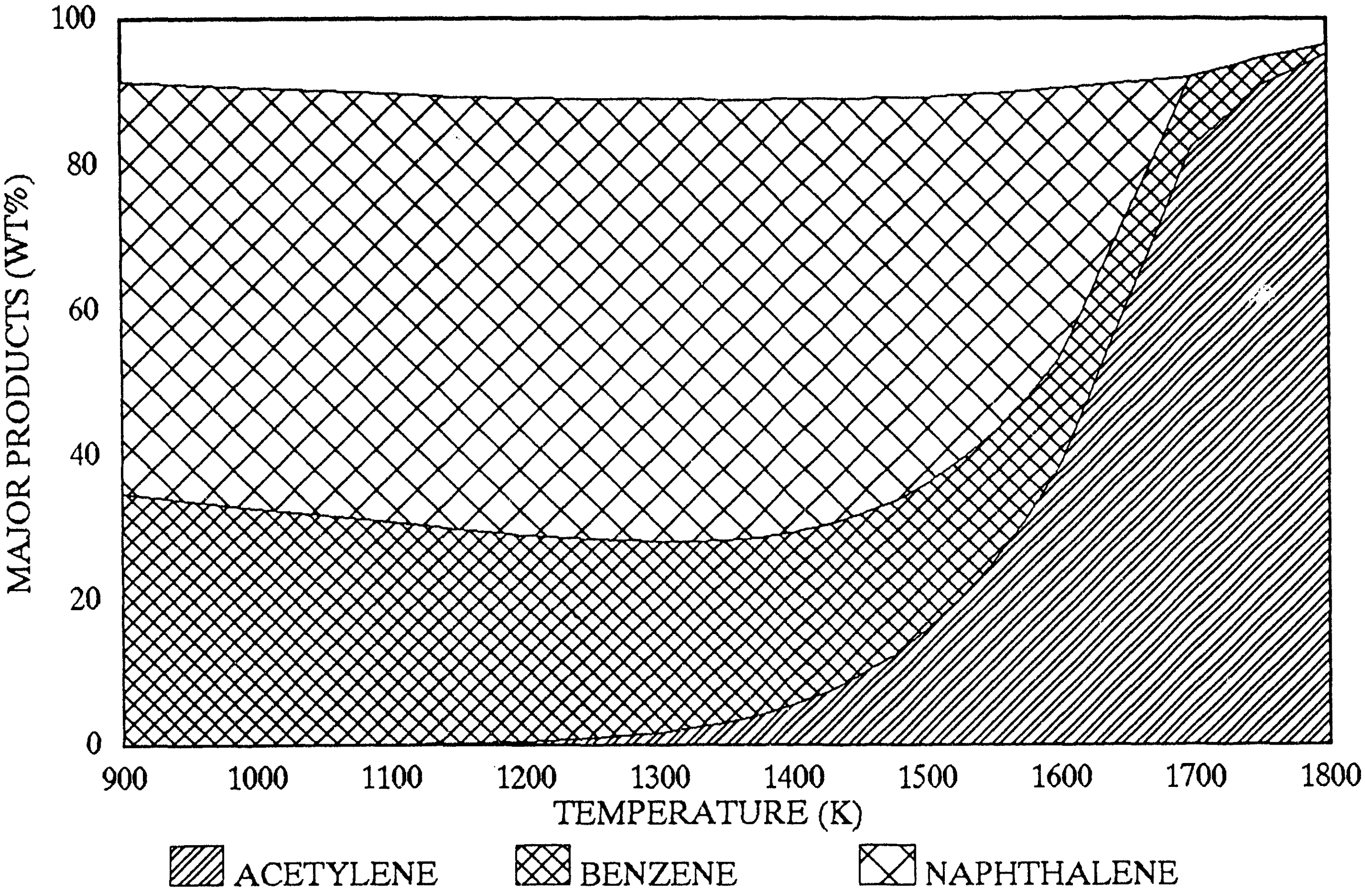


Figure 5.



EQUILIBRIUM PRODUCT DISTRIBUTION

(EXCLUDING HYDROGEN)

Figure 6.

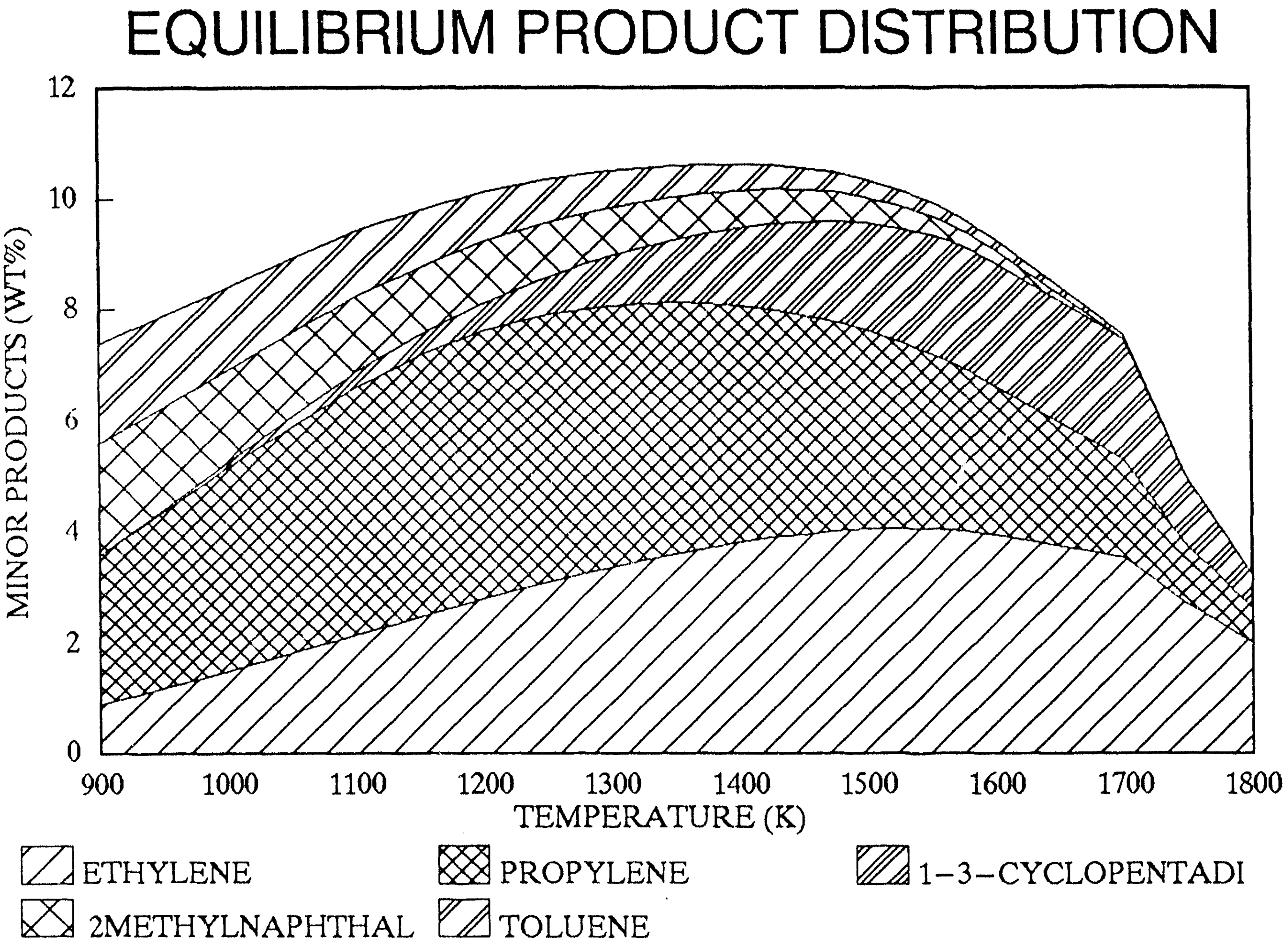

EQUILIBRIUM PRODUCT DISTRIBUTION
MINOR PRODUCTS (WT%)
0
2
4
6
8
10
12
TEMPERATURE (K)
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
ETHYLENE
PROPYLENE
1-3-CYCLOPENTADI
2METHYLNAPHTHAL
TOLUENE

Figure 7.

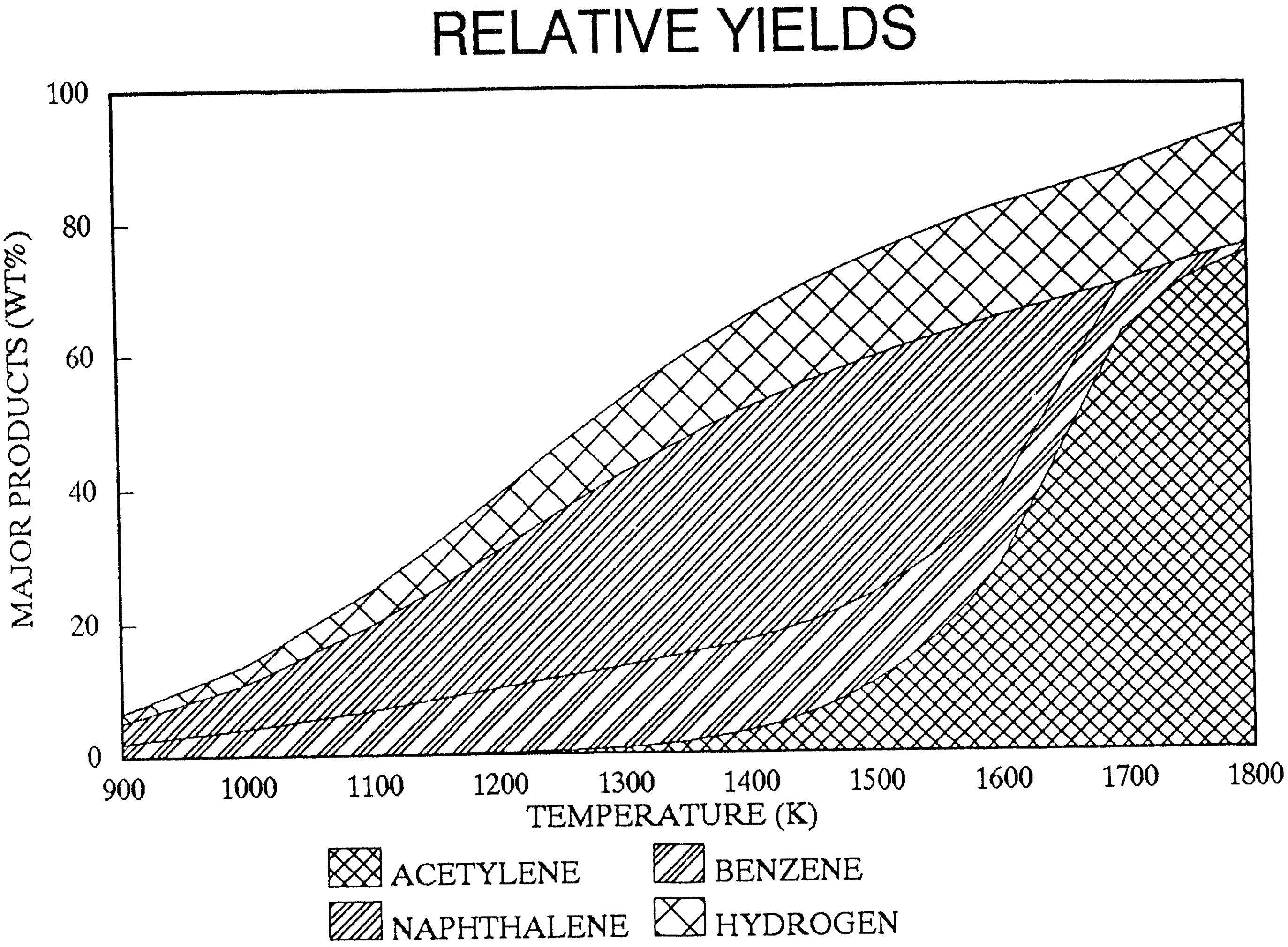

RELATIVE YIELDS
MAJOR PRODUCTS (WT%)
0
20
40
60
80
100
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
TEMPERATURE (K)
ACETYLENE
BENZENE
NAPHTHALENE
HYDROGEN

Figure 8.

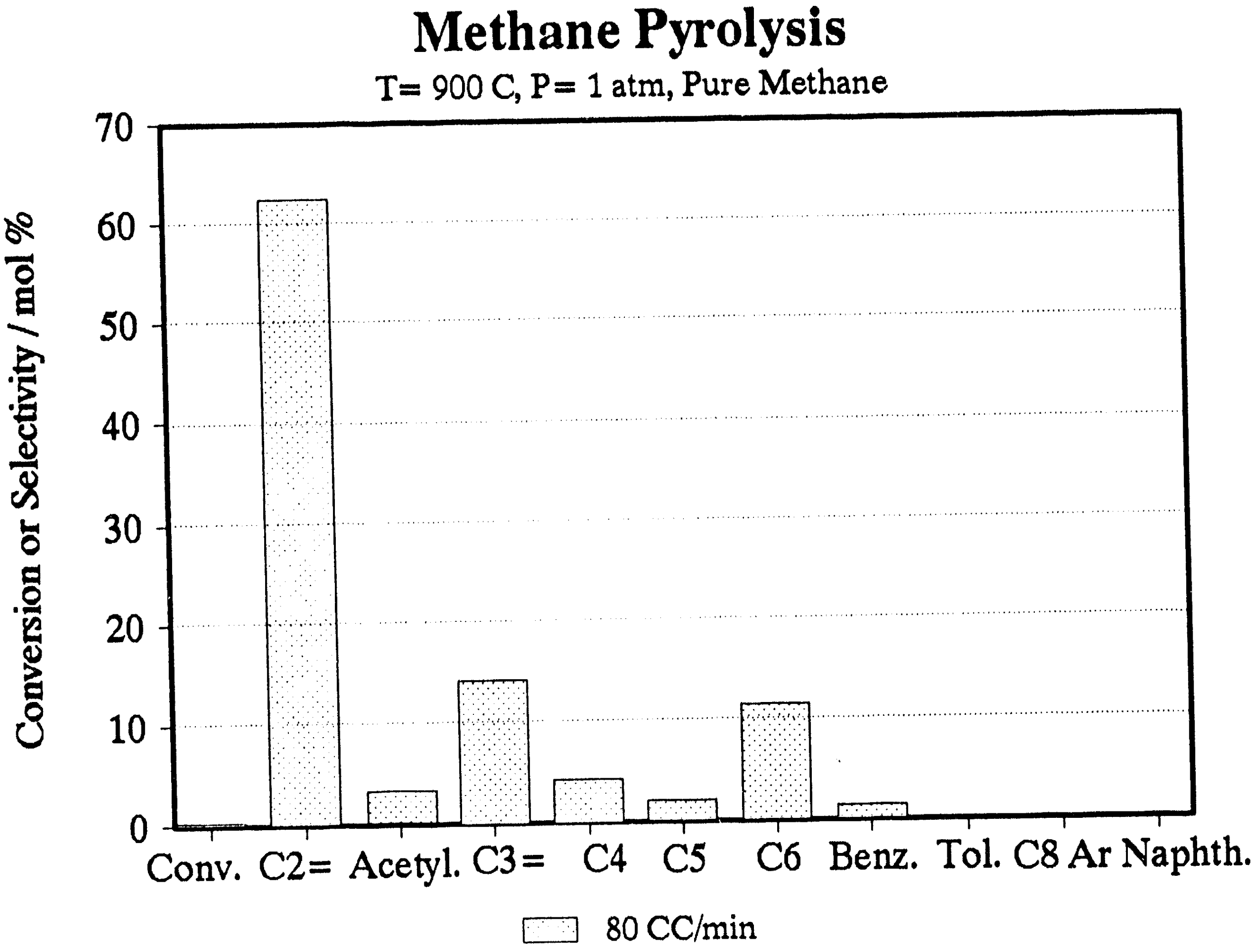
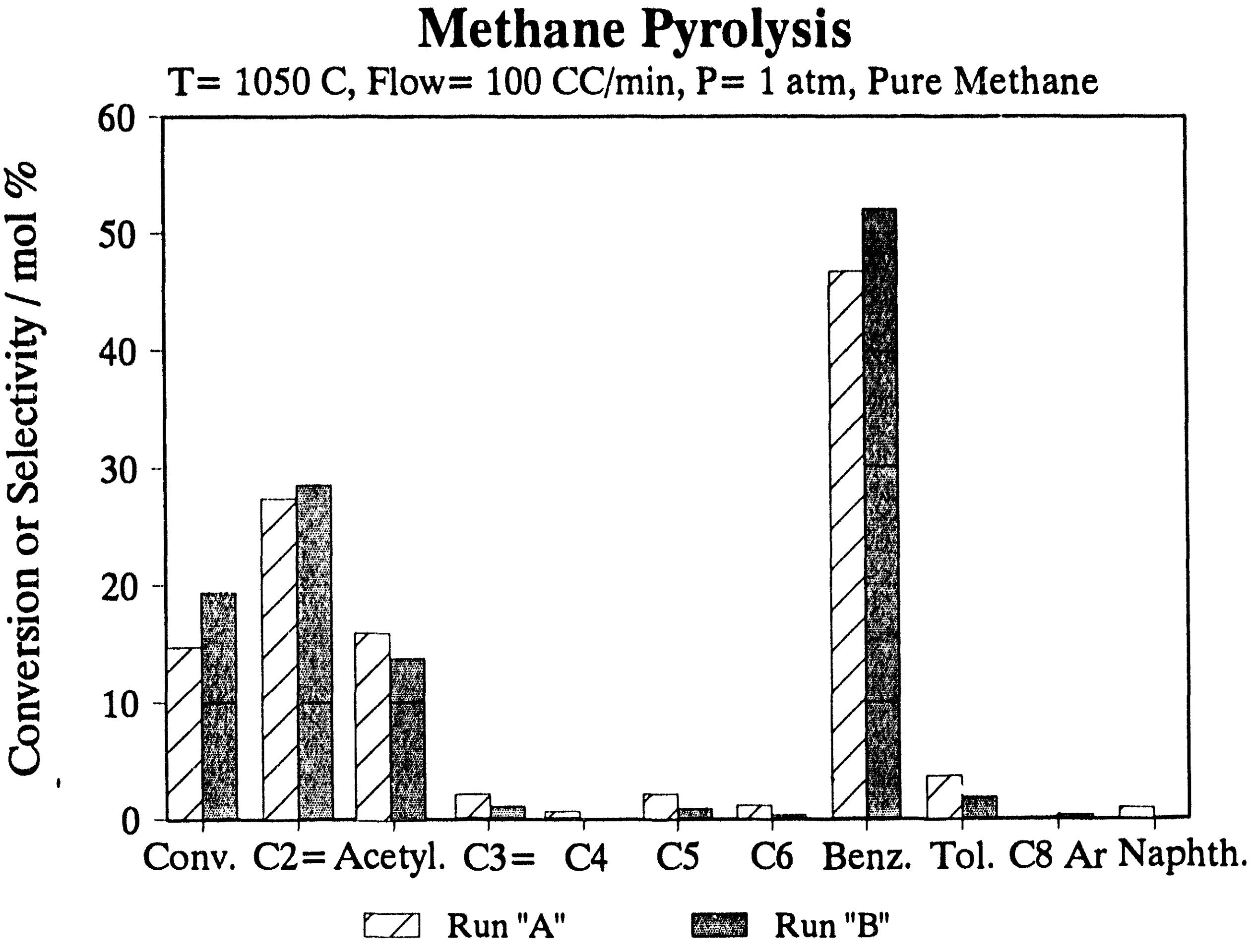
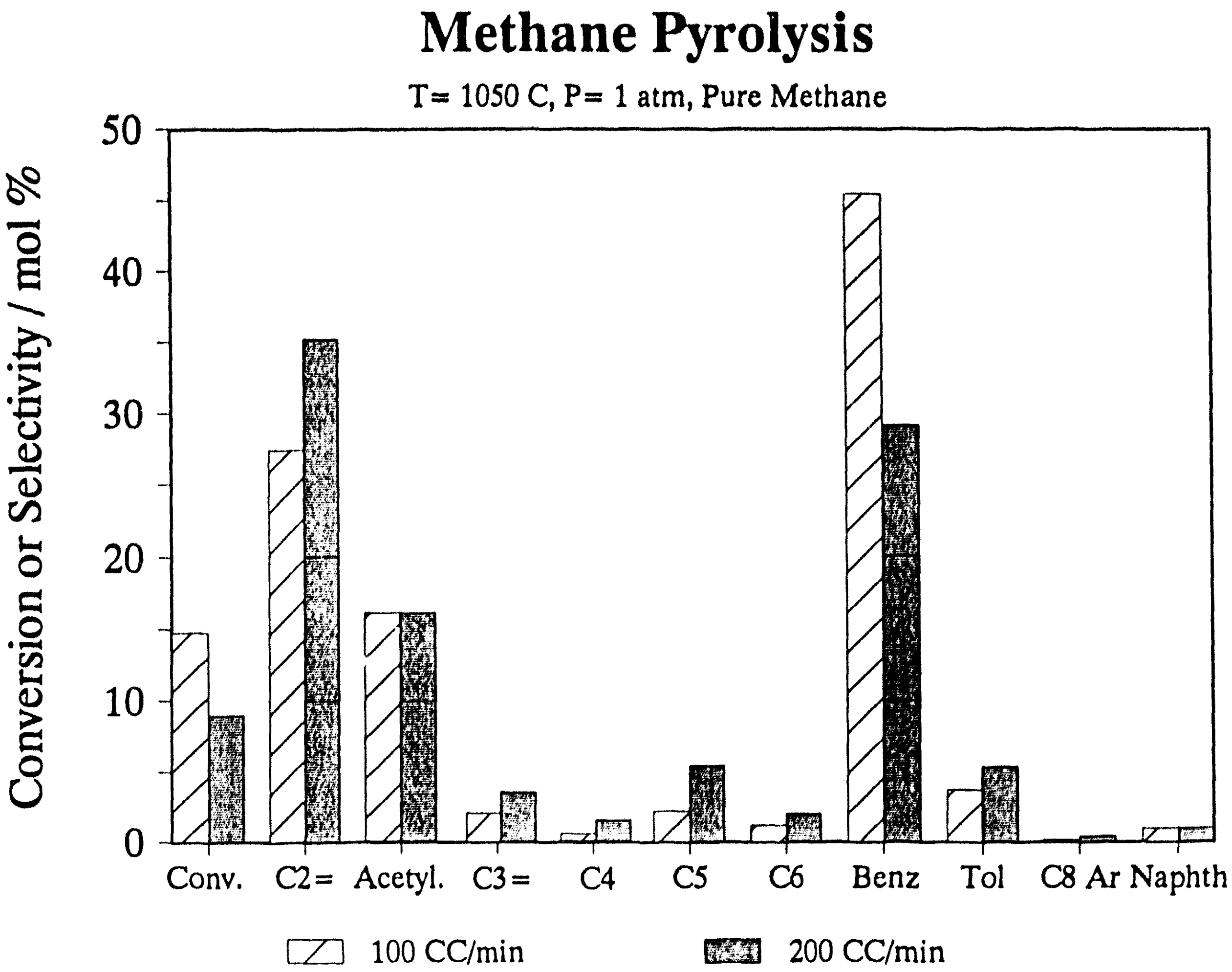

Methane Pyrolysis
T= 900 C, P= 1 atm, Pure Methane
Conversion or Selectivity / mol %
70
60
50
40
30
20
10
0
Conv.
C2=
Acetyl.
C3=
C4
C5
C6
Benz.
Tol.
C8 Ar
Naphth.
80 CC/min

Figure 9.



Methane Pyrolysis
T= 1050 C, Flow= 100 CC/min, P= 1 atm, Pure Methane
Conversion or Selectivity / mol %
60
50
40
30
20
10
0
Conv.
C2=
Acetyl.
C3=
C4
C5
C6
Benz.
Tol.
C8 Ar
Naphth.
Run "A"
Run "B"

Figure 10.


Methane Pyrolysis
T= 1050 C, P= 1 atm, Pure Methane
Conversion or Selectivity / mol %
50
40
30
20
10
0
Conv.
C2=
Acetyl.
C3=
C4
C5
C6
Benz
Tol
C8 Ar
Naphth
100 CC/min
200 CC/min

DIRECT LIQUEFACTION

PROOF OF CONCEPT FACILITY FOR DIRECT LIQUEFACTION

A.G. COMOLLI
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COAL AND GAS CONVERSION CONTRACTORS' REVIEW CONFERENCE

DIRECT LIQUEFACTION

THURSDAY, OCTOBER 7, 1993

9/93
93/AGC/213

INTRODUCTION

The U.S. Department of Energy and participants have been developing and scaling-up direct coal liquefaction technologies at the 3-5 ton/day Wilsonville Advanced Coal Liquefaction Research & Development Center for about 20 years until its closure in early 1992. A contract was then awarded to Hydrocarbon Research in October of 1992 to conduct demonstrations of Direct Coal Liquefaction in a 3 ton/day Proof Of Concept facility located at the Hydrocarbon Research Development Center in Lawrenceville, N.J.

Modifications are underway on HRI's process development unit (PDU) to upgrade and prepare for a three year program, consisting of four run campaigns (*Figure 1*). The first Proof Of Concept demonstration run is on Illinois No. 6 Coal. The modifications include an on-line hydrotreater, a new second-stage reactor and reactor structure, a Rose-SR™ solid separation unit, a new pulverized coal storage and handling system, new preheaters, new flare system and, a computerized automated data collection and control system and additional back-up systems. A schematic of the PDU section of the Proof Of Concept facility is shown in *Figures 2 & 3*. Note that both filtration and Rose-SR™ solid separation options are included.

FIGURE 1

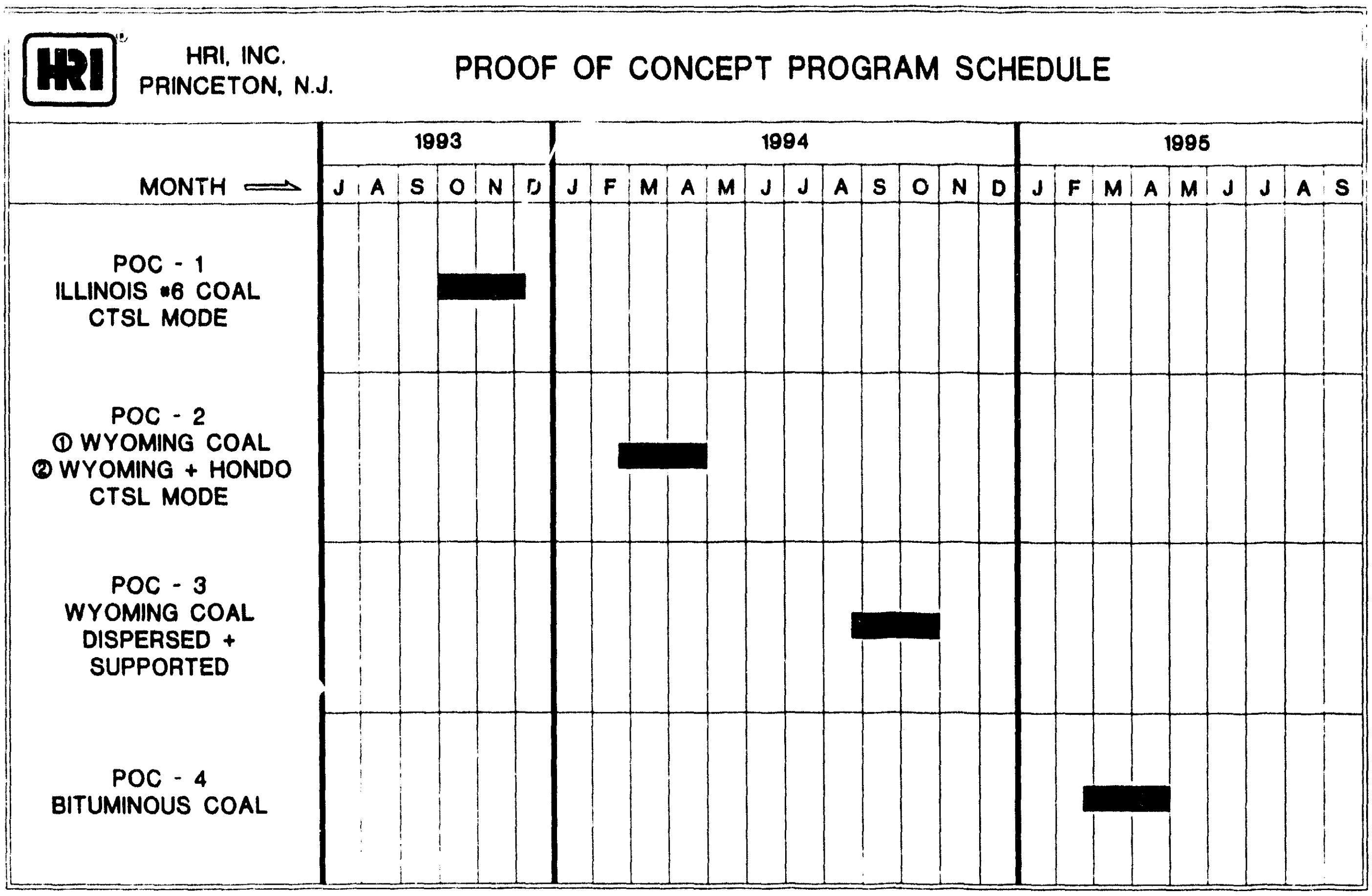

HRI
HRI, INC.
PRINCETON, N.J.
PROOF OF CONCEPT PROGRAM SCHEDULE
1993
1994
1995
MONTH
J A S O N D J F M A M J J A S O N D J F M A M J J A S
POC - 1
ILLINOIS #6 COAL
CTSL MODE
POC - 2
① WYOMING COAL
② WYOMING + HONDO
CTSL MODE
POC - 3
WYOMING COAL
DISPERSED +
SUPPORTED
POC - 4
BITUMINOUS COAL

FIGURE 2

PROCESS DEVELOPMENT UNIT NO. 260
SIMPLIFIED PROCESS FLOWSHEET

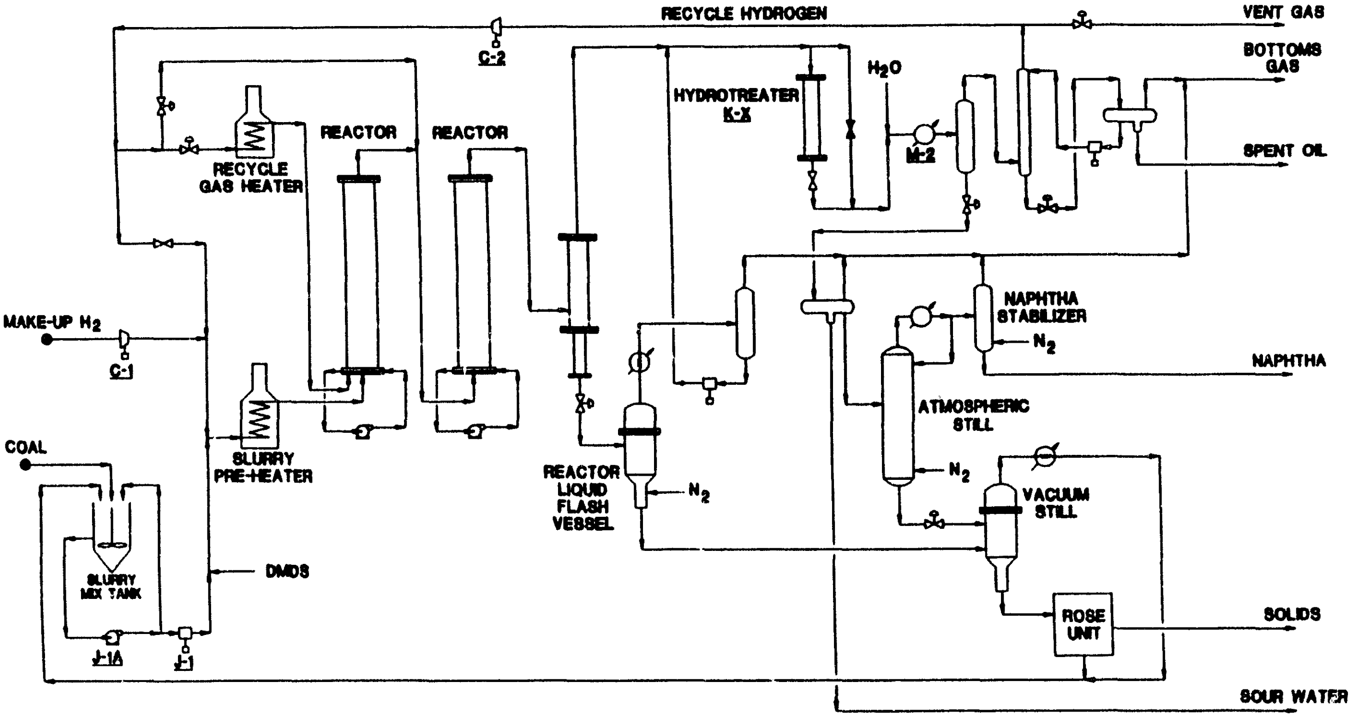
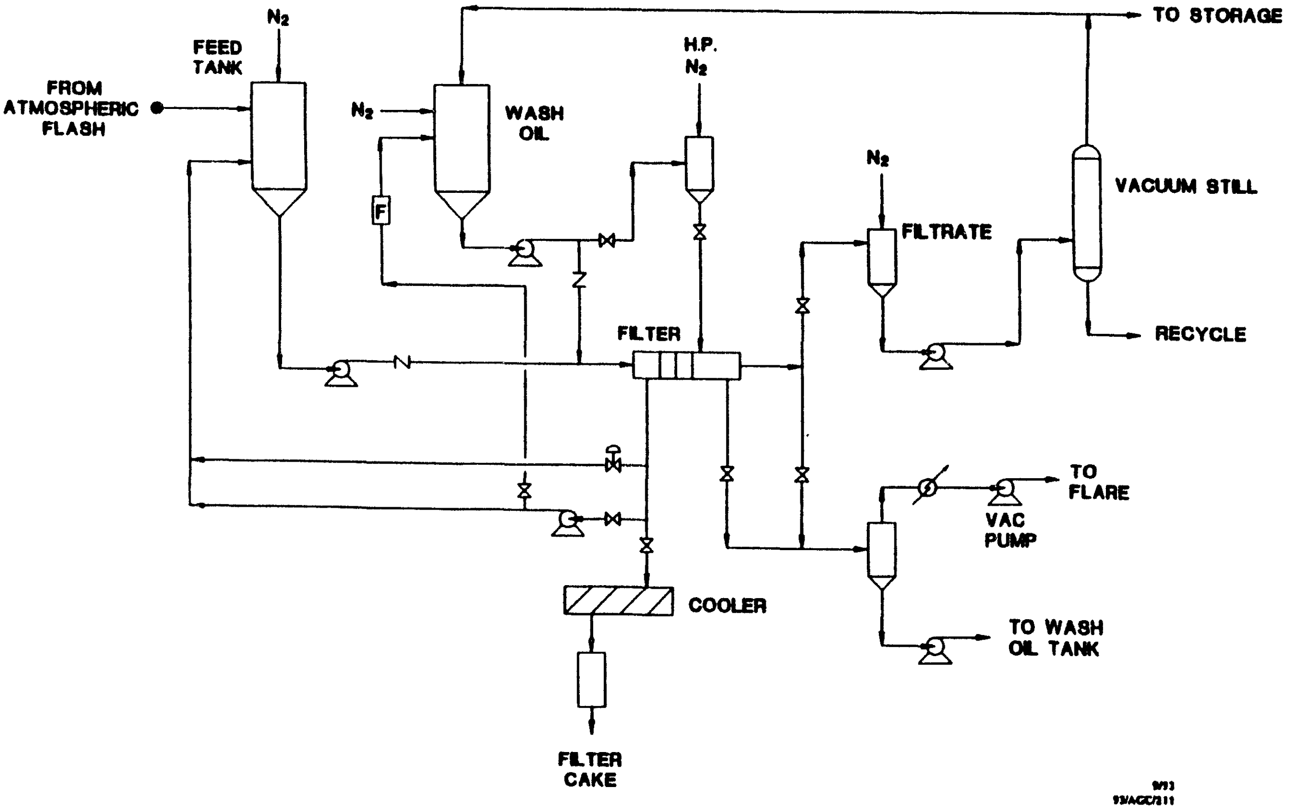


FIGURE 3

PROCESS DEVELOPEMENT UNIT NO. 260
SIMPLIFIED PROCESS FLOWSHEET, RUN 3



9/93
93/AGC/311

PROGRAM

The overall objective of the Proof Of Concept program is to develop Direct Coal Liquefaction and associated transitional technologies towards commercial readiness for economically producing premium liquid fuels from coal in an environmentally acceptable manner.

The program will focus on developing the two-stage liquefaction (TSL) process by utilizing geographically strategic feedstocks, commercially feasible catalysts, new prototype equipment, and testing co-processing or alternate feedstocks and improved process configurations.

Other high priority objectives include dispersed catalyst studies, demonstrating low rank coal liquefaction without solids deportion, improving distillate yields on a unit reactor volume basis, demonstrating ebullated bed operations while obtaining scale-up data, demonstrate optimum catalyst consumption using new concepts (e.g. regeneration, cascading), produce premium products through on-line hydrotreating demonstrate improved hydrogen utilization for low rank coals using novel heteroatom removal methods, define and demonstrate two-stage product properties for upgrading; demonstrate efficient and economic solid separation methods, examine the merits of integrated coal cleaning, demonstrate co-processing, study interactions between the preheater and first and second-stage reactors, improve process operability by testing and incorporating advanced equipment and instrumentation, and to demonstrate operation with alternate coal feedstocks.

The Proof Of Concept (PDU unit) is being readied for the first run under this program. POC Run No. 1 has as its main objective to scale-up and to demonstrates the CTSL™ process with extinction recycle operations while processing Illinois No. 6 Crown II Mine Coal. A comparison of Crown II with Burning Star Mine 2 is shown in *Table 1*; Burning Star Mine 2 coal is no longer available. Other POC-1 objectives are to:

- Confirm equipment operability and continuity of operations.
- Evaluate Rose-SR™ and filtration solid separation technologies.
- Obtain data on catalyst consumption and catalyst performance at lined-out conditions.
- Produce premium products and obtain data on on-line hydrotreating.

PROGRAM
(Cont'd)

- Study the interaction between the first and second-stage reactor stages.
- Provide data on reactor hydrodynamics, bed exotherms, hydrogen gas rates, flashes and flows for design of a commercial size unit.
- Collect products and samples for characterization, upgrading and as solvent for other programs.
- Obtain data on materials of construction and test new equipment and instrumentation.

The run plan for the 60 day POC Run No. 1 at 2-3 tons/day of dry coal scheduled to start in mid October is shown in *Table 1*.

TABLE 1

CANDIDATE ILLINOIS NO. 6 FEED COALS

MINE NAME	CROWN II	BURNING STAR 4	BURNING STAR 2
PROXIMATE, W% DRY			
Volatiles	42.05	39.6	38.6
Fixed Carbon	48.86	50.0	49.6
Ash	9.09	10.4	11.8
ULTIMATE, W% MAF			
Carbon	78.2	78.5	79.5
Hydrogen	5.5	5.4	5.5
Nitrogen	1.4	1.5	1.5
Oxygen (Diff)	10.5	10.1	9.6
Sulfur, Total	4.3	4.4	3.7
Pyritic	1.5	2.2	1.5
Organic	2.6	2.1	2.1
Chlorine	0.2	0.08	0.2
MICROAUTOCLAVE (CATALYTIC)			
THF Coal Conversion	95.2	96.2	91.7
TGA Resid Conversion	66.3	61.2	57.5

TABLE 2

RUN PLAN FOR POC-01
COAL: ILLINOIS NO. 6 CROWN II MINE
CATALYST: AKZO AO-60 1/16" EXTRUDATE

CONDITION	PERIOD	NO. OF DAYS	SOLID SEPARATION	ON-LINE HYDROTREATER	SPACE VELOCITY	TEMPERATURE °F		SOLV/COAL RATIO	CATALYST REP. RATE
						K1	K2		
L/O	1-2	2	Vac. Still	Yes	Base	715-735	750-775	2.0	0.25xBase
L/O	3-4	2	Vac. Still	Yes	Base	735-750	775-800	1.5	0.25 Base
1	5-12	8	ROSE-SR™	Yes	Base	770	815	1.2	0.25xBase
2	13-20	8	ROSE-SR™	Yes	Base	770	815	1.2	0.25xBase
3	21-28	8	ROSE-SR™	Yes	Base	770	815	1.2	2xBase
4	29-36	8	ROSE-SR™	Yes	1.5xBase	775	825	1.2	2xBase
5	37-44	8	ROSE-SR™	Yes	1.5xBase	775	825	0.9	2xBase
6	45-60	8	FILTER	Yes	1.5xBase	775	825	0.9	Base

PROGRAM
(CONT'D)

The initial low catalyst replacement rate of 1/4 base rate is to hasten the approach to catalyst equilibrium. Solid separation is switched from vacuum still operation to Rose-SR^{TM} with some solids (ashy) recycle to the feed system. In condition 2 operation is without ashy recycle followed by a 50% higher space velocity in condition 4, higher coal feed concentration in condition 5 and the base catalyst replacement rate in conditions 6. In condition 3 the catalyst replacement rate is 2xbase or 1.5 and 3.0 lbs/ton coal. Operation switches from the Rose-SR^{TM} unit to the filter in condition.

Figure 4 attached illustrates the approach to catalyst equilibrium with respect to residual oil conversion based on this run plan. Note that 90% of resid equilibrium is obtained in 13 days with the initial lower catalyst addition rate. *Figures 5&6* show the respective catalyst age distribution based on catalyst addition rate and coal feed rate.

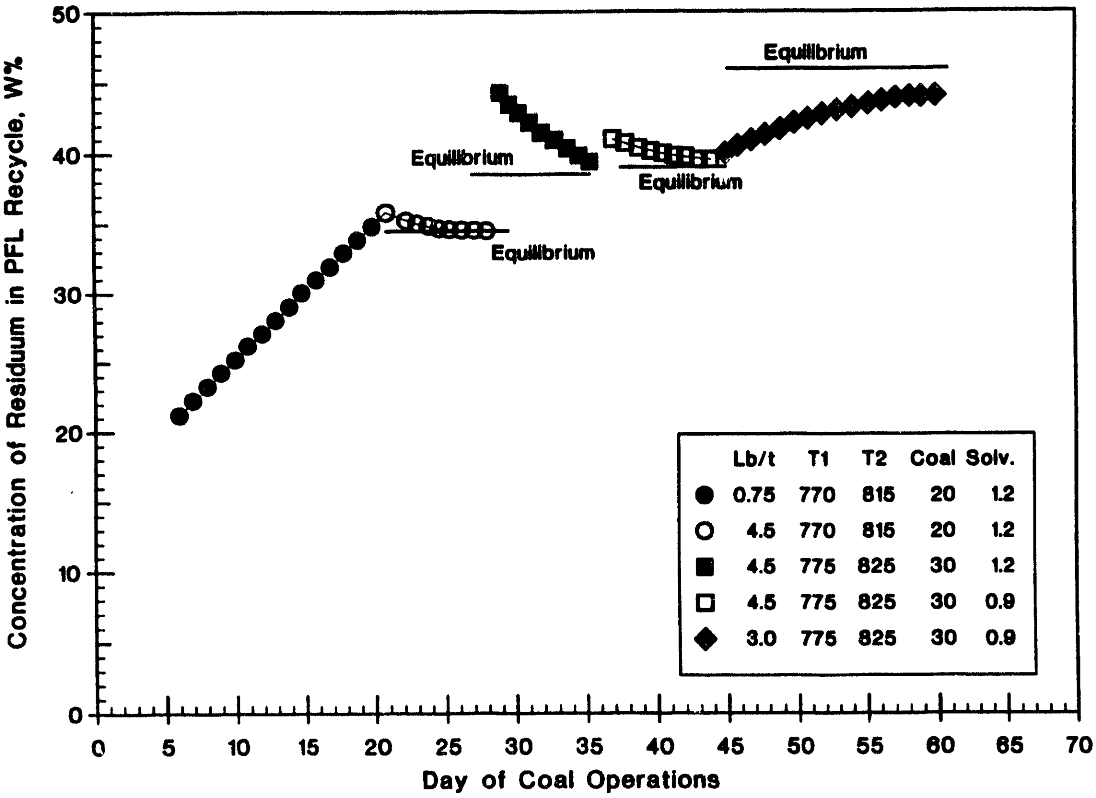
In order to scale-up on-line hydrotreating from the bench-scale to PDU, a series of off-line tests were conducted on both bituminous and sub-bituminous derived naphtha feedstocks. Based on a run of 58 days to a catalyst age of 1400 hrs, a deactivation rate of 46°F/1000 hrs for the initial 600 hrs down to 11°F/1000 hrs after 600 hrs results in a projected catalyst life of 1.5 Years. *Table 2* shows the large reduction in heteroatoms achieved on Illinois No. 6 Coal derived liquids using Criterion 411 catalyst at a bed temperature level of 725°F. Sulfur content was reduced to 9 ppm and nitrogen to 1 ppm from 297 and 161 ppm, respectively.

Based on bench data and process simulation, a 2 bed, down-flow hydrotreater has been installed on the PDU and will be on-line, except for sampling, the entire 60 day run.

The target process performance for the CTSL process in POC No. 1, based on a bench-scale extinction recycle demonstration run of 30 days with cleaned Illinois No. 6 Burning Star Mine 2 coal is to approach the distillate yields of the bench-scale run with mine washed Illinois No. 6 Crown II Coal.

FIGURE 4

EQUILIBRATION FOR RUN POC-01*



* Idealized with no allowance for inventory lags

FIGURE 5

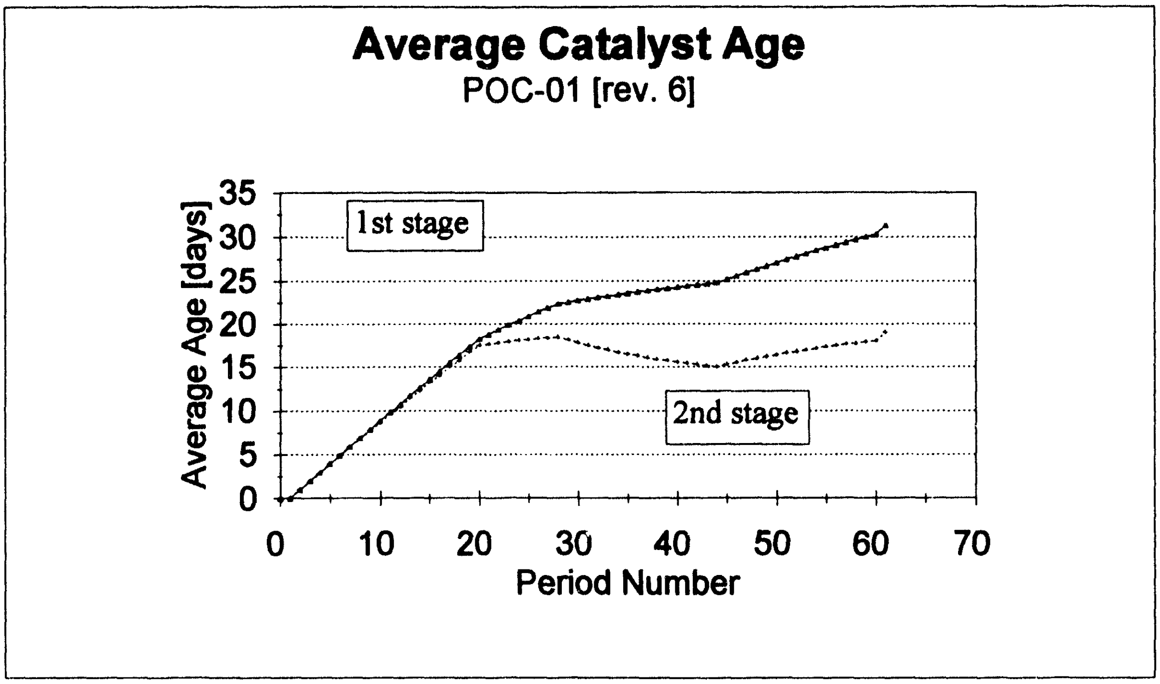


FIGURE 6

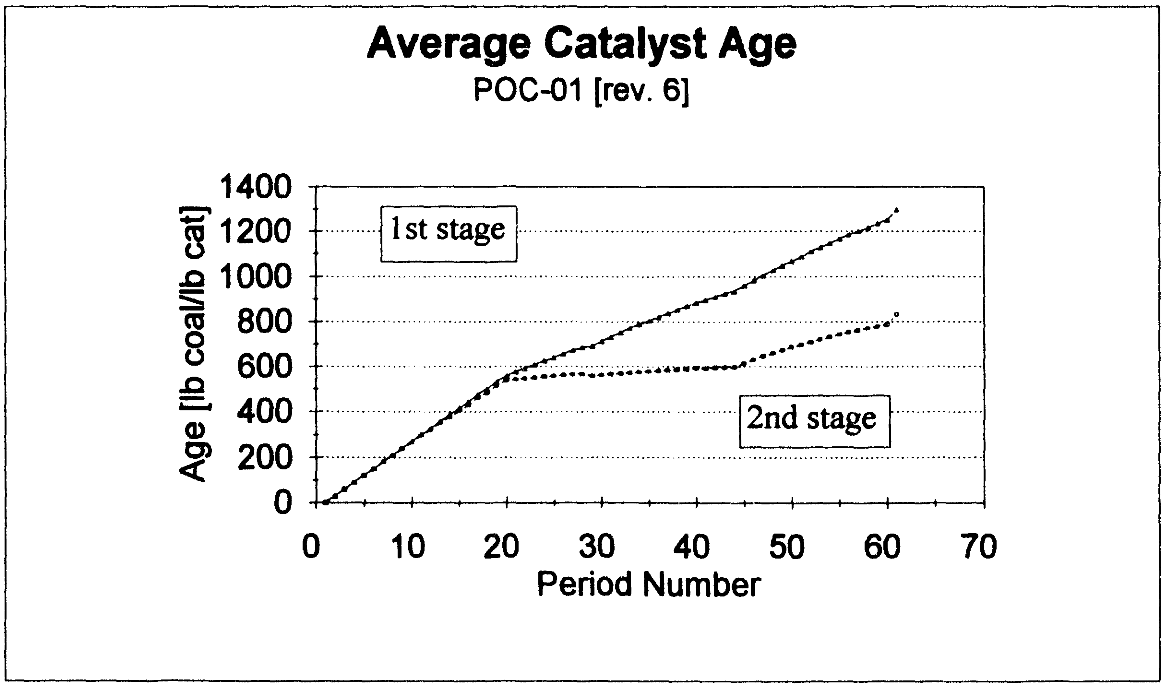


TABLE 3

HYDROTREATING OF COAL LIQUIDS OF ILLINOIS ORIGIN

	FEED	PRODUCT
GRAVITY, °API	39.6	46.2
C, W%	86.20	86.3
H, W%	13.16	13.49
S, PPM	297	9
N, PPM	161	1

PONA (IBP-350°F), PNA (350-650°F)	FEED IBP-350°F	FEED 350-650°F	PRODUCT IBP-350°F	PRODUCT 350-650°F
PARAFFINS	22.8	12.2	24.3	13.7
OLEFINS	0.5		0.3	
NAPHTHENES	67.0	48.2	69.3	55.7
AROMATICS	8.4	39.6	7.4	30.6
CETANE INDEX		38.0		39.5
CETANE NUMBER				39

TABLE 4

CTSL DEMONSTRATION RUN PERFORMANCE

Distillate W% MAF Coal	77.5
Distillate Bbls/Ton MAF	5.0
CH-750°F W% MAF	72.6
Coal Conversion W% MAF[1]	97.1
975°F Conversion W% MAF	94.0

[1] Illinois Coal cleaned to 5.8% Ash

RESULTS AND CONCLUSIONS

Plans have been formulated for 60 day PDU run with Illinois No. 6 Crown II Mine Coal as the feedstock. The run will demonstrate the CTSL extinction recycle made of operation, on-line hydrotreating, solid separation and operation at catalyst equilibrium at two space velocity levels.

Distillate yields of up to 5 bbls/ton of MAF coal are anticipated.

PLANS

Referring to *Figure 1* Proof Of Concept program schedule, four runs are planned in Fiscal 1993, 94 & 95. Run POC-2 scheduled for the first of 1994 will be to operate on a Western Coal and in the later stages with Western Coal and Hondo resid. The run plan is shown in *Table 5* and feedstock analysis are included in *Table 6*. The Hondo resid is high in sulfur and metals. By combined processing with Western Coal the synergism of metals removal on the coal ash and excellent desulfurization will be demonstrated.

Run POC-3 is planned as a demonstration of sub-bituminous coal processing in the presence of dispersed and supported catalysts and the substitution of syngas for hydrogen feed.

POC Run-4 is planned for the processing of a bituminous coal with interactive catalyst systems and interstage separation of heterogases.

TABLE 5

PROOF OF CONCEPT RUN 2

BASIC CONDITIONS	
Configuration -	Two close coupled ebullated bed reactors with on-line hydrotreating, filtration and Rose-SR™ solid separation.
CTSL -	Western Coal/Recycle
Co-Pro 1 -	Hondo/Western Coal
Catalyst -	AKZO, AO-60
System Pressure -	2,750 PSIG (18.96 MPA) 1,800 PSI Outlet Hydrogen Partial Pressure (12.41MPA)
TEMPERATURES	
First Stage -	400-440°C (750-825°F)
Second Stage -	400-400°C (750-825°F)
On-Line Hydrotreater -	370°C (700°F)
Coal Concentrations -	33% to 50%

TABLE 6

OIL/COAL FEEDSTOCK QUALITIES

OIL FEED STOCK QUALITIES

OIL FEEDSTOCK	HONDO
Atmospheric Residuum	
API Gravity	7.8
Carbon, W%	82.8
Hydrogen, W%	10.6
Nitrogen	0.8
Sulfur, W%	5.4
NI + V, WPPM	385
CCR, W%	14.3
975°F$^+$, w%	68

COAL FEEDSTOCK QUALITIES

COAL FEEDSTOCK	BLACK THUNDER
Proximate Analysis, W% Dry	
Volatile Matter	44.4
Fixed Carbon	49.4
Ash	6.2
Ultimate Analysis, W% Dry	
Carbon	68.9
Hydrogen	4.2
Nitrogen	0.9
Sulfur	0.5
Ash (SO$_3$-Free	6.2
Oxygen (By Difference)	19.3
H/C Atomic Ratio	0.73
O/C Atomic Ratio	0.21

Direct Coal Liquefaction – Capital Cost and Economics for Improved Baseline Design

S. K. Poddar
Bechtel Corporation

S. J. Kramer
Amoco Oil Company

and

A. Basu
Amoco Chemical Company

DIRECT COAL LIQUEFACTION -- CAPITAL COST AND ECONOMICS FOR IMPROVED BASELINE DESIGN

S. K. Poddar
Bechtel Corporation

S. J. Kramer
Amoco Oil Company

and

A. Basu
Amoco Chemical Company

OBJECTIVE

The primary scope of this improved baseline study is similar to that of the original baseline case. The results of the original baseline study are the basis for this study.

Thus, the objectives of this study were to:

- develop overall material balance, overall utility requirements and overall flow distributions (hydrogen and water) for the entire complex,
  - o develop material balance, utility requirements, equipment sizing and capital costs for the directly affected plants,
  - o make adjustments to the above entities described in the baseline design for each of the indirectly affected plants,
- generate capital cost estimates for the entire complex following the same approach as used in the baseline design
- carry out economic evaluations utilizing the LOTUS 1-2-3 Spreadsheet Economic Model developed in the baseline design, and
- develop an ASPEN/SP process simulation model with required modifications of the baseline simulation model

INTRODUCTION

Over the last two decades under the sponsorship of the Federal Government, several detailed designs and cost estimates of commercial size direct coal liquefaction complexes were carried out. One of these, known as the Breckinridge Project, was the 1981 Bechtel study on the design and estimation of capital cost of an H-Coal plant [1]. This conceptual design was based on the single-stage H-Coal process developed by Hydrocarbon Research Inc. In 1986, Bechtel, with Amoco's sponsorship, [2,3] studied the impact of technology improvements associated with the two-stage coal liquefaction technology practiced at the Advanced Coal Liquefaction Research facility in Wilsonville, Alabama.

In 1990, Bechtel/Amoco were awarded a contract by the U.S. Department of Energy (DOE), under contract number DEAC22 90PC89857, to update the design and economics of a conceptual commercial size direct coal liquefaction plant for Illinois No. 6 bituminous coal. Results of this study were presented in last year's Contractors Review Meeting.[4]

The basis for the study was the then available pilot plant data generated at the advanced coal liquefaction facility (pilot plant) at Wilsonville, Alabama in run 257E [5]. This design basis was felt to be rather conservative. While the baseline study was at the final stage of completion, a separate set of data became available based on Wilsonville run Nos. 257J, 261B and 261D. These data were for a relatively higher space velocity through the liquefaction reactor.

Because of the potential favorable economic impact of the higher space velocity, DOE modified the subject contract and authorized the Bechtel/Amoco team to extend the study to include the higher space velocity data as an additional design basis and designate that as the improved baseline case. In addition, this contract modification included the incorporation of the best option of the baseline case as an option to the improved baseline. This option, as discussed in the baseline design case, refers to the case whereby the required hydrogen is produced by natural gas reforming and the ash concentrate is fed to a fluidized bed combustion (FBC) plant to generate energy. Thereby, waste production is minimized and electrical energy is produced.

This paper summarizes the results of the extension to the baseline study. The methodology utilized is to identify the impact of the changes in design basis on the baseline design in terms of plants which are directly affected, and those which are indirectly affected. The directly affected plants were redesigned in the same way they were in the baseline design; whereas for the indirectly affected plants, adjustments were made based on their respective flow rate or throughput changes. The directly affected plants are the coal liquefaction plant - plant 2, hydrogen production plant - plant 9, and steam and power generation plant - plant, 31. In addition to plant 2 for the improved baseline, plant 3 (Gas Plant), plant 4 (Naphtha Hydrotreater), and plant 5 (Gas Oil Hydrotreater) are also considered as directly affected plants. These are considered as directly affected plants because for plant 3 the gas flow is significantly different when compared to the baseline, and for plants 4 and 5 the design is for a single train for each of these two plants, as opposed to two trains in the original baseline design. In this study the overall plant complex reliability was assumed to be the same as the baseline, 88.4%. The capital cost estimates were carried out following the procedure of the baseline case, and are of a budgetary type with an associated accuracy of ± 30%.

ASPEN/SP modeling of the various ISBL plants was conducted following the approach used for the baseline case.

The design, capital cost estimates and modeling were then extended to the improved baseline case coupled with the best option. The best option (based on minimal capital cost) was established while studying seven different options with reference to the baseline case. The best option is Option 6, where hydrogen is produced by natural gas reforming plus a Fluid Bed Combustion (FBC) unit to generate energy using the waste (ash concentrate) from the ROSE-SR unit as feed.

The economic evaluation was carried out utilizing the LOTUS 1-2-3 spreadsheet economics model developed for the baseline study and making appropriate input changes for these cases.

DESIGN BASIS AND PROCESS DESCRIPTION

The improved baseline design basis data are shown in Table 1 [6,7]. A simplified block flow diagram of the overall baseline case is shown in Figure 1. The interconnected process plants are supported by several offsite facilities. Run of Mine coal enters the complex through the coal cleaning and handling plant (Plant #1), which is a Jig plant. Clean coal containing 11.47% ash (MF) is further ground and dried to a moisture level of 2 wt% in Plant 1.4 before entering the liquefaction plant (Plant 2).

The light products are sent to the gas plant (Plant 3) to separate the fuel gas, propane and mixed butanes. The C_5-350°F stream goes to the Naphtha hydrotreater (Plant 4). The 350-850°F fraction from Plant 2 goes to the Gas Oil hydrotreater (Plant 5). Required hydrogen for the complex is provided via coal gasification from Plant 9 utilizing Texaco technology. The coal liquefaction bottoms goes to Kerr McGee's Rose-SR plant (Plant 8) which produces:

(1) an extract that is recycled back to the liquefaction plant, and

(2) an ash concentrate stream that goes to the gasifier (Plant 9).

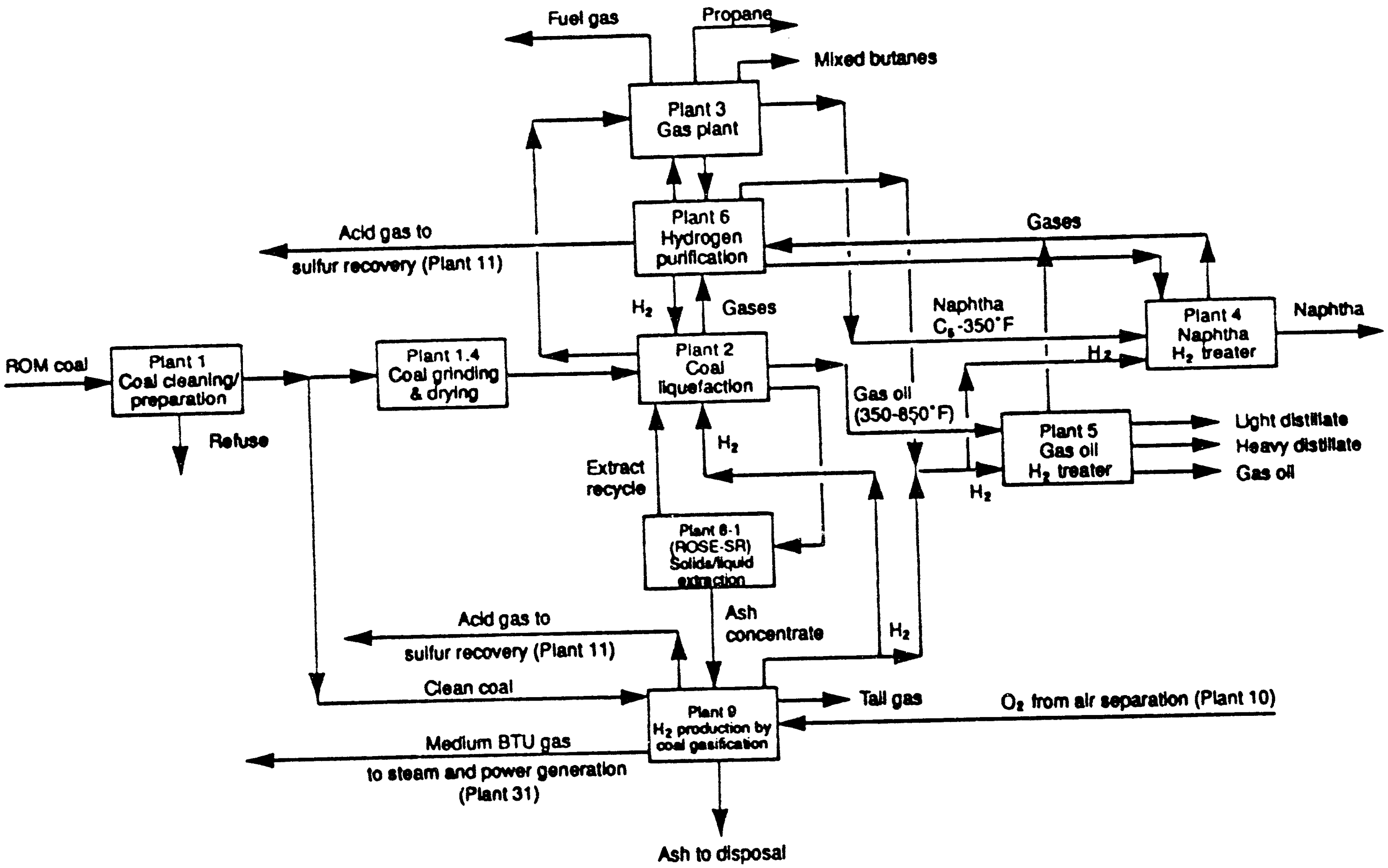


Fig. 1 Simplified Block Flow Diagram

Table 1

Improved Baseline Design Basis

• Based on Wilsonville Pilot Plant Runs 257J, 261B and 261D (Cat-Cat Reactor, Illinois Number 6, Burning Star Mine Coal)	
• Reactor operating conditions	
Coal feed	
Rate, ton (MAF)/day	16503
Ash (MF), wt%	11.47
Temperature, °F	
First Stage	810
Second Stage	760
Catalyst Space velocity (lb MAF coal/hr/lb catalyst)	1.95
Solvent/MAF Coal	2.26
Hydrogen consumption, wt% MAF	6.3

The hydrogen purged from Plant 2 is recovered by the hydrogen purification plant (Plant 6) which is a combination of membrane and PSA units. The treated hydrogen is recycled back to Plant 2. Sulfur is recovered by a sulfur recovery plant (Plant 11). Sour water collected from the various plants is sent through an ammonia recovery plant (Plant 38). Part of this treated water is sent to the coal gasification plant and the rest to the phenol recovery plant (Plant 39) followed by a waste water treatment plant (Plant 34). The oxygen required by the coal gasifier is produced in the air separation plant (Plant 10).

PRODUCTS AND BYPRODUCTS YIELDS

The hydrocarbon product and byproduct yields from the plant with 16,503 tons per day of MAF feed coal to liquefaction reactor are shown in Table 2.

Table 2

Hydrocarbon Product Yields

Coal (MAF) Feed Rate to liquefaction reactor	**TPSD** 16503
Hydrocarbon Product Yields	**BPSD**
Propane	3,884
Mixed Butanes	2,230
Naphtha	18,519
Light Distillate	7,403
Heavy Distillate	27,590
Gas Oil	21,370
	Total 80,996
Byproduct Yields	**TPSD**
Sulfur	859
Ammonia	277
Phenol	39
	Total 1,175

In addition to the improved baseline study one option was included. In this option, the required hydrogen is produced by natural gas reforming, and the ash concentrate is fed to a fluidized bed combustion (FBC) plant to generate energy. This approach minimizes the production of waste and produces electrical energy. This option was selected because this was the lowest capital cost option identified during the baseline study [4].

OVERALL MATERIAL BALANCE FOR THE ENTIRE COMPLEX

The overall material balance for the entire complex for the improved baseline and the improved baseline with the option of producing hydrogen via reforming of the methane are shown in Tables 3 and 4 respectively. It is worth to note that the coal feed rate shown as a part of the input stream in Table 3 is the total amount of coal per hour (both for the gasifier, Plant 9, and the liquefaction reactor, Plant 2 entering the fence line of the complex. In Table 4, however, the total coal input rate shown indicates the amount of coal (per hour) entering only to the liquefaction reactor, Plant 2. This is obvious because, in this case, there is no coal gasifier to produce required hydrogen.

Table 3

Overall Material Balance for Improved Baseline

Input to Complex		**Output from Complex**	
Stream Description	Quantity M Lbs/Hr	Stream Description	Quantity M Lbs/Hr
Coal (Maf)	2,401.5	Propane	28.6
Coal (Ash)	311.2	Mixed Butanes	18.6
Air to Gasifier	3,684.9	Naphtha	203.3
Air to Sulfur Recovery Plant	379.5	Light Distillate	91.5
Reaction Stream	783.7	Heavy Distillate	360.3
		Gas Oil	292.2
		Sulfur	71.6
		Ammonia	23.1
		Phenol	3.2
		Reaction Water	168.9
		Refuse-Solids	542.4
		Ash/Slag	263.4
		Flue Gas	70.8
		Medium Btu Gas	74.0
		Gas to Incinerator	459.7
		Nitrogen	2,708.4
		Tail Gas (to Atm)	2,180.8
Total Input	**7,560.8**	**Total Output**	**7,560.8**

Table 4

Overall Material Balance for Improved Baseline with H2 by Natural Gas Reforming

Input to Complex		**Output from Complex**	
Stream Description	Quantity K Lbs/Hr	Stream Description	Quantity K Lbs/Hr
Coal (Maf)	1,718.9	Propane	28.6
Coal (Ash)	222.7	Mixed Butanes	18.6
Air to Sulfur Recovery Plant	202.8	Naphtha	203.3
Air to Fluid Bed Combustion Unit	3,898.7	Light Distillate	91.5
Reaction Stream	981.1	Heavy Distillate	360.3
Natural Gas	348.9	Gas Oil	292.2
Limestone	47.8	Sulfur	38.2
		Ammonia	22.2
		Phenol	4.1
		Reaction Water	579.1
		Ash	243.3
		Refuse	388.2
		Flue Gas	4,095.2
		Medium Btu Gas	796.3
		Tail Gas	0.4
		Fuel Gas	70.2
		Gas to Incinerator	189.3
Total Input	**7,421.0**	**Total Output**	**7,421.0**

METHODOLOGY FOR CAPITAL COST ESTIMATES

The capital cost estimate for the improved baseline, like the baseline design, was for an Nth plant case. The Nth plant is defined as the Nth commercial plant built when the technology basis, plant design and operation are well established. The Nth plant has the following characteristics:

- Lowest reasonable plant cost contingency
- No spare trains
- Lowest reasonable engineering cost
- Shortest possible project schedule to erect and start-up
- Matured technology allowing the overall stream factor of the complex to be same as that of the First plant.

The overall plant cost was estimated by developing cost estimates (field cost) for each Inside Battery Limit (ISBL) plant and each Outside Battery Limit (OSBL) plant. For each plant (ISBL as well as OSBL), the total field costs were estimated by summing the estimated costs of: 1) major equipment, 2) bulk materials, 3) subcontracts, 4) direct labor and 5) distributables (indirect costs).

The Nth plant installed plant costs for the baseline case were calculated by 1) taking the estimated ISBL plant cost for each ISBL plant, 2) adding the respective proportional amount of total OSBL costs, and then 3) adding the proportional amount of home office fees, engineering fees, and contingency.

CAPITAL COSTS

The installed plant costs along with the number of trains for each plant are shown in Table 5. Because these cost estimates are for the "Nth plant" scenario, the number of operating trains and the total number of trains for any ISBL plant are the same since no spare trains are used.

Table 5

Nth Plant Capital Costs for the Complex

Improved Baseline

Plant #	No. of Oper. Trains	Total No. of Trains	ISBL Plant Field Costs 1000$	ISBL Plant Cost Adj. with OSBL Costs 1000$	Installed Plant Costs 1000$
1	6	6	104,900	151,700	182,000
1.4	12	12	96,800	140,000	171,800
2	4	4	854,800	1,236,400	1,517,000
3	1	1	23,600	34,100	41,900
4	1	1	13,600	19,700	24,100
5	1	1	82,900	119,900	147,100
6	1	1	130,000	188,000	230,700
8	1	1	41,700	60,300	74,000
9	6	6	303,300	438,700	538,200
10	6	6	222,500	321,800	394,800
11	5	5	55,100	79,700	97,800
38	1	1	45,000	65,100	79,900
39	1	1	16,000	23,100	28,400
Total			**1,990,200**	**2,878,500**	**3,531,900**

CAPITAL COSTS FOR THE IMPROVED BASELINE WITH HYDROGEN PRODUCTION FROM NATURAL GAS

The total installed cost for this option was re-estimated from the baseline estimates by replacing the cost of the directly affected baseline plant with the cost of the optional plant. All other cost modifications impacting the indirectly affected plants were done using cost vs. capacity correlations.

Thus, the installed costs reported in the last column of Table 6 are the Nth plant costs for the entire complex with hydrogen production by steam reforming of natural gas (Option 6 of the baseline design).

For this option the directly affected plants are hydrogen production plant (plant 9), air separation plant (plant 10), and the additional fluid bed combustion (FBC) unit in plant 31.4-01 for processing the ROSE-SR bottoms. For this option, the air separation plant (plant 10) is not required.

Table 6

Nth Plant Capital Costs for the Complex

Improved Baseline with H2 Produced by Natural as Reforming

Plant #	No. of Oper. Trains	Total No. of Trains	ISBL Plant Field Costs 1000$	ISBL Plant Cost Adj. with OSBL Costs 1000$	Installed Plant Costs 1000$
1	6	6	86,000	115,800	142,100
1.4	12	12	96,800	130,400	160,000
2	4	4	854,800	1,151,300	1,412,600
3	1	1	23,600	31,700	38,900
4	1	1	13,600	18,300	22,500
5	1	1	82,900	111,700	137,000
6	1	1	129,900	174,900	214,700
8	1	1	41,700	56,200	68,900
9-01	3	3	224,700	302,600	371,300
11	5	5	33,700	45,400	55,700
38	1	1	42,500	57,300	70,300
39	1	1	18,500	24,900	30,500
Total			**1,648,700**	**2,220,500**	**2,724,500**

PRODUCT VALUATION

The coal liquid products were valued utilizing Bechtel's linear programming modeling tool, PIMS (Process Industry Modeling Systems). A typical PAD II refinery configuration and crude mix with a fixed price were assumed. Also, it was assumed that the coal liquid naphtha (C5-350°F) was sent to a reforming unit, the light distillate (350-450°F) was used for blending (diesel and fuel oil), the heavy distillate (450-650°F) was used for diesel and fuel oil blending and/or FCCU feed, and the vacuum gas oil (650-850°F) was used as a fuel oil blending stock and/or FCCU feed. The product valuation was then determined for various scenarios and expressed as "Syn-Crude Premium" (SCP). The SCPs varied between 1.07 and 1.27.

BY-PRODUCT VALUATION

The by-products for this complex are sulfur, ammonia, phenol, propane and mixed butanes. The production rates of these streams for the improved baseline case and their assumed respective prices are shown below in Table 7.

Table 7

By-product Values

By-Product	Production Rate	Price
Sulfur	858.8 STPD	$80/ton
Ammonia	276.6 STPD	$120/ton
Phenol	38.5 STPD	$400/ton
Propane	3884 BPSD	$7.50/bbl
Mixed Butanes	2230 BPSD	$14.50/bbl

ECONOMICS AND SENSITIVITIES ON ECONOMICS

The economic analysis to determine the Crude Oil Equivalent price (COE) in $/bbl was carried out using the LOTUS 1-2-3 based spreadsheet model developed by Amoco. There were several key assumptions made in carrying out this analysis. These key assumptions are listed below.

Key Assumptions

Years of construction	4
Years of operation	25
Depreciation, Years	10
Maintenance, % initial capital	1
Working capital, % revenue	10
Working capital, % liquid	50
Owner's cost, % initial capital first year operation	5
Bank interest rate	8
Federal income tax rate, %	34
Percent equity	25
Percent IRR* on equity	15
General inflation %	3
Raw material price escalation	same as general inflation of 3%
State and Local Tax	0
SCP	1.07

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* IRR is the internal rate of return

Economic Results

The results of the economic analysis are presented in Table 8. These results are based on mid-1991 capital cost estimates, and the project start date is six months later. The results are expressed in terms of Crude Oil Equivalent (COE) for a 15% IRR on equity. Results thus obtained are summarized for four cases. Two of these cases refer to the baseline, and baseline with the best option. Though not directly relevant to the subject of this paper, these two cases are included in this table for the sake of completion. The four cases are 1) baseline design, 2) improved baseline design, 3) baseline design with hydrogen production by natural gas reforming, and 4) improved baseline design with hydrogen production by natural gas reforming. As shown in this table, the best economic case studied in this project is the improved baseline case with hydrogen production by natural gas reforming.

Table 8

Results on Economics

Case	**COE $/bbl**
Baseline	38.55
Improved Baseline	33.45
Baseline with H2 Production by Natural Gas Reforming	36.00
Improved Baseline with H2 Production by Natural Gas Reforming	31.00

Sensitivity on Economics

The economics sensitivity analysis was carried out to determine the impact of changes in capital costs, raw material pricing, owner's equity, price escalation (per EIA) on coal, natural gas and crude oil, and syncrude premium, respectively.

For comparison, the results of the sensitivity analysis for the baseline are included in this paper in addition to those for the improved baseline, and they are shown in Tables 9 and 10.

For the baseline case, a change in capital cost by 10% changes the Crude Oil Equivalent price by $2.35/bbl, and a 25% change causes a change of $5.90/bbl in the Crude Oil Equivalent price. For the improved baseline case, similar changes cause the Crude Oil Equivalent price to change by 1.95/bbl and $4.95/bbl respectively. A 25% change in coal and natural gas price individually changes the equivalent crude oil price by $2.30/bbl and $0.65/bbl, respectively, for the baseline, and $2.10/bbl and $0.55/bbl for the improved baseline.

Increasing the owner's equity by 100% (a change from 25% to 50% equity) increases the Crude Oil Equivalent price by $3.05/bbl for both cases.

When coal, natural gas and crude oil are individually allowed to escalate per the EIA forecast, instead of at the fixed 3% inflation rate, the equivalent crude oil price decreases by $8.70/bbl and $7.45/bbl for the baseline and the improved baseline, respectively. The increase in syncrude premium to 1.27 results in a drop of the Crude Oil Equivalent price by $6.15/bbl and $5.35/bbl, respectively.

Table 9

Sensitivities on Economic Results for Baseline

ECONOMICS	
Case	**COE $/bbl**
Baseline	38.55
Baseline with H_2 production from natural gas	36.00

SENSITIVITIES		
Item	**Change**	**Δ $/bbl**
• Capital	± 10% ± 25%	± 2.35 ± 5.90
• Raw Material		
Coal	± 25%	± 2.30
Natural Gas	± 25%	± 0.65
• Owner's Equity	± 100%	± 3.65
• Price Escalation, per EIA		- 8.70
Coal	+ 1.6	
Natural gas	+ 3.5	
Crude oil	+ 2.9	
• Syncrude Premium	+0.20%	- 6.15

Table 10

Sensitivities on Economic Results for Improved Baseline

ECONOMICS	
Case	**COE $/bbl**
Improved Baseline	33.45
Improved Baseline with H_2 production from natural gas	31.00

SENSITIVITIES		
Item	**Change**	**Δ $/bbl**
• Capital	± 10% ± 25%	± 1.95 ± 4.95
• Raw Material		
Coal	± 25%	± 2.10
Natural Gas	± 25%	± 0.55
• Owner's Equity	± 100%	± 3.05
• Price Escalation, per EIA		- 7.45
Coal	+1.6	
Natural Gas	+3.5	
Crude oil	+2.9	
• Syncrude Premium	+0.20	- 5.35

MODELING TOOLS

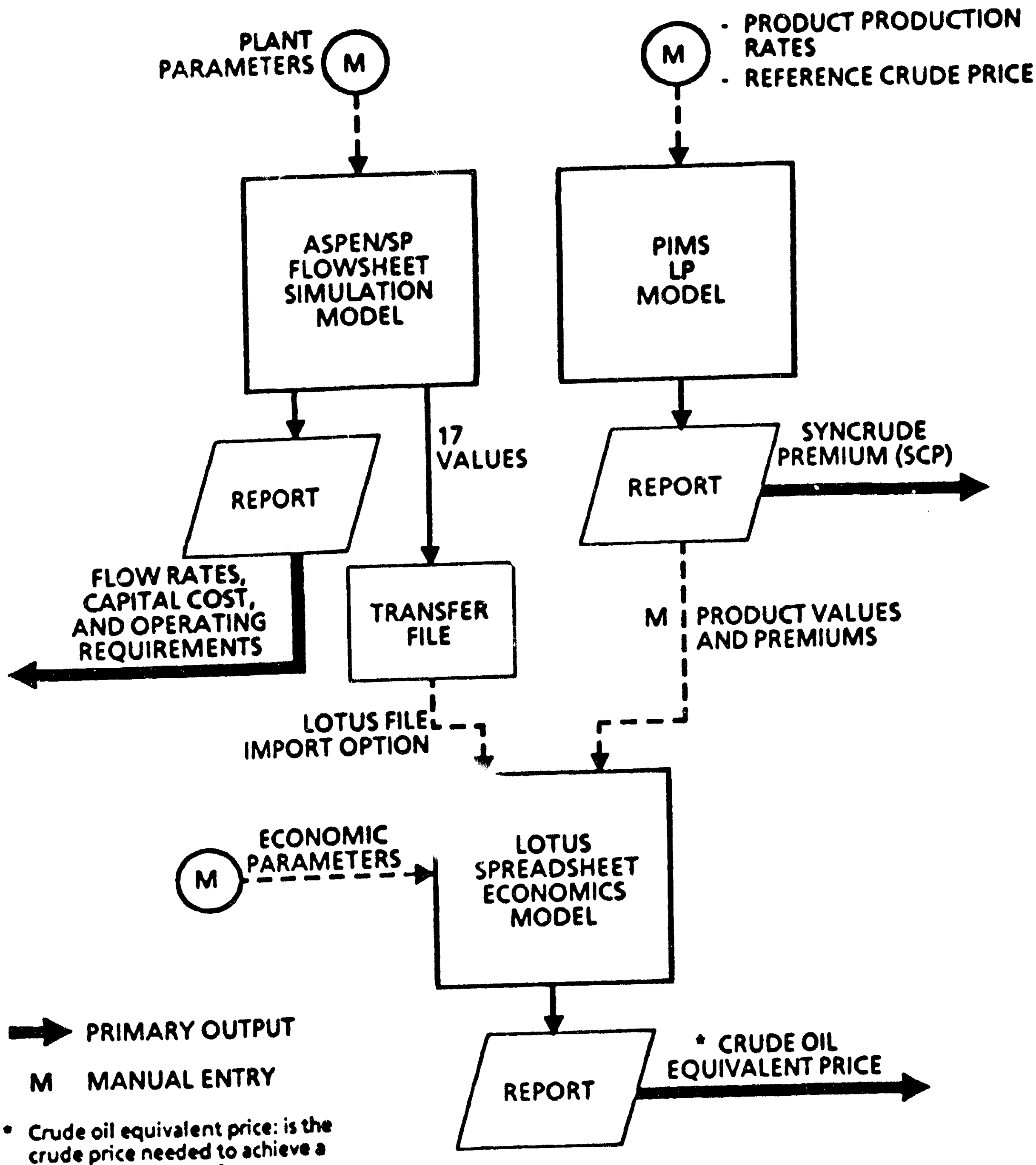
The complete modeling package that was developed under this project was designed to be a research guidance tool to study technology advances and options in a case study approach. It does not feature optimization capabilities and is not a detailed process design tool. It was designed to predict the effects of various process and operations changes on the overall plant material and utility balances. It also was designed to predict the effects on the capital cost and operating labor. The modeling tools were developed in a way so that they are applicable for the baseline as well as for the improved baseline cases.

A separate LOTUS spreadsheet economics model was developed that does a discounted cash flow analysis of the project taking results directly from the process simulation model output to calculate project economics.

Figure 2 shows a simplified user input-output diagram of the various computer models used in this project, and how they interact with each other. The ASPEN/SP process simulation model is the heart of the modeling system. Although this model resides in a detailed process simulation model, many simplifying assumptions and approximations were made to keep the model manageable and still satisfy the requirements of being a research guidance tool, and not a design tool. If detailed process simulation models for design were developed, the system would have become unmanageable and would have required excessive computer facilities.

The ASPEN/SP process simulation model is based on the detailed plant designs developed for both the baseline and improved baseline designs. Fortran user block models are used to simulate most of the plants, and to predict their utilities consumptions, labor requirements and capital costs. Results are available in several forms including the normal ASPEN/SP reports, specific plant summary reports, and an overall management summary report. A small output file also is generated for transferring the key process simulation model results to the LOTUS spreadsheet economics model.

Bechtel's linear programming tool, PIMS (Process Industry Modeling Systems) was used to value the coal liquid products by simulating a typical PADD II (mid-western) refinery. The product valuation expressed as Syncrude premiums was used for the LOTUS spreadsheet economics model. The product valuations were calculated for various scenarios as case studies. For these scenarios, different amounts of coal liquid products were fed into the refinery with corresponding amounts of petroleum being backed out. In general, it was assumed that the naphtha fraction of the coal liquid (C_5 - 350) was sent to the reforming unit, the light distillate fraction (350-450) went to blending (diesel and fuel oil), the heavy distillate fraction (450-650) was for diesel and fuel oil blending and/or used as Fluid Catalytic Cracking Unit (FCCU) feed, and the vacuum gas oil (650-850) was used as a fuel oil blending stock and/or FCCU feed.



* Crude oil equivalent price: is the crude price needed to achieve a 15% internal rate of return.

Fig. 2 Simplified User Input - Output Diagram for Computer Models Used in Direct Coal Liquefaction Study

The LOTUS spreadsheet economics model takes the results from the other two models along with user supplied economic parameters and does a complete discounted cash flow analysis. This spreadsheet generates the net present value of the project at a specified internal rate of return (IRR) on equity. It also can be used to calculate what crude oil price is required to obtain a specific internal rate of return. In addition, this spreadsheet model allows studying the effects of other economic assumptions on project economics.

The basic process simulation model developed under this project simulates the baseline design. Seven optional cases also were simulated. These optional cases were simulated either by minor modifications to the basic ASPEN/SP input file, or by the use of a separate, but similar ASPEN/SP input file. Separate input files were required because some cases have a different flowsheet logic which could not be blended into the basic simulation model input file.

RECOMMENDATIONS

Over the past years, significant improvements have reduced the cost of direct coal liquefaction. However, further advancement is necessary to make the process economical [2,8,9]. The sensitivity analysis suggests that both capital costs and raw material costs significantly impact on direct coal liquefaction economics. Efforts should be directed at investigating the effect of 1) lower rank coals, 2) coal cleaning on coal conversion, 3) different types of reactor designs (e.g., slurry reactor), different plant locations (e.g., gulf coast location) and "close-coupled" upgrading of coal liquids [3,10]. In addition, there is a continued need to continue basic research to reduce the liquefaction pressure and to develop improved liquefaction catalysts. A need for a coal liquid product quality data reference library has also been identified. Availability of such data are needed to make definitive assessments of coal liquid economics by defining the effects of product quality on such assessments.

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COAL LIQUEFACTION AND GAS CONVERSION CONTRACTORS' REVIEW CONFERENCE

TITLE: Improved Coal Liquefaction through Enhanced Recycle Distillate Quality

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Abstract

The DOE is sponsoring R & D programs in direct coal liquefaction with the objective of developing new processing concepts that may lead to significant reductions in the cost of producing liquids. The authors of this paper are engaged in one such program, and are investigating concepts that concern the first stage of a two-stage process, and involve modification of the coal and solvent feeds, and achieving more effective use of dispersed catalysts. Emphasis is given to the conversion of low-rank coal (Black Thunder, subbituminous). The research is conducted on a laboratory scale, and attempts to simulate process conditions as realistically as possible through the use of process derived solvents, and through the selection of operating conditions that can be related to the performance of the Wilsonville pilot plant in run period 263J. The expectation is that these concepts or combinations thereof that show promise for improving liquefaction economics will be selected for testing and assessment in a larger scale continuous unit at PETC.

This paper describes the results of a specific combination of concepts that are concerned with improving the recycle solvent quality, through pretreatment of the heavy distillate fraction by dewaxing, hydrotreatment, and dewaxing followed by hydrotreatment. It has been demonstrated that each of these measures increases IOM conversion, increases oil yield, and reduces the yield of preasphaltenes and asphaltenes. The dewaxing step produces, in addition, a by-product wax. The reasons for improvement are considered to relate to the reduction of retrograde reactions due to the removal of paraffins and naphthenes, and to increases in H-donor capacity. Further research will help to establish the configuration and to optimize operation of these processing steps to have the most beneficial effect on liquefaction economics.

Introduction

The Department of Energy has defined the goal of substantially lowering the cost of producing coal liquids by direct liquefaction, through the development and evaluation of new and promising concepts. To this end, several projects are under DOE sponsorship. The authors of this paper represent four organizations that are collaboratively engaged in one such project: the University of Kentucky Center for Applied Energy Research (CAER); CONSOL Inc.; the Sandia National Laboratory; and LDP Associates.

The program is concerned with concepts that involve the first stage of a two-stage process, and relate to modifications to the coal and solvent feeds, and to the use of dispersed catalysts. The primary focus is on the use of low-rank coal feedstocks. The specific concepts are illustrated in Figure 1, where they are shown on a schematic of the Wilsonville pilot plant operation, run period 263J, which was selected as the base case against which to assess the extent of any improvements in performance. The run used Black Thunder subbituminous coal, and iron oxide and molybdenum dispersed catalysts. The numbers shown on the Figure were calculated on an SO_3-free ash basis.

Briefly, the CAER is investigating: low severity CO pretreatment of the coal, with the aims of rejecting oxygen, inhibiting the propensity for regressive reactions, and increasing coal reactivity; the application of more active, low-cost, Fe-based dispersed catalysts to increase the rate and extent of conversion; and the possible use of fluid coking for solids rejection, and to generate an overhead product for recycle. CONSOL is investigating: oil agglomeration for coal ash rejection, for the possible rejection of ash in the recycled resid, and for catalyst addition and recovery; and distillate dewaxing for the removal of naphthenes and paraffins, and to generate a suitable feed for recycle distillate hydrogenation. At Sandia, research is concerned with the production of active hydrogen donor distillate solvent fractions, produced by the hydrogenation of dewaxed distillate, and by fluid coking via low severity reaction with $H_2/CO/H_2O$ mixtures, using hydrous metal oxide and other catalysts. The technical and economic evaluation of the experimental data, and the impact on liquefaction process economics is being made by LDP Associates.

The present phase of the program involves small scale laboratory experiments, in which individual and integrated concepts are tested and assessed. A particular strength is the use of process-derived liquids rather than model compounds. Although this creates some difficulties in experimental operation and in the interpretation of data, it lends additional credibility to the results. In a later phase, it is intended that the more promising concepts will be subjected to more detailed testing in a larger-scale continuous unit.

In this paper, results are described to show the extent of process improvement that is indicated by a specific combination of concepts, namely, distillate dewaxing (CONSOL), followed by hydrogenation of the dewaxed distillate (Sandia), and the effect on coal liquefaction of substituting the hydrogenated product for the normal distillate fraction in the Wilsonville composite solvent (CAER). A preliminary indication of the impact on liquefaction economics (LDP Associates) is presented.

Recycle Distillate Dewaxing - CONSOL

Dewaxing Process and Products

Approximately 4-5 wt% yield (MAF coal basis) of paraffinic waxes, and some naphthenic compounds, is produced during the liquefaction of subbituminous coals. These relatively stable materials tend to concentrate in the recycle distillate stream, reaching levels of 15-20 wt% or more, in continuous two-stage liquefaction processes. Their accumulation dilutes the hydrogen donors in the process recycle solvent and, as the waxes are poor physical solvents for the coal reaction products, they can contribute to the retrograde reactions that are thought to impair the dissolution and upgrading of low-rank coals. Their removal by solvent dewaxing offers a method to improve the performance of the process solvent and, as a result, improve the overall performance of coal liquefaction. At the same time, potentially valuable by-product waxes can be recovered. Solvent dewaxing fits into the overall advanced liquefaction concept as a solvent pre-treatment step, Figure 1, in which all or part of the distillate portion of the recycle solvent may be dewaxed to a desired degree, by either physical or chemical means. Only physical solvent dewaxing was tested under the present project. However, it is likely that the degree of process solvent improvement attained by dewaxing depends primarily on the degree of dewaxing and not on the dewaxing method.

All of the dewaxing work to date was done with the V-1074 distillate material from Wilsonville Run 262E. The material was obtained from a period of operation between Run Periods D and E while the plant was being operated at the conditions used in Period E. Initial tests with 100 mL batches of distillate were made to determine the conditions suitable for preparing larger batches of dewaxed distillate for hydrogenation and solvent quality studies.

A series of ketone (acetone) dewaxing tests was carried out at temperatures from 0 to -35 °C. For each run, 100 mL of sample was mixed with 300 mL of HPLC-grade acetone in a beaker. The mixture was gradually cooled, with stirring, to the test temperature using a bath of dry ice and acetone. At the desired temperature, the precipitated wax was suction-filtered and washed with cold acetone. The filter cake was then dissolved and washed through the filter into a separate container using THF at room temperature or warmer. The wax and dewaxed oil fractions were recovered by rotary evaporation, followed by vacuum drying at 70 °C. The yields of each fraction and the total recovered material were calculated from the weights of feed oil and recovered fractions (Table 1). Each sample was analyzed by ^{1}H-NMR for proton distribution, and the feed and dewaxed oils were tested for liquefaction donor solvent quality by a standard assay in use in CONSOL's laboratory. Test conditions were: 9 g subject oil, 6 g Old Ben Coal (Indiana V seam), 30 minutes, 750 °F, autogenic pressure.

The results in Table 1 show that with decreasing temperature: the dewaxed oil yield decreased (wax yield increased, with a progressive reduction in wax purity); and the solvent quality of the dewaxed oil increased (levelling off at about 83% at -5 °C and lower). A decrease in wax purity with decreasing dewaxing temperature is expected from prior experience at CONSOL (1). This trend was also evident in the darker color of the filter cake, and by the increasing proportions of aromatic and alkyl alpha protons, and decreasing proportion of alkyl beta protons in the wax. Material balances were 99.8 to 100.0 wt % for these trial runs. GC-MS analysis, performed on the set of feed and product samples from these runs, showed the wax to be highly aliphatic, but not purely paraffinic. It also showed that virtually all of the n-paraffins were removed from the oil at -5 °C.

The results of these preliminary studies provided the basis for selecting the conditions to prepare two large batches (about 1 L) of dewaxed oil for Sandia to use as a hydrogenation feedstock. Although the oil dewaxed at -5 °C was essentially free of n-paraffins, dewaxing at -35 °C resulted in a product with a greater proton aromaticity (26.3 vs 20.3). The increased aromaticity, however, came at the expense of dewaxed product yield (56% vs 80%). Based on the results of these preliminary trials, it was decided to produce two batches of acetone-dewaxed oil for hydrogenation. The first batch was dewaxed at -35 °C and the second at -5 °C.

Samples of Wilsonville Run 262E V-1074 distillate were also dewaxed at -35 °C in 100% MEK and in 50/50 (vol %), 55/45 (vol %) and 60/40 (vol %) acetone/MEK mixtures. The wax yields from the runs with acetone/MEK mixtures were 11 wt%, 16 wt% and 17 wt%, respectively versus 10 wt% in 100% MEK and 44 wt% in 100% acetone, Table 2. The solvent quality index of the oil dewaxed in the 50/50 acetone/MEK mixture was 78% while that dewaxed in the 55/45 MEK/acetone mixture was 83%. This is a substantial increase over the 74% solvent quality of the oil obtained by dewaxing with 100% MEK at the same temperature.

A plot of the dewaxed oil solvent quality index against wax removal is shown in Figure 2. The data are from the preliminary dewaxing tests, the -5 °C and -35 °C production dewaxing runs, and from the tests with solvents other than acetone (e.g., MEK). It is apparent that the solvent quality of the dewaxed oil is strongly dependent on the quantity of wax removed up to about 15 wt% wax removal (~85 wt% dewaxed oil yield). At wax removals above ~15 wt%, the solvent quality is essentially constant at about 84%. This result suggests that the solvent quality of the dewaxed oil depends primarily on the extent of wax removal and not directly on the specific dewaxing solvent used or the dewaxing temperature. The production of a high-solvent-quality dewaxed oil, commensurate with minimal wax removal (thus, a more pure wax product), is desirable for optimization of distillate use and the production of by-product wax. The higher the purity of the initial slack wax, the higher will be the yield of clean wax.

Based on these studies, a large batch (~1 L) of dewaxed distillate was prepared by dewaxing the V-1074 distillate at -35 °C in 55/45 (vol %) acetone/MEK. This material was used in hydrogenation experiments at Sandia, and by CONSOL in the development of a microautoclave test for evaluating the effects of solvent treatment on the liquefaction of Black Thunder coal.

Solvent Quality Testing

CONSOL's standard microautoclave solvent quality test involves the liquefaction of Indiana V coal under relatively mild conditions (750 °F, 30 min, no H_2) to provide a relative measure of the donor hydrogen content of the solvent (2). In the present program, it is important to have a more reliable measure of the absolute improvement in process performance that can be achieved by the various solvent pretreatment steps, principally dewaxing and hydrogenation, that are envisioned in the integrated process. Therefore, a series of microautoclave tests was made using simulated Wilsonville Run 262E recycle solvent to define conditions for solvent testing.

In these tests, the recycle material was a composite of the three recycle component streams used at Wilsonville: distillate (V-1074), ashy resid (V-1082), and deashed resid (V-130). The streams were obtained from Wilsonville Run 262E and blended in the correct proportions: 42.8 wt % distillate, 50.6 wt % ashy resid, and 6.6 wt % deashed resid. In some cases, the original V-1074 was replaced in the recycle mix with dewaxed or hydrogenated-dewaxed V-1074. Coal conversions were measured by the THF solubility of the reaction products, corrected for the ash contents of the coal and recycle materials, on an SO_3-free ash basis. The conversions are expressed both on an MAF-coal-fed basis and on a total-IOM-fed basis (i.e., including the IOM in the ashy resid in the denominator of the conversion calculation). Expressing the conversion on an MAF coal basis gives an indication of the steady-state conversion one might expect in a recycle system. Expressing the conversion on an IOM-fed basis gives a better indication of the per-pass conversion activity.

The results of these experiments are given in Table 3. The variables included residence time, recycle distillate component, and recycle ratio. The first tests were made at residence times of 15-30 min, a rough approximation of the residence times in the Wilsonville reactors. However, coal conversions at these conditions were well over 100 wt % MAF coal (because of the conversion of solvent IOM), compared to approximately 90% observed at Wilsonville with subbituminous coals. As these conditions were too severe to provide a reasonable simulation of Wilsonville conversion, and an indication of the relevance of the data, the reaction time was reduced to five minutes.

The results of the five-minute runs were evaluated as a function of recycle-to-coal ratio. These results are plotted in Figure 3. Conversions in the 90% range were obtained at recycle-to-coal ratios of 1.5 and above. Therefore, it appears that microautoclave tests at these conditions (i.e., 824 °F, 5 min, 1.5 recycle-to-coal) provide a reasonable simulation of Wilsonville coal conversion results. Furthermore, at these conditions, there was a clear improvement in conversion when the dewaxed V-1074 and the hydrogenated-dewaxed V-1074 were substituted for the original V-1074 distillate in the recycle mixture. The overall improvement is in the range of 4-5 wt % MAF coal. It is significant that the high coal conversions (~90 wt %) currently attained in two-stage liquefaction processes can be further improved by solvent dewaxing and subsequent hydrogenation of the dewaxed solvent.

A potential benefit of dewaxing and/or hydrogenation of the recycle solvent is the reduction of retrograde reactions at more severe liquefaction conditions. To test this idea, a study was made of the effect of reaction temperature on the conversion of Black Thunder coal in the five-minute microautoclave test. Tests were made with the original V-1074 and with the Sandia hydrotreated -5 °C acetone dewaxed V-1074 oil substituted for the original V-1074 portion of the composite recycle solvent at 824 °F, 840 °F, 860 °F, 880 °F, and 900 °F. All conditions, except for temperature and the distillate portion of the solvent were the same for each run. The Wilsonville Run 262E composite solvent was used with a 1.5 solvent/coal (MF) ratio. The results of these tests are plotted in Figure 4.

Coal conversion with either distillate generally increases with increasing temperature up to 860 °F. At 880 °F conversion continues to increase for the hydrogenated solvent case and to level off for the untreated V-1074 case. Several repeat determinations were made at 880 °F, Figure 4, and the reproducibility of the conversion data from these repeat runs is reflected by the error bars shown for the 880 °F points. Thus, at more severe operating conditions, i.e., at temperatures >860 °F, the benefit (reflected by coal conversion) of using hydrogenated-dewaxed distillate in the recycle solvent is magnified. The relatively higher coal conversions obtained with the hydrotreated solvent at the highest temperatures are attributed to the increased H-donor capacity, and the reduction of retrograde reactions resulting from the removal of paraffins from the distillate. Increased conversion at higher temperatures with hydrogenated solvent suggests a potential benefit of solvent dewaxing/hydrogenation (i.e., the ability to operate the process at higher temperatures to attain higher single-pass conversions than are possible with current solvents).

Solvent Hydrogenation - Sandia

This portion of the program involves hydrotreating distillate solvent fractions of the composite recycle solvent, in order to enhance their H-donor capacity, and improve the effectiveness of coal conversion in the first stage. Samples of heavy distillate (V-1074) from Run 262E at Wilsonville, and dewaxed distillates prepared by acetone dewaxing V-1074 at -5 and -35 °C, were provided by CONSOL. These materials were used as feedstocks for hydrotreating at Sandia in a laboratory-scale, trickle-bed reactor, using a synthesis gas mixture (50: 50 vol % CO: H_2) and steam; in the latter part of the experiments, pure hydrogen was used. The *in situ* water-gas shift (WGS) reaction provides an alternate source of hydrogen and has the potential for eliminating the need for high-purity, high-pressure hydrogen for solvent hydrogenation (3, 4). Hydrogenation at lower temperatures can lead to increased donor content because larger amounts of hydroaromatics are produced at equilibrium with any given hydrogen pressure.

Two types of catalyst were investigated: a commercial NiMo catalyst, Shell 324M, and a platinum catalyst, which was a hydrous titanium oxide (HTO) compound synthesized at Sandia National Laboratories. A fixed bed microflow reactor was used for hydrogenation, and consisted of liquid and gas feed systems connected to a stainless steel tubular reactor (0.5" O.D.), with an internal volume of 23 cm^3, holding about 20 g of catalyst.

The experiments involved three days of testing for each combination of catalyst and feed. The first two days of experiments used the *in situ* water-gas shift reaction to hydrotreat the distillate. To test the effect of varying the partial pressure of hydrogen gas on solvent hydrogen uptake, only hydrogen gas was used for reactions on the third day. The catalyst was first packed in the reactor tube and then pretreated in the appropriate fashion. The commercial nickel molybdenum on alumina catalyst (NiMo) was presulfided with a 9% H_2S/H_2 mixture for four hours at 390 °C. The platinum (Pt HTO) catalyst was pre-reduced in hydrogen at 200 °C for two hours.

After catalyst pretreatment, the reactor was pressurized to 1000 psig with a 50:50 mixture of carbon monoxide and hydrogen. The reactor temperature was increased to the operating value (300-325 °C), while the distillate and a 1:1:1 molar mixture of $CO:H_2:H_2O$ were fed to the reactor. The carbon monoxide component of the "synthesis gas" was set to flow at 3.6 L/hr, giving a gas hourly space velocity of 150 hr^{-1}. The distillate liquid weight hourly space velocities (WHSV) were varied between 0.4 hr^{-1} and 0.8 hr^{-1}. All reactants flowed downward over the packed bed into a reservoir which was used to separate the gases and liquids. Liquid and gas products were sampled from this reservoir during operation. Distillates and hydrotreated distillates were analyzed by high resolution gas chromatography, proton NMR spectroscopy and for solvent quality (SQ) using the modified equilibrium test developed by CONSOL (2).

The results of hydroteating the heavy distillates with the combined water-gas shift reaction and the NiMo catalyst are shown in Table 4. In general the heavy distillate samples gained from 0.3 to 0.8% hydrogen under the reaction conditions, with attendant decreases in aromatic hydrogen concentration. Solvent quality improved by about five to seven points for each of the hydrogenated samples, whether dewaxed or not, although much higher values were obtained with the dewaxed distillates.

The water-gas shift reaction is essentially complete at 300 to 325 °C under these conditions (carbon monoxide conversion was greater than 95% for all experiments involving synthesis gas), and the estimated hydrogen partial pressure from the combined water-gas shift solvent hydrogenation experiment with "near equilibrium" conversions of carbon monoxide is approximately 670 psig (2/3 of system pressure). Sample 110602 in Table 4 was produced on the third day of testing using 1000 psig of hydrogen pressure to hydrogenate the -35 °C dewaxed distillate and showed that the increased hydrogen partial pressure improved hydrogenation over the WGS case, further reducing the aromatic hydrogen content from 20.4% to 18.9%.

The effect of hydrogen pressure on hydrogenation of the -5 °C dewaxed heavy distillate, with the platinum HTO catalyst, at 325°C and WHSV = 0.8 hr^{-1}, is shown in Table 5. Each result was obtained on the third day of testing (after the bulk of the catalyst deactivation had taken place) using only hydrogen as the gas phase. Decreasing the hydrogen pressure from 1000 psig to 333 psig reduced the hydrogen content of the distillate from 9.6% to 8.6%, confirming that the degree of hydrogenation is directly related to the hydrogen partial pressure in the reactor. The 1000 psig product showed the most extensive hydrogenation, as indicated by the aromatics content, which was the lowest produced under all the conditions and catalysts tested.

The analyses of samples sent to CONSOL and CAER for microautoclave liquefaction tests are shown in Table 6. Sample SC-1 was a composite of many -5 °C acetone dewaxed heavy distillate samples hydrogenated at 300 to 325 °C in the trickle-bed reactor. A composite sample labeled HYD V1074 (hydrogenated at 300 °C) was shipped to CAER for testing the effect of hydrotreating the original V1074, and a sample of -5 °C dewaxed distillate hydrotreated with pure hydrogen at 1000 psig (HYD Dewax -5°C V-1074) was also sent.

This research has demonstrated that synthesis gas mixtures can be used to effectively hydrogenate heavy distillate solvents at low temperatures (300-325 °C), with significant improvements in solvent quality arising from the combined effects of dewaxing and hydrotreatment. To determine the merits of using pure hydrogen versus the *in situ* WGS reaction for solvent pretreatment, issues such as catalyst deactivation, gas purification and separation, and possible over-hydrogenation, with the formation of alicyclic and paraffinic compounds, will have to be considered in more detail.

Wyodak Coal Liquefaction in Modified Recycle Solvent - CAER

Microautoclave experiments were conducted to evaluate the effect of modifying the distillate portion of the Wilsonville composite recycle solvent, through the dewaxing and hyrotreatment operations described above, on the liquefaction of Black Thunder subbituminous coal. The liquefaction procedure and product analysis scheme has been described in detail elsewhere (5). Experiments were conducted in 50 mL microautoclaves at 415 °C, and 1000 psig H_2 cold. The charge was 3 g as-received coal, 5.4 g solvent. The gaseous products were analyzed by gas chromatography and the solid products were separated into THF-insoluble (IOM), THF-soluble, pentane-insoluble (PA+A), and pentane soluble fractions. The yield of each fraction was calculated by subtracting, for each fraction, the amount in the feed from the amount in the product. Based upon the assumption of complete ash recovery, the oil yields are calculated by difference from the coal feed, less moisture and SO_3-free ash; hence, they include water.

The Black Thunder subbituminous coal was ground to -200 mesh, riffled and stored under nitrogen at 4°C prior to use. The recycle material was a composite of the three recycle component streams used at Wilsonville in Run 262E, as described earlier. The distillate fraction material was varied to examine the comparative effects of the original fraction V-1074, the hydrotreated equivalent of this fraction, dewaxed V-1074 (-5°C), and hydrotreated dewaxed distillate.
The solvent fractions were characterized by solvent solubility. Properties of the coal, composite solvent fractions, composite solvent, and heavy distillates are given in Tables 7-9.

The effects of the different distillate fractions on coal liquefaction are shown in Table 10, which shows the product distributions from both 30 and 60 minute runs. The effect of simply hydrotreating the V-1074 distillate causes a significant increase in oil yield, and reductions in IOM and PA+A yields (negative IOM yields arise from the method of calculation, which assumes that the solvent IOM does not convert). This result alone demonstrates that the normal distillate fraction is H-donor deficient, and that significant potential improvements could be made through a distillate hydrogenation step.

Distillate dewaxing also has a substantial influence on liquefaction performance: after 30 min reaction, the effect on product distribution is less pronounced than that caused by V-1074 hydrogenation, but after 60 min the product distributions are more similar. Some further improvement is produced by hydrotreatment of the dewaxed distillate.

From these results, it is apparent that pretreatment of the distillate solvent fraction can cause substantial improvements in liquefaction performance. Continuing work will be directed to determine how best to utilize this information in order to most advantageously influence liquefaction economics.

Techno-economic assessment - LDP Associates

The evaluation of the process modifications developed in this program necessitated the establishment of a baseline case, which was developed using data from Wilsonville Run period263J, Figure 1. In this run the Wilsonville unit was operated with Black Thunder subbituminous coal in a hybrid mode with the use of both dispersed and supported catalysts. Dispersed iron and molybdenum catalysts were added upstream of the first stage thermal reactor, and a supported nickel-molybdenum catalyst was used in the second stage reactor. The unit was operated at relatively high space velocity and at relatively high temperatures. As a consequence of this high severity of operation, the solvent quality of the recycle process solvent was poor, as indicated by CONSOL's modified equilibrium test (2). It was also noted during Wilsonville Runs 262 and 263 that waxy material accumulated in the distillate portion (V-1074) of the recycle solvent. For this reason, and as already described, dewaxing and hydrotreating of the distillate portion of the recycle process solvent was considered to present a viable route to improving solvent quality and overall liquefaction system economics.

The positions of the dewaxing and hydrotreating processes are shown in Figure 1. Coal and a three-stream recycle process solvent are fed to the liquefaction reactors. The heaviest product from the second stage is fed to a vacuum tower which separates a heavy distillate fraction from the ash-containing residue fraction. Part of the ashy residue is recycled while a smaller portion is fed to a ROSE unit where the net ash fed to the system is removed and a clean resid material is recovered and recycled. In the proposed scheme, the approximately 650^{0}F+ heavy distillate stream from the vacuum tower is at least partially dewaxed and then hydrotreated before being recycled back to the liquefaction system.

The dewaxing step involves solvent precipitation and filtration of the wax species below ambient temperatures. Dewaxing is a commonly applied technique in the petroleum refining industry to remove paraffinic hydrocarbons from lube oil stocks. The waxy material or slack wax removed in the dewaxing unit is highly paraffinic. Several processing options can be used with this material. Through the use of additional processing steps (deoiling and hydrotreatment) a high value, fully refined paraffin wax can be recovered. On a weight basis, fully refined paraffin wax sells for approximately 3 times the price of gasoline. Alternatively, the highly paraffinic slack wax stream can be sent to a fluid cat cracking unit where it is readily converted into gasoline and other refinery type by-products. The choice of processing options for the slack wax will depend on the quantity of fully refined paraffin wax which could be produced versus current market demand for this product, along with the costs associated with the additional processing steps required to produce the product.

The results described earlier show that the solvent quality of the heavy distillate stream is significantly improved by dewaxing. However, for projected commercial operation a cost-benefit analysis is required to determine the optimum level of wax-like constituents in the distillate recycle solvent. A good parameter to be used in such an analysis is the concentration of alkyl beta protons in the stream. Alkyl beta protons are representative of the (undesirable) paraffinic content of the solvent.

Using the CONSOL experimental batch dewaxing data and commercial dewaxing information, estimated steady-state simulations of commercial dewaxing operations were developed as a function of the amount of the heavy distillate fed to the dewaxer. The results of these simulations are shown in Figure 5 and Table 11. Naturally, as the proportion of heavy distillate fed to the dewaxer increases, the alkyl beta proton concentration of the recombined distillate decreases and its quality as a solvent increases. Unfortunately, dewaxing costs increase with increasing feedrates. It is also noteworthy, that the most significant drop in alkyl beta content is achieved when only 25% of the heavy distillate is fed to the dewaxer. Future evaluation work is directed to quantifying: (1) dewaxing costs for a range of feed rates, and (2) the benefits of better solvent quality at several levels of dewaxing. Later, the proposed testing in fully continuous and integrated mode will allow confirmation of these results and and an evaluation of the economic impact with a much higher level of confidence.

Further gains in solvent quality are effected by dewaxing followed by hydrotreatment. Preliminary estimates indicate that the capital cost of hydrotreating will be lower than the capital cost of dewaxing. Nonetheless, the hydrotreating unit capital cost will be a significant factor in determining the economic viability of this process concept. It is intended to assess the dewaxing-only option in order to fully evaluate the use of hydrotreating. It is further expected that the hydrotreater reactor cost will the most important determinant of the hydrotreating unit cost.

Therefore, higher space velocity operation would appear to be desirable, especially since heteroatom removal is not a criterion of performance. Catalyst stability and life will also be important factors in the hydrotreating unit costs. Once again continuous operation will be required to confirm estimates made from batch data.

Synopsis

This paper has described the results of a specific combination of concepts that form part of a broader program to examine routes to reducing the cost of producing coal liquids. In the research, data from the Wilsonville pilot plant are used as a base case against which to assess the extent of improvements in performance. For this reason, the experimental work is conducted using process-derived materials. The present study has been concerned with improving the recycle solvent quality, through pretreatment of the heavy distillate fraction by dewaxing, hydrotreatment, and dewaxing followed by hydrotreatment. It has been demonstrated that each of these measures increases IOM conversion, increases oil yield, and reduces the yield of preasphaltenes and asphaltenes. The dewaxing step produces, in addition, a by-product wax. The reasons for improvement are considered to relate to the reduction of retrograde reactions due to the removal of paraffins and naphthenes, and to increases in H-donor capacity. Further research will help to establish the configuration to optimize operation of these processing steps to have the most beneficial effect on liquefaction economics.

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Table 1. Results of Acetone Dewaxing

Temp, °C	Dewaxed Oil Yield, wt %	^{1}H-NMR Analysis Aromatics[a], %	Paraffinics[b], %	Solvent Quality[c], %
Feed	—	14.9	46.9	64
0	90.5	17.3	41.0	72
-5	80.4	20.3	34.8	83
-10	79.2	20.1	34.0	84
-20	70.7	23.0	28.9	85
-35	55.7	26.3	26.6	83

a = Condensed aromatic protons + uncondensed aromatic protons
b = Alkyl beta + gamma protons
c = % MAF conversion of Indiana V coal to THF solubles at 750 °F, 30 min, S/C = 1.5

Table 2. Data for Acetone/MEK Dewaxing at -35 °C

		^{1}H-NMR Analysis		
Acetone/MEK, vol %	**Dewaxed Oil Yield, wt %**	**Aromatics[a], %**	**Paraffinics[b], %**	**Solvent Quality[c], %**
Feed	-	14.9	46.9	64
100/0	55.7	23.5	29.1	83
60/40	83.5	19.1	39.0	81[d]
55/45	83.9	20.2	35.6	83
50/50	89.0	18.3	38.5	78
0/100	90.1	17.5	42.9	74

a = Condensed aromatic protons + uncondensed aromatic protons
b = Alkyl beta + gamma protons
c = % MAF conversion of Indiana V coal to THF solubles at 750 °F, 30 min, S/C = 1.5
d = calculated from ^{1}H-NMR data, Reference B.

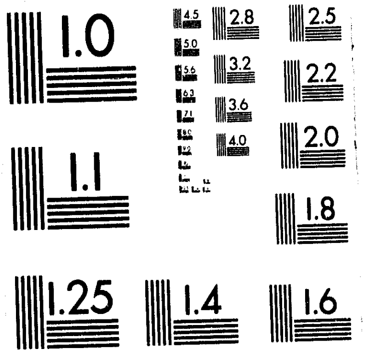
1.0
4.5
5.0
5.6
6.3
7.1
8.0
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

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Table 3. Exploratory Microautoclave Tests with Black Thunder Coal

Run	Temp.	Time	Recycle/	Coal		Recycle						Conversion, %MAF		Comments
No.	°F	Min[1]	MF Coal[3]		wt.g	Comp1	wt.g	Comp2	wt.g	Comp 3	wt.g	Coal[2]	IOM[2]	
19	824	5	1.04	BT[3]	6.16	V-1074	2.18	V-130	0.34	V-1082	2.59	71.8	64.1	5-minute runs using the original V-1074 as the distillate portion of the recycle. Recycle/coal ratio variable. 824°F. Concentrations as in original Wilsonville composite solvent.
14	824	5	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	87.5	74.6	
12	824	5	2.3	BT	3.84	V-1074	3.00	V-130	0.46	V-1082	3.56	88.8	70.3	
20	824	5	1.04	BT	6.16	-35°C DW	2.18	V-130	0.34	V-1082	2.59	76.6	68.4	Same as above but with dewaxed V-1074
16	824	5	1.51	BT	4.55	-35°C DW	2.33	V-130	0.36	V-1082	2.76	89.0	76.0	
15	824	5	2.3	BT	3.84	-35°C DW	3.00	V-130	0.46	V-1082	3.56	89.7	71.1	
21	824	5	1.04	BT	6.16	SC-1	2.18	V-130	0.34	V-1082	2.59	79.7	71.2	Same as above but with hydrogenated, dewaxed V-1074
18	824	5	1.51	BT	4.55	SC-1	2.33	V-130	0.36	V-1082	2.76	92.1	78.6	
27	824	5	2.3	BT	3.84	SC-1	3.00	V-130	0.46	V-1082	3.56	93.6	74.1	
11	824	15	2.3	BT	3.84	V-1074	3.00	V-130	0.46	V-1082	3.56	106.4	84.2	15-minute run with V-1074
8	824	30	1.51	BT	4.55	V-1074	2.33	V-130	0.36	V-1082	2.76	103.5	88.3	30-minute runs with V-1074 in Wilsonville composite solvent. Recycle/coal ratio variable.
5	824	30	2.3	BT	3.84	V-1074	3.00	V-130	0.46	V-1082	3.56	109.5	86.7	
6	824	30	2.3	BT	3.84	V-1074	3.00	V-130	0.46	V-1082	3.56	109.0	86.3	
9	824	30	1.51	BT	4.55	-35°C DW	2.33	V-130	0.36	V-1082	2.76	104.4	89.1	30-minute runs with dewaxed V-1074. Recycle ratio variable.
7	824	30	2.3	BT	3.84	-35°C DW	3.00	V-130	0.46	V-1082	3.56	108.8	86.2	

[1] Residence time includes 2.5-minute heatup. All runs at 1500 psig (cold) H_2

[2] SO_3 - free ash basis

[3] BT - Black Thunder, subbituminous

Table 4. Properties of hydrogenated distillates (NiMo catalyst; $CO/H_2/H_2O$)

Feed	Hydrotreating Temp (°C)	Hydrogen %	Aromatics %	Paraffinics %	Hydroaromatics %	Solvent Quality
V1074	NA	9.9	14.9	46.9	30.5	63.8
92804	300	10.7	11.0	49.9	31.8	70.9
92906	325	10.2	12.7	49.1	30.9	70.7
-5 °C	NA	8.5	21.6	33.4	35.8	82.1
102205	300	≈ 8.9	16.0	35.9	38.1	90.8
102305	325	≈8.8	18.3	33.7	38.3	88.6
-35 °C	NA	8.0	23.5	29.1	37.1	85.3
110507	325	NA	20.4	30.9	38.6	89.1
110602	325*	NA	18.9	31.1	38.3	90.3

*Hydrogen pressure only, no concurrent WGS reaction

Table 5. Properties of distillates hydrogenated at various hydrogen pressures (Pt HTO catalyst)

Feed	Hydrogen Pressure (psig)	Hydrogen %	Aromatics %	Paraffinics %	Hydroaromatics %	Solvent Quality
-5 °C Dewax	NA	8.5	21.6	33.4	35.8	82.1
111903	1000	9.6	10.3	46.6	35.4	89.2
111905	670	9.0	ND	ND	ND	ND
111907	333	8.6	19.6	35.8	35.4	88.4

Table 6. Properties of samples for microautoclave testing at CONSOL and CAER

Feed	Hydrogen source	Hydrogen %	Aromatics %	Paraffinics %	Hydroaromatics %	Solvent Quality
V1074*	NA	9.9	14.9	46.9	30.5	63.8
HYD V1074*	WGS	10.5	ND	ND	ND	ND
-5 °C V1074*	NA	8.5	21.6	33.4	35.8	82.1
HYD -5 °C V1074*	Hydrogen gas	8.9	16.7	34.3	39.5	ND
SC -1**	WGS and Hydrogen	ND	16.6	37.3	36.1	90.0

* Used for tests at CAER with Black Thunder Coal
** Composite sent to CONSOL

Table 7. (from CONSOL, INC.) Analysis of Materials from Wilsonville Run 262E (September 16, 1991)

	Black Thunder Coal	V-1082 Ashy Resid	V-130 Deashed Resid	V-1074 Distillate
Moisture, wt% as received	22.40	-	-	-
Ultimate, wt% dry				
Carbon	70.32	72.59	89.79	88.86
Hydrogen	4.68	5.40	7.26	9.91
Nitrogen	1.04	0.88	0.86	0.44
Sulfur	0.50	1.93	0.03	<0.03
Chlorine	0.035	N.D.	N.D.	N.D.
Ash	6.69	20.28	0.73	N.D.
SO_3-free basis	5.54	16.04	N.D.	N.D.
Oxygen, by diff	16.74	-1.08	1.33	0.79
SO_3-free basis	17.89	3.15	N.D.	N.D.
Molybdenum, mg/kg as det	20	298	53	2
Sulfur forms, wt% dry				
Pyritic	0.08	—	—	—
Sulfate	0.08	—	—	—
Organic	0.34	—	—	—

Table 8. Wilsonville Run 262E Solvent Composition, wt%

	Heavy Distillate V-1074	Deashed Resid V-130	Ashy Resid V-1082	Composite Solvent V-131B
Concentration	42.7[a]	6.6[a]	50.7[a]	100[a]
1050°F- Distillate	100 (assumed)	16.0[a]	2.5[a]	43.8[a]
Cresol Soluble Residue	0 (assumed)	83.9[a]	58.8[a]	36.6[a]
Cresol Insolubles	0 (assumed)	0.01[a]	18.3[a]	9.2
Ash	0 (assumed)	0.11[a]	20.4[a]	10.4
Iron	not determined	100	3.3	1.7
Mo, ppmw	2	53	300[b]	160[b]

a. Values supplied by Wilsonville personnel

b. Calculated from component fraction analysis

Table 9. Solvent Characterization of Wilsonville Run 262E Recycle Solvent Components

Solvent Separation Results	Oils	PA+A	IOM	Ash
Heavy Distillate (V-1074)	95.91	0.74	3.09	0.26
Deashed Resid (V-130)	63.51	32.63	3.43	0.43
Ashy Resid (V-1082)	29.78	31.89	18.31	20.03
Hydrotreated Heavy Distillate	95.0	0.1	4.9	
-5 °C Dewaxed Heavy Distill.	91.3	5.5	3.2	
Hydrotreated Dewaxed Heavy Distillate	93.6	0.8	5.6	

Table 10. Effect of Distillate Component on Liquefaction of Black Thunder Coal at 415 °C (wt% maf coal)

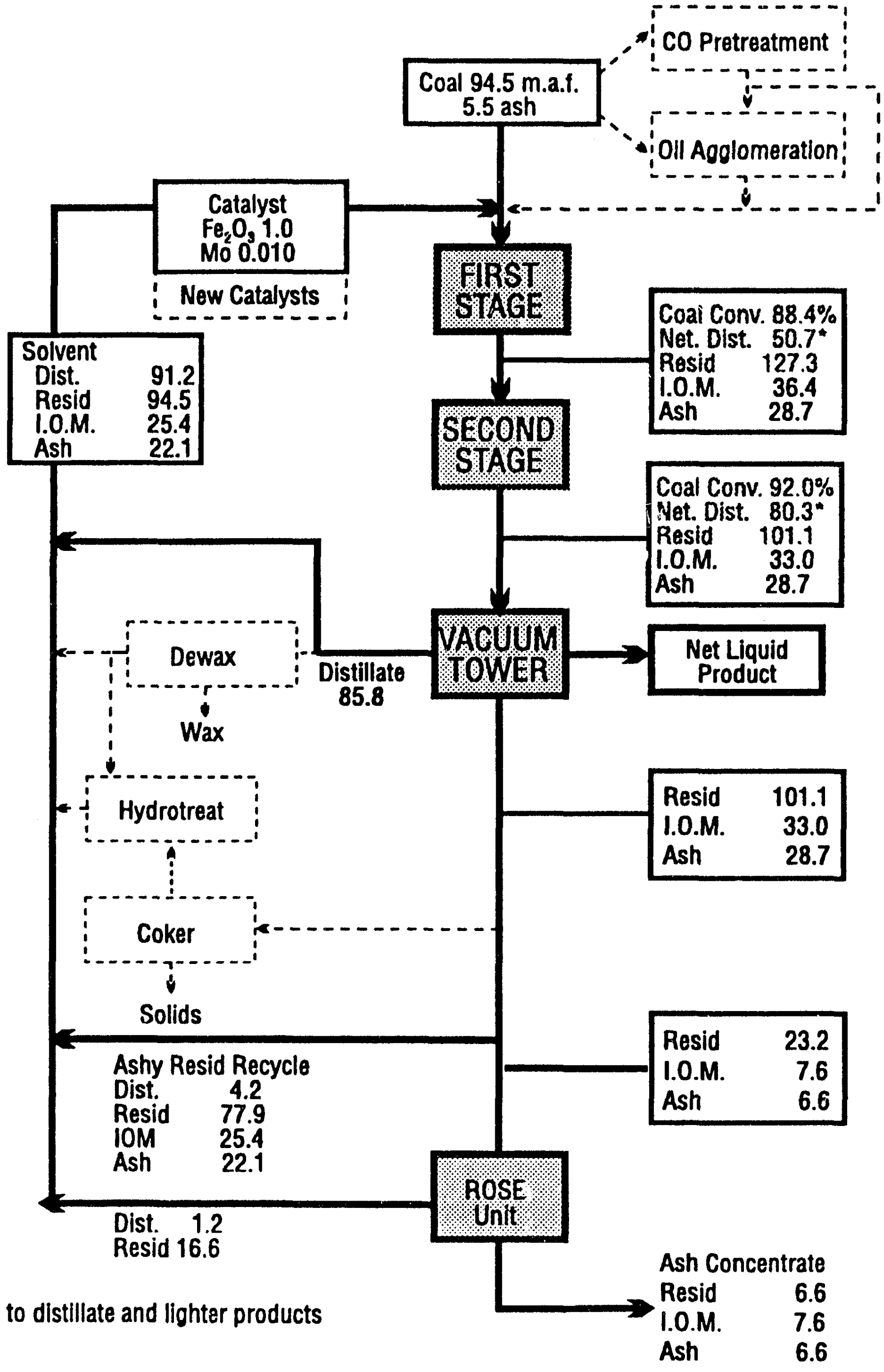
	$1050^{\circ}F^{-}$ Distillate Source			
30 minute runs	V-1074	HYD V-1074[a]	Dewax V-1074	HYD/Dewax[b] V-1074
HC Gases	1	1	1	1
$CO+CO_2$	5	5	5	5
Oils	34	53	42	51
PA+A	53	40	50	44
IOM	6	0	2	-2
mg H_2/g maf coal	43	43	42	44
60 minute runs				
HC Gases	2	2	2	2
$CO+CO_2$	5	6	6	6
Oils	49	62	58	63
PA+A	46	36	42	35
IOM	-1	-6	-7	-6
mg H_2/g maf coal	56	51	49	48

a - hydrogenated by WGS

b - hydrogenated with pure hydrogen

Table 11. Dewaxing & Hydrotreating of Distillate Recycle Solvent : Dewaxing Unit Options

% FED TO DEWAXING UNIT:	None	25	50	100
DEWAXING UNIT FEED				
- Feedrate, Lb/100lb MF Coal	None	24.37	46.95	91.09
- % Alkyl Beta Protons	-------	26.80	25.06	23.62
- Wt.% Hydrogen	-------	9.36	9.22	9.10
SLACK WAX YIELD				
- Wt.% of Feed	-------	11.06	7.64	4.81
lb/100lb MF Coal	-------	2.70	3.59	4.38
SLACK WAX PROPERTIES				
- % Alkyl Beta Protons	-------	67.66	67.19	66.80
- Wt.% Hydrogen	-------	14.60	14.35	14.15
- Watson 'K' Factor	-------	12.05	12.04	12.02
DEWAXED OIL PROPERTIES				
- % Alkyl Beta Protons	-------	21.72	21.57	21.44
- Wt.% Hydrogen	-------	8.71	8.79	8.84
DISTILLATE RECYCLE SOLVENT				
- % Alkyl Beta Protons	34.64	25.53	23.31	21.44
- Wt.% Hydrogen	9.91	9.20	8.95	8.84



* Conversion to distillate and lighter products

Figure 1. Schematic of all-distillate mode operation based on Wilsonville pilot plant operation, Period #263J (SO_3-free ash basis)

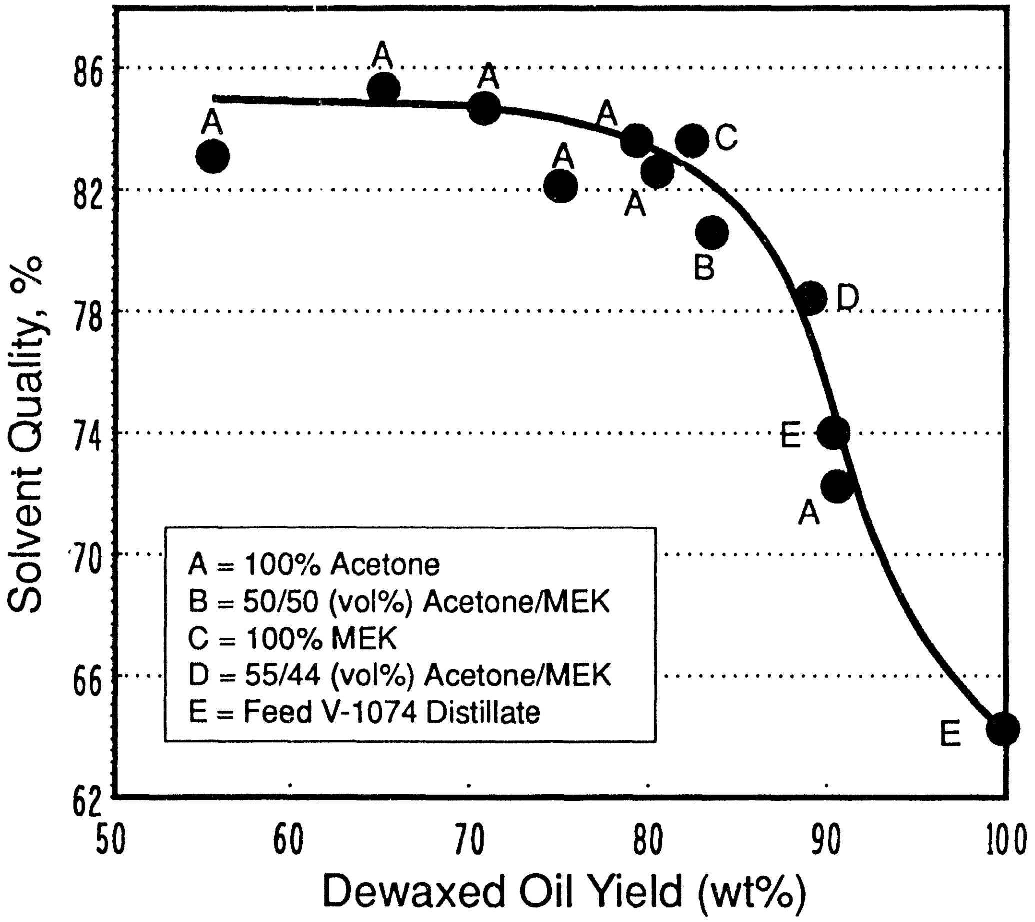


Figure 2. Solvent Quality Changes with Dewaxed Oil Yield

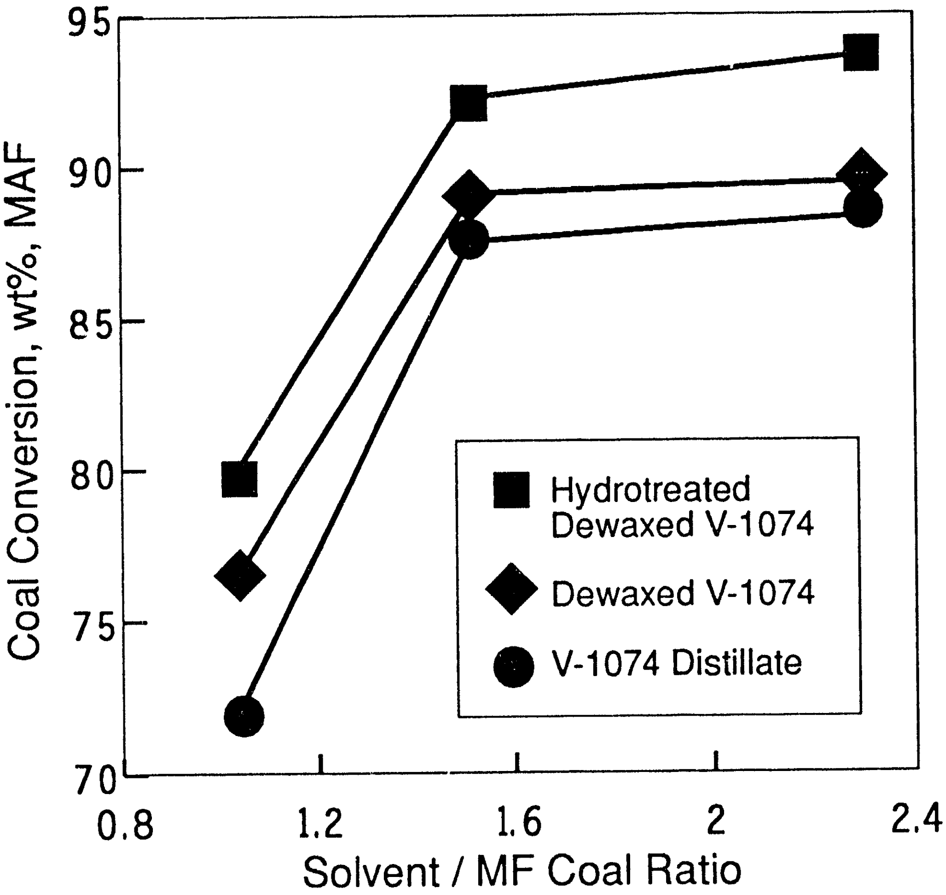


Figure 3. Conversion of Black Thunder Coal vs. Solvent / Coal Ratio (824 °F, 5 min., 1500 psig H_2).

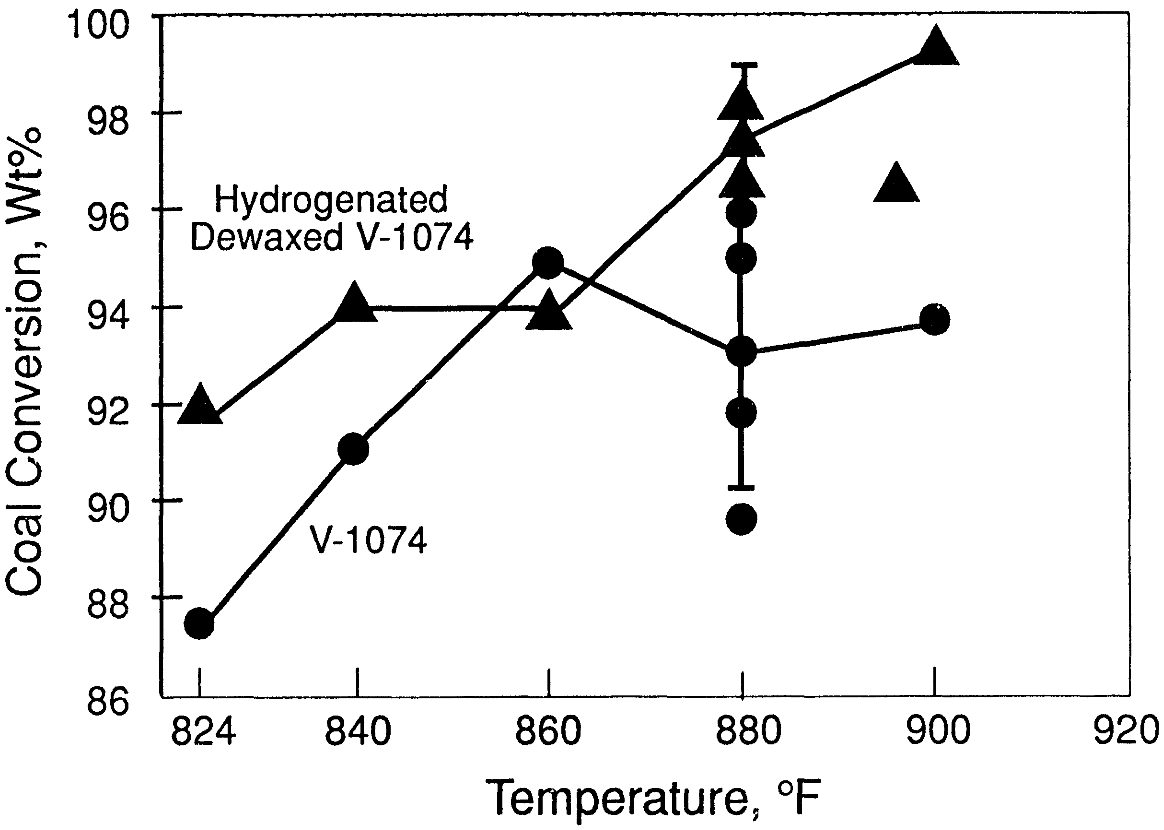


Figure 4. Distillate Quality Affects the Relationship Between Black Thunder Coal Conversion and Temperature

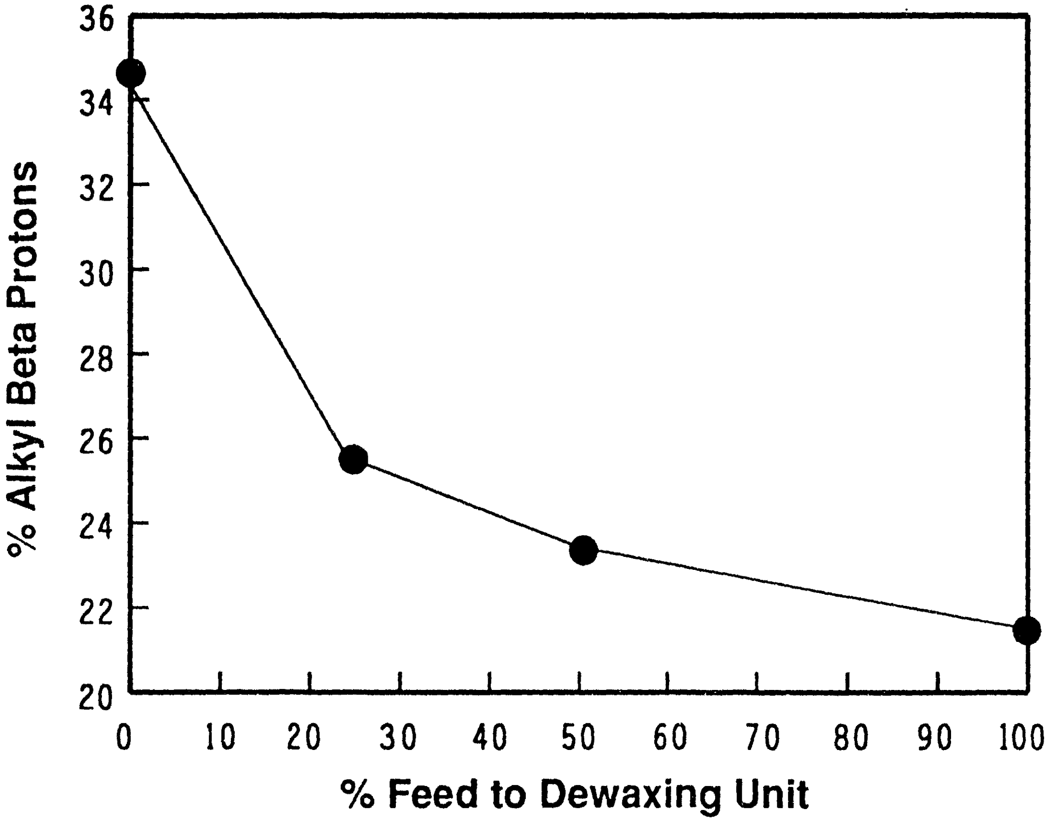


Figure 5. Effect of Dewaxing Unit Bypass on Solvent Quality

Advanced Liquefaction Using Coal Swelling and Catalyst Dispersion

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Contract No. DE-AC22-91PC91051
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INTRODUCTION

The objective of this project is to develop an improved liquefaction process to generate an all-distillate product slate at a sizable cost reduction over current technology. All aspects of the liquefaction process are involved including coal selection, pretreatment, coal swelling with catalyst impregnation, coal liquefaction with solvent evaluation, product recovery with characterization, alternate bottoms processing, and a technical assessment. The research is being carried out in cooperation with Foster Wheeler Development Corporation (FWDC), Auburn University (AU), Pennsylvania State University (PSU), and Hazen Research Inc.

RESEARCH PROGRESS

Coal Selection and Beneficiation:

The primary coals selected for this study were Burning Star (Illinois No. 6) bituminous, Black Thunder (Wyoming) subbituminous, and Martin Lake (Texas) lignite. All of these coals had been tested in the Wilsonville Advanced Coal Liquefaction Facility, and the first two were converted effectively in their two-stage, close-coupled unit. The conversion of the lignite was less than desired. In addition, these coals are considered somewhat representative of their rank.

Coal beneficiation consists of one or several of the following: size selection (crushing followed by screening), treatment with mild acids to remove alkaline metals, gravity separation (sink/float), and agglomeration with or without froth flotation. The effectiveness of each procedure depends upon coal characteristics, that are typically related to rank. Extensive beneficiation using physical techniques has been reported for Illinois No. 6 coal. A representative ash level of 5 to 6% has been achieved with feed coals containing in excess of 10% ash. Because treatment with mild acid does not demineralize this coal further, it was not studied in this program.

A schematic of the treatment of a sample of Martin Lake lignite is given in Slide 1. This sample was crushed and screened to generate a high yield (86%) of material in the size range of 8x60 mesh. The lignite was contacted for 2-4 hours with sulfurous acid (5%) and flushed with water on a screen to remove the acid. Additional (2%) fines were collected. The 8x60 mesh lignite was gravity separated in a heavy media (magnetite) cyclone, and recovered. The overall yield of beneficiated sample was 62% of the feed. Analyses of this and similarly treated Black Thunder coal are given in Slide 2. It is noted that ash removal of these low rank coals is very effective, but there is some retention of sulfur.

Flotation/agglomeration experiments were carried out with raw and sulfurous acid-treated Black Thunder coal. The results and recommendations are summarized in Slide 3. In summary, a 96% recovery of a coal containing only 2.1% ash was achieved at the best operating conditions in the laboratory. In pilot-scale units, these figures were 88% and 2.3%, respectively, but the system was not optimized.

Coal Swelling:

Coals are postulated to consist of three-dimensionally cross-linked macromolecular networks. The controlling factors in coal swelling are the solvent-coal interactions and the cross-link density of the coal. Coal can exist in the glassy state, in which the macromolecular chains are constrained and diffusion is slow. They can also exist in the rubbery state, in which the chains move freely and diffusion is high. Solvents can change the coal from one to the other state. Solvents can be considered to be hydrogen-bond disrupting (coal-coal bonds are replaced with solvent-coal) or charge-transfer disrupting (i.e. tetrahydrofuran in Illinois coal).

The results of swelling the above coals with selected solvents and mixtures of solvents are presented in Slides 4 and 5. A comparison of swelling effectiveness of the raw and sulfurous acid-treated coals is given in Slide 6. The conclusions are given in Slide 7.

Coal Liquefaction Experimentation:

Both laboratory- and bench-scale experiments are underway; the goals are: (1) evaluate the effect of coal pre-treatment (beneficiation) on conversion, (2) test slurry phase catalysts, and (3) determine the effect of coal pre-swelling on conversion.

The reference laboratory-scale liquefaction reactions were performed with raw and sulfurous acid-treated Black Thunder coals using pyrene as both a probe hydrogenation species and a solvent. Subsequent runs were made with the addition of liquefaction solvents (1-methylnaphthalene (1-MN), V-1074 Wilsonville gas oil, or dihydroanthracene (DHA)). The results of selected experiments are given in Slides 7 through 10.

The following conclusions were drawn from the above runs and preliminary bench-scale runs:

1. SO_2-pretreatment enhanced coal conversion with and without solvent swelling.

2. Nickel octoate and Molyvan-L were the most active catalysts for both conversion and pyrene hydrogenation.

3. Coal conversion increased with solvent donor quality.

4. Hydrogenation was dependent upon catalyst type and sulfur addition.

5. Preswelling was more positive for untreated than SO_2-treated Black Thunder coal.

6. Molyvan-L was a more effective catalyst precursor that nickel octoate for pre-swelled coal.

7. Dimethyl sulfoxide was an effective swelling agent , but it was detrimental for coal conversion.

8. Initial bench-scale runs indicated that the effect of pre-swelling in combination with catalyst impregnation was marginal for both Black Thunder and Illinois No. 6 coals.

Emphasis in the future will be directed toward developing a better understanding of the role of dispersed catalyst precursors using laboratory and bench scale experiments and observing catalyst impregnation and stability.

Bottoms Processing:

Experimentation is underway to recover recycle solvent and products that are generated in the reactors. The goals are to: (1) evaluate the FWDC ASCOT process, which consists of coupling solvent deasphalting with delayed coking, and (2) maximize the production of coal-derived liquids while rejecting solids within the coke drum. Bench-scale deasphalting runs are being made in a unit of 16 L capacity. Coking runs are being made in a mini-delayed coker consisting of two 4" by 4' coke drums. Experimentation also consists of product and feed characterization and carrying out asphalt/solvent fluidity and pumping tests.

The schematic of the ASCOT process is given in Slide 11; specifically, the solvent-deashing (SDA) option. Experimentation has been carried out testing both options with a comparison to the vacuum distillation/ROSE-SR process combination that was used at Wilsonville using the same feed slurry blend. See Slide 12 for the Wilsonville results, and the feedstock inspection is given in Slide 13.

The comparison of yields for the three options to process atmospheric tower bottoms product is summarized in Slide 14. The maximum yield of total oils (distillate plus deasphalted heavy bottoms) was achieved with the ASCOT process; namely 65%. The total yield of distillate oil plus resid for the Wilsonville approach was 59%, and that of direct delayed coking was only 53%.

PROGRAM SUMMARY

The following observations/conclusions are drawn:

1. Emphasis in coal selection is centering upon subbituminous and bituminous coals. Limited experimentation will be done with Texas lignite.

2. The study of beneficiating Black Thunder subbituminous coal is nearing completion. A coal containing 4% ash has been achieved using sulfurous acid-treatment in combination with size selection. With the subsequent use of froth flotation and agglomeration, the ash level was reduced to 2.2%. Recoveries were high in the laboratory runs, but they have not been optimized in bench-scale runs (such optimization studies are not included in this program.)

3. Data is available for the beneficiation of Illinois No. 6 and similar bituminous coals.

4. The study of beneficiating Martin Lake lignite using size selection, acid treatment, and froth flotation/agglomeration is underway.

5. Pertinent coal swelling data is available.

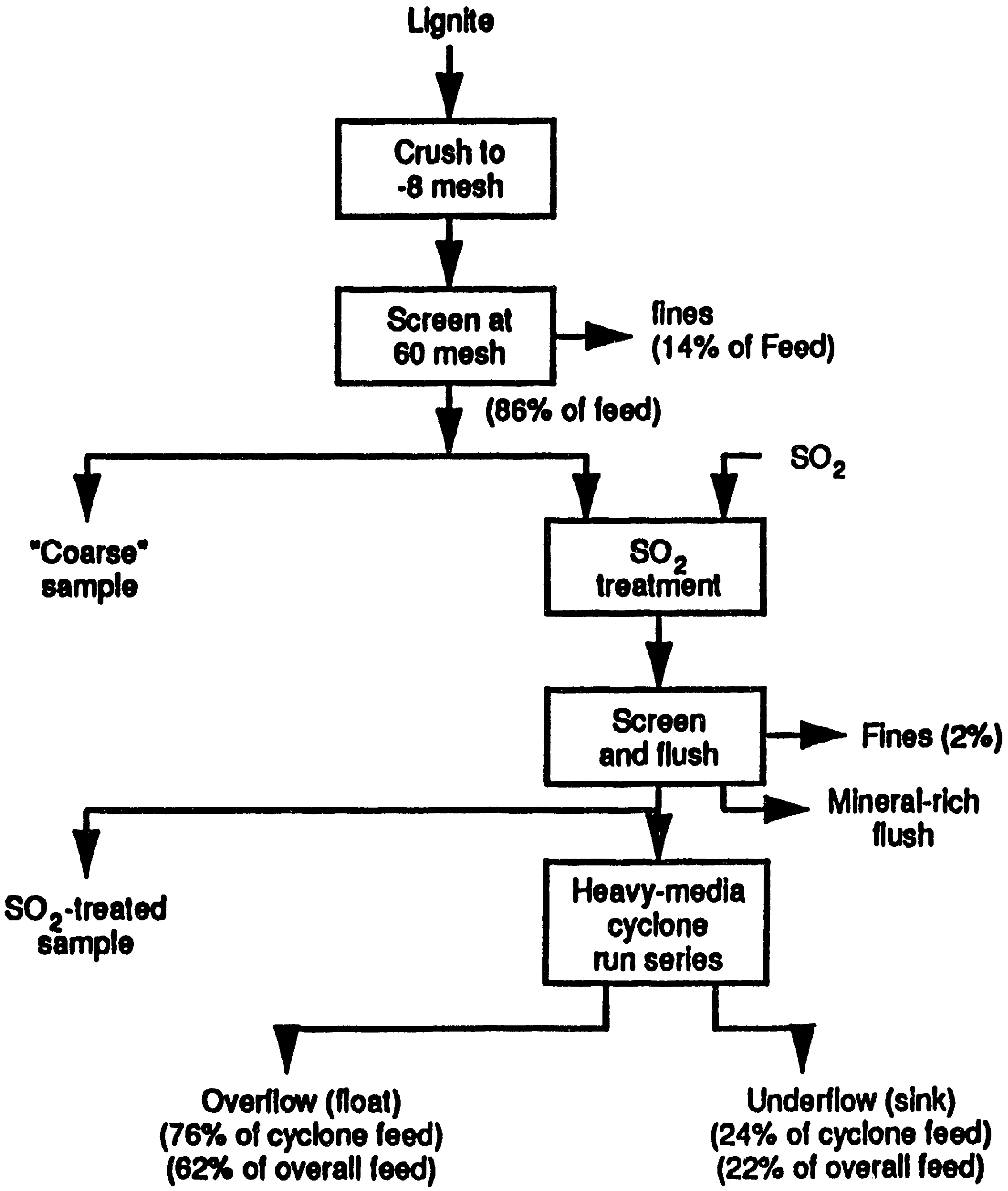
6. Laboratory- and bench-scale coal swelling plus catalyst impregnation experimentation is underway. Improvements will have to be generated to achieve a major change in process concepts.

7. In the study of bottoms processing, the ASCOT approach is favorable. Experimentation with Wilsonville samples is nearing completion, and that with Amoco-generated bench-scale product will have to be done.

8. The calculation of an economic evaluation of process options is being delayed pending the completion of an on-going Bechtel/Amoco project.

SLIDE 1

Lignite Beneficiation Procedure



Lignite

Crush to -8 mesh

Screen at 60 mesh

fines (14% of Feed)

(86% of feed)

"Coarse" sample

SO_2

SO_2 treatment

Screen and flush

Fines (2%)

Mineral-rich flush

SO_2-treated sample

Heavy-media cyclone run series

Overflow (float)
(76% of cyclone feed)
(62% of overall feed)

Underflow (sink)
(24% of cyclone feed)
(22% of overall feed)

COAL ANALYSES

Coal	Black Thunder		Martin Lake		Burning Star
	Subbituminous		Lignite		Bituminous
	Raw	SO_2-T	Raw	SO_2-T Float	
Ultimate: (Dry Basis, Wt%)					
Carbon	69.7	70.5	62.5	68.3	69.5
Hydrogen	4.9	5.0	4.4	4.9	4.6
Nitrogen	0.9	0.9	1.4	1.4	1.2
Sulfur	0.4	0.8	1.5	1.0	3.3
Ash	6.1	3.4	13.4	5.6	9.4
Oxygen (diff.)	18.0	19.4	17.3	18.3	12.0
	100.0	100.0	100.0	100.0	100.0

SLIDE 3

FLOTATION/AGGLOMERATION EXPERIMENTS
(Untreated and SO_2-treated BT coal)

Laboratory Treatment:

- Grinding: 400 mesh

- Dispersant during Grinding: Sodium hexametaphosphate (calgon) addition had a marginal effect.

- Solids Concentration: Low coal concentrations (2%) desired.

- Flotation: Dodecane (collector) and methyl iso-butyl carbinol (MIBC/frother) are effective (2.2% ash).

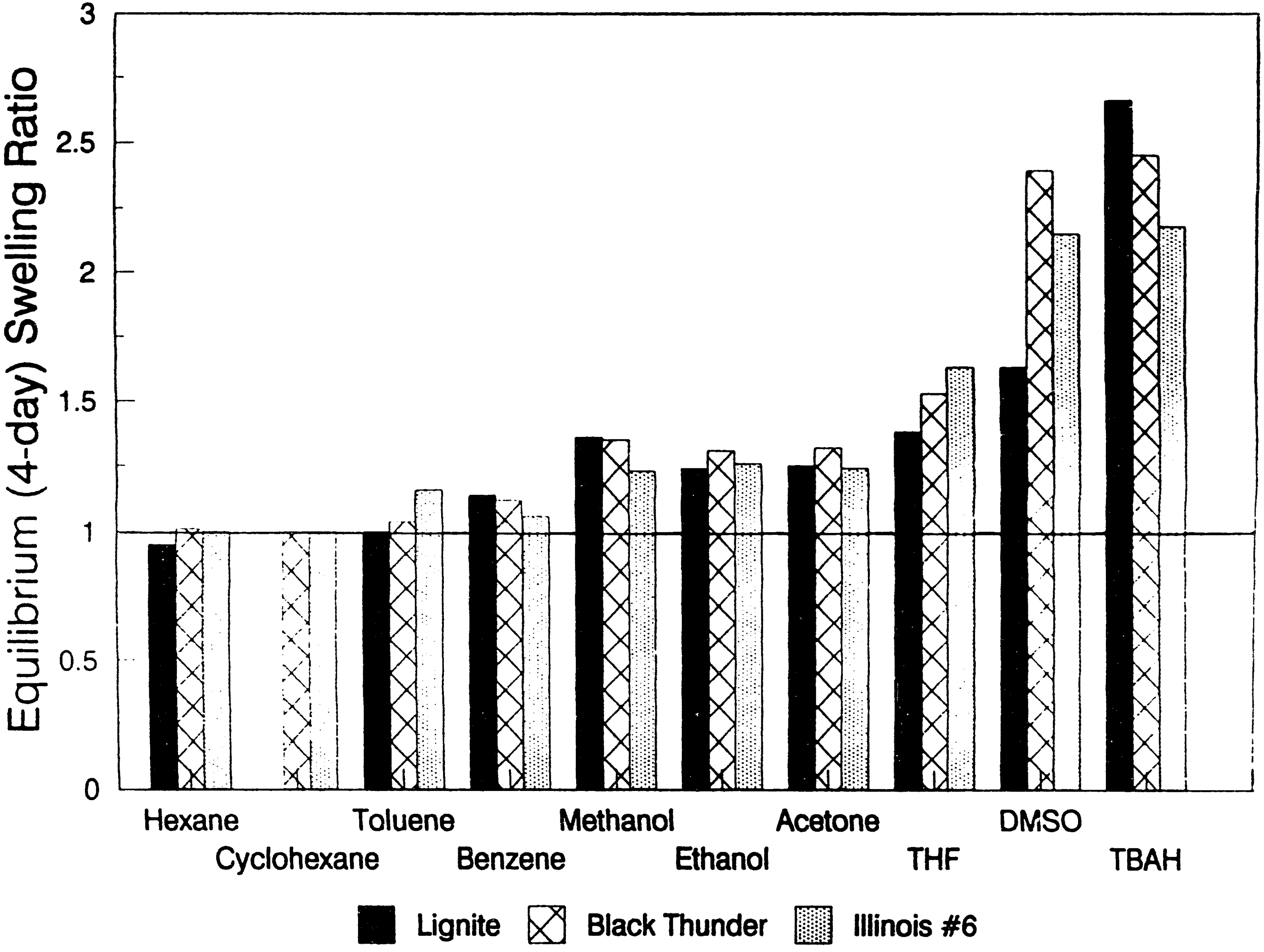
- Spherical Agglomeration: S/A is necessary with oil prior to flotation; there was no benefit from ultrasonic pre-treatment.
  (30 and 120 sec, CMR was 46% and 85% with 2.23% ash)

- Surfactant: Flotation efficiency increased with a surfactant.
  (96% CMR with 2.11% ash)

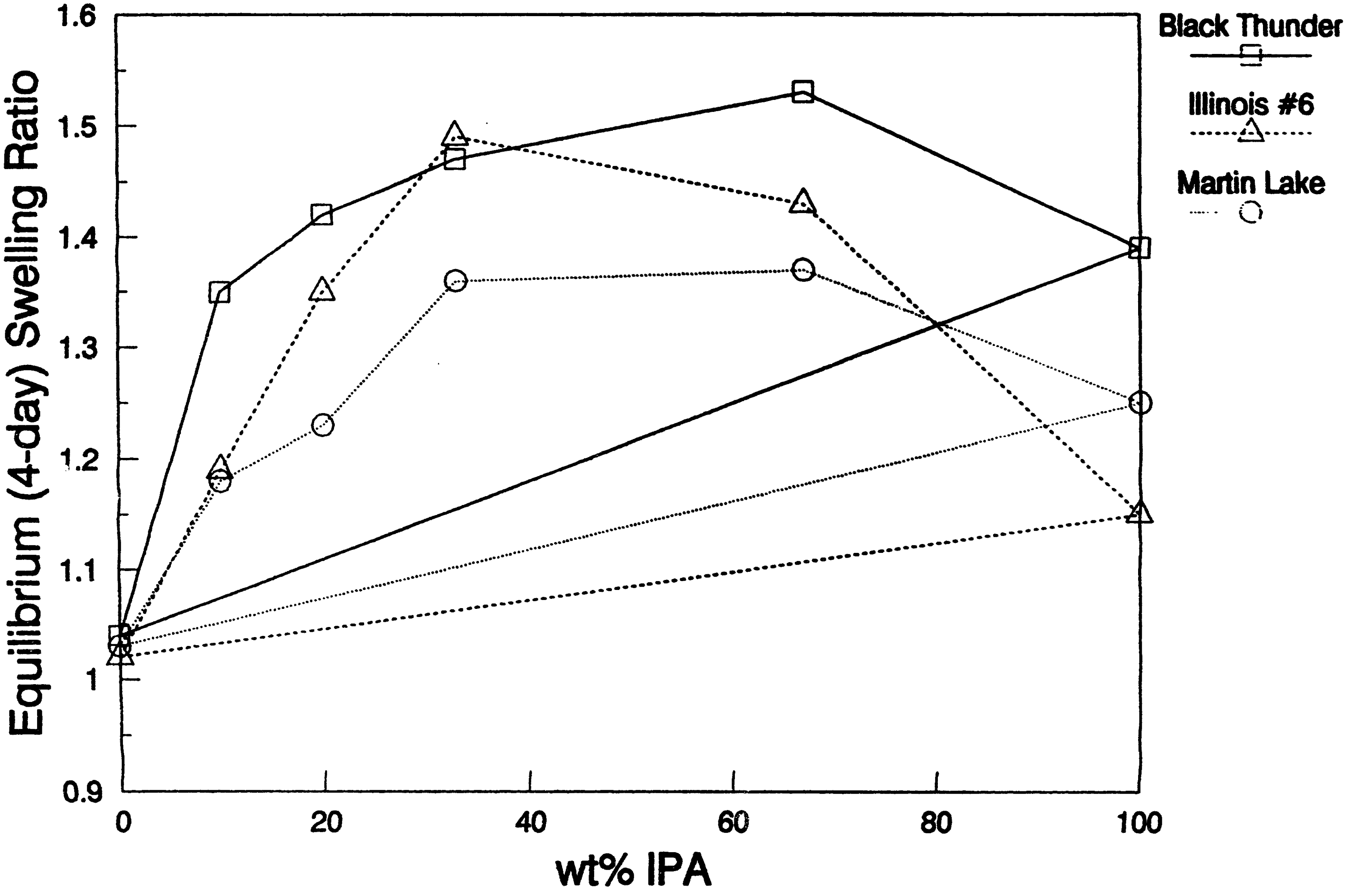
Bench-scale Treatment:

- CMR recovery of 88% with an ash level of 2.31%.

Swelling Ratios of Raw 325-mesh Coal

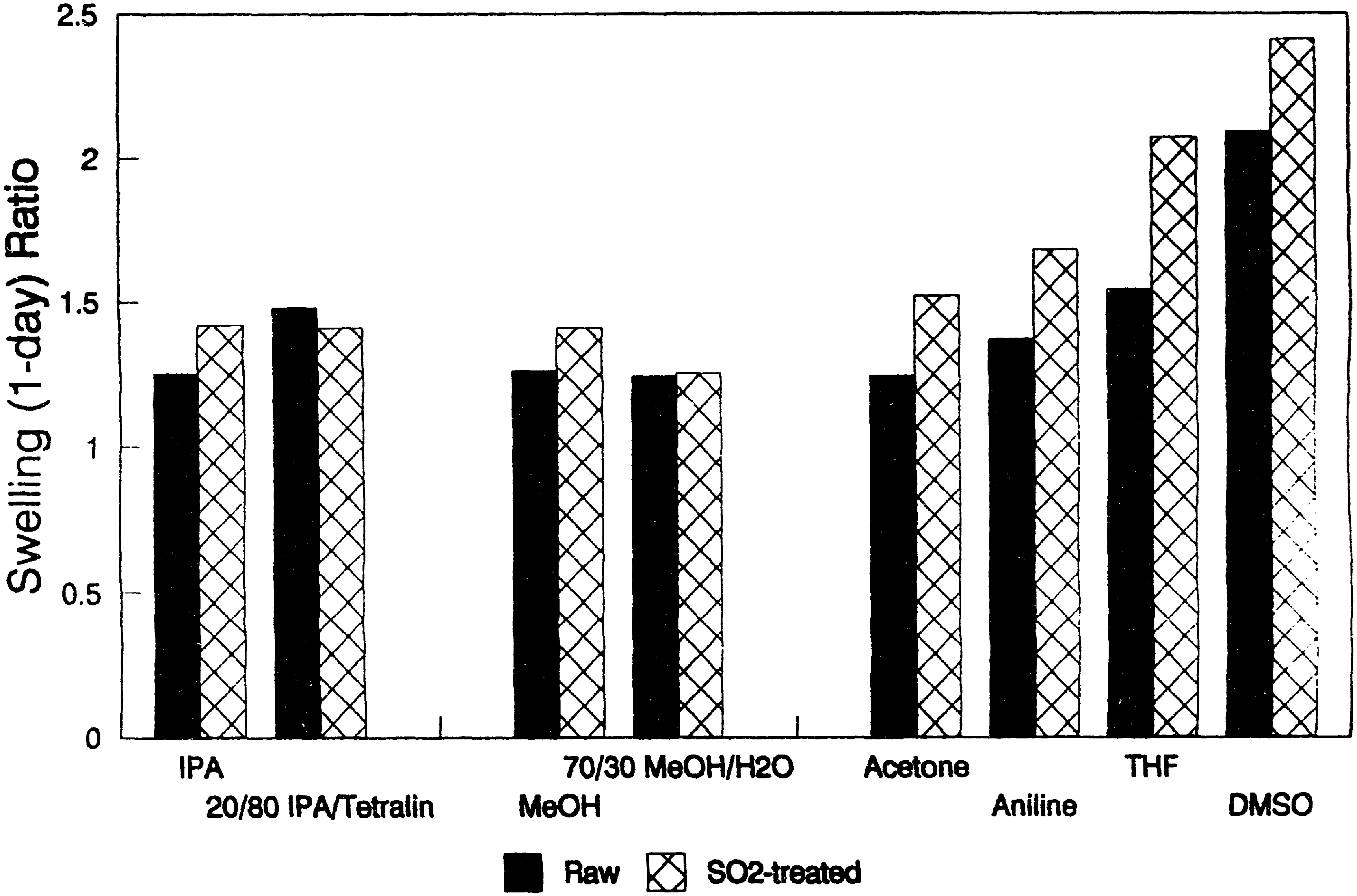


Swelling Ratios of Raw 325-mesh Coals With the IPA/Tetralin System



SLIDE 6

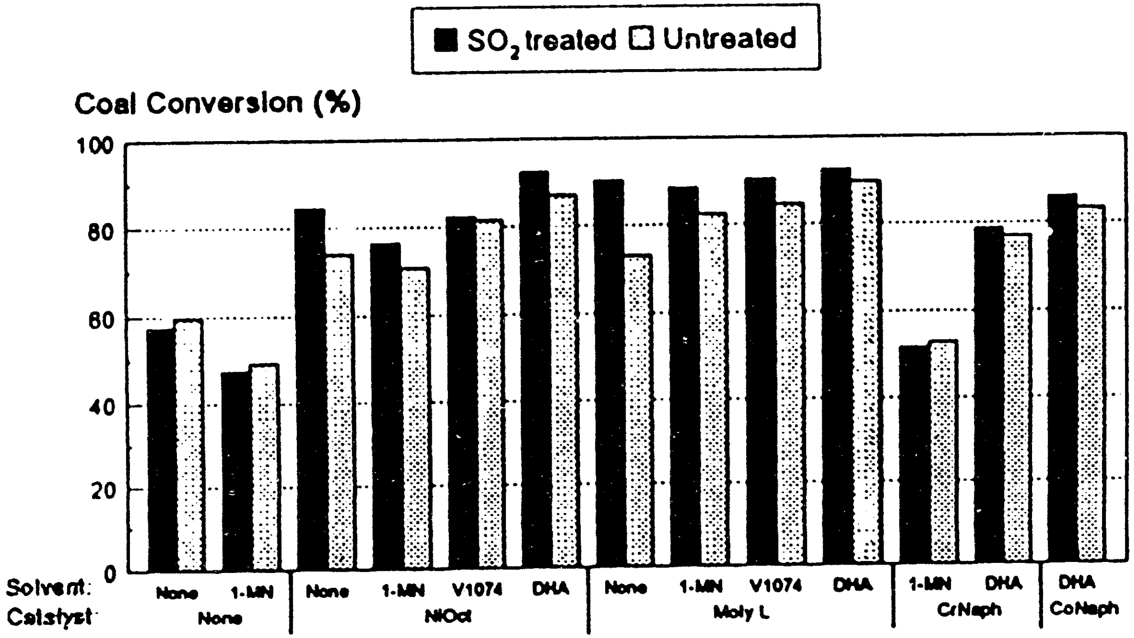
Swelling Ratios of Raw and SO2-treated Coal
8 x 60 mesh Black Thunder



SLIDE 7

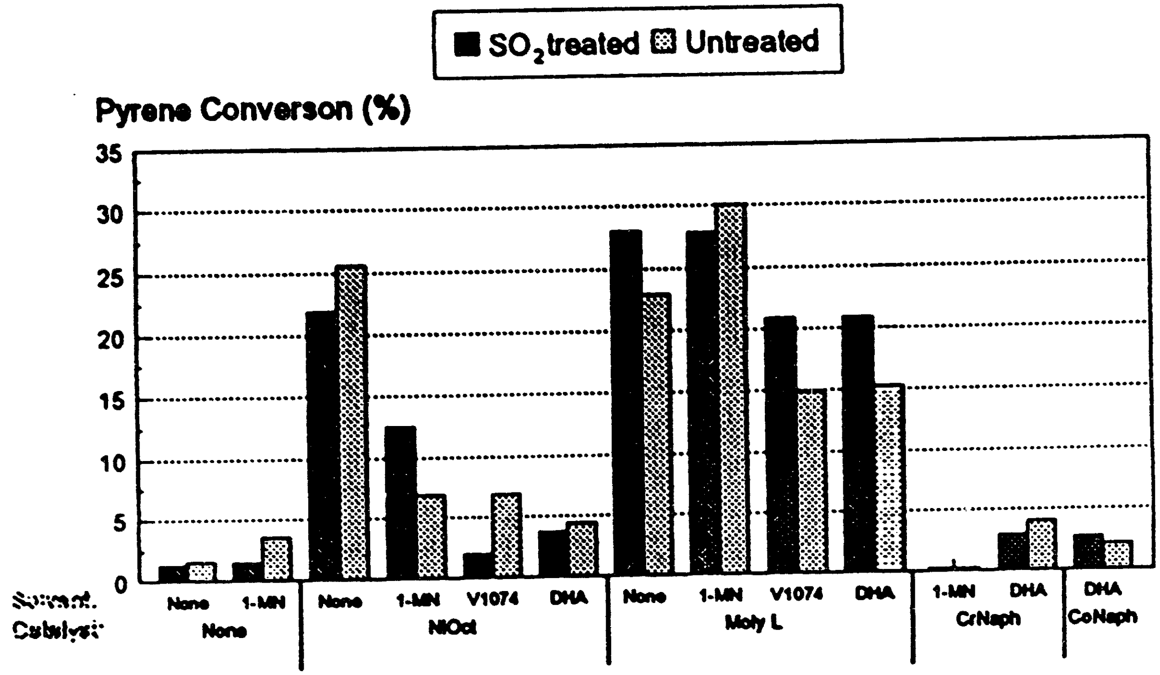
Effect of Catalyst Type on Coal Conversion

(With and Without Solvents)



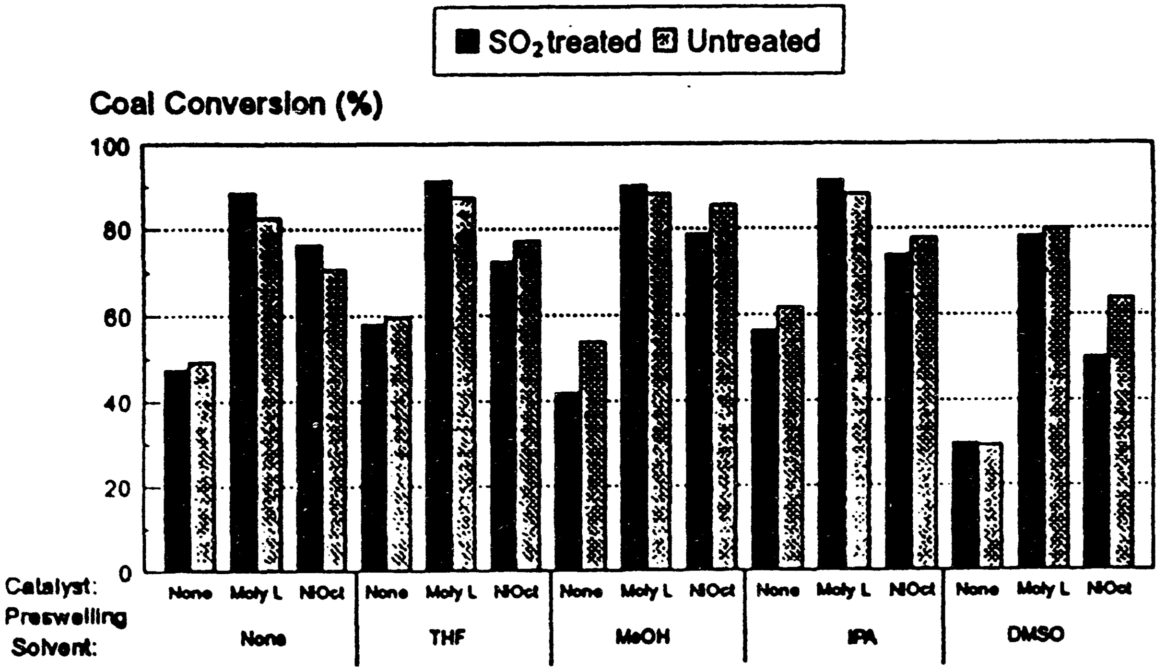
Effect of Catalyst Type on Pyrene Conversion

(With and Without Solvents)



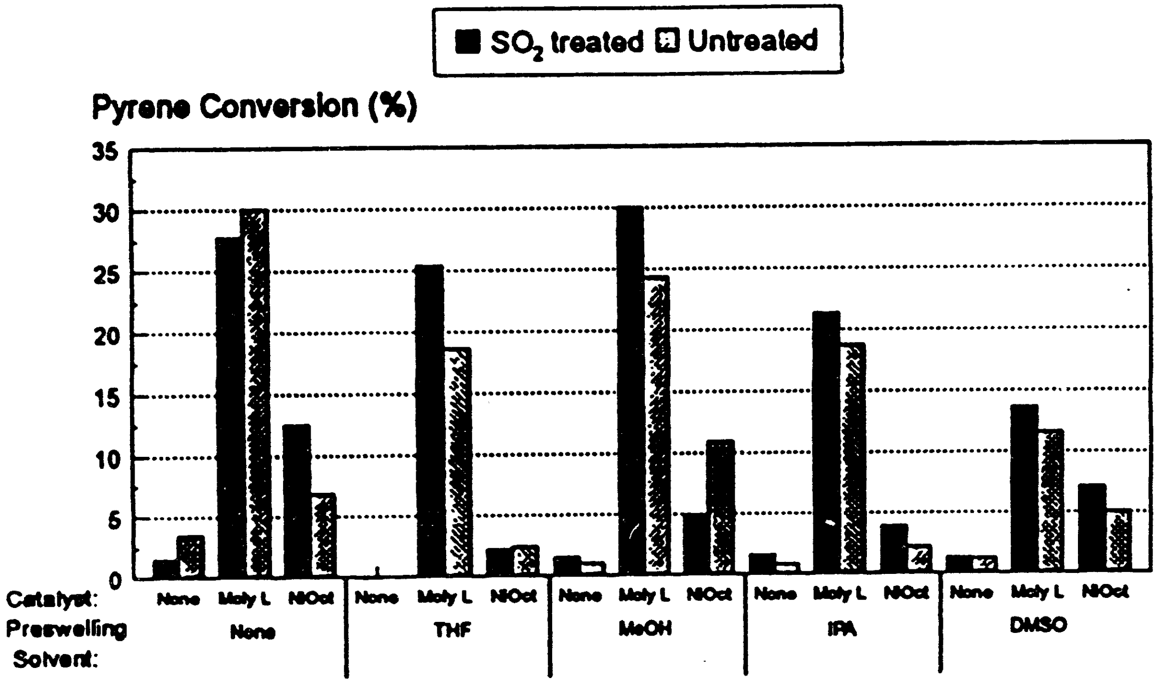
SLIDE 9

Effect of Solvent Preswelling on Coal Conversion



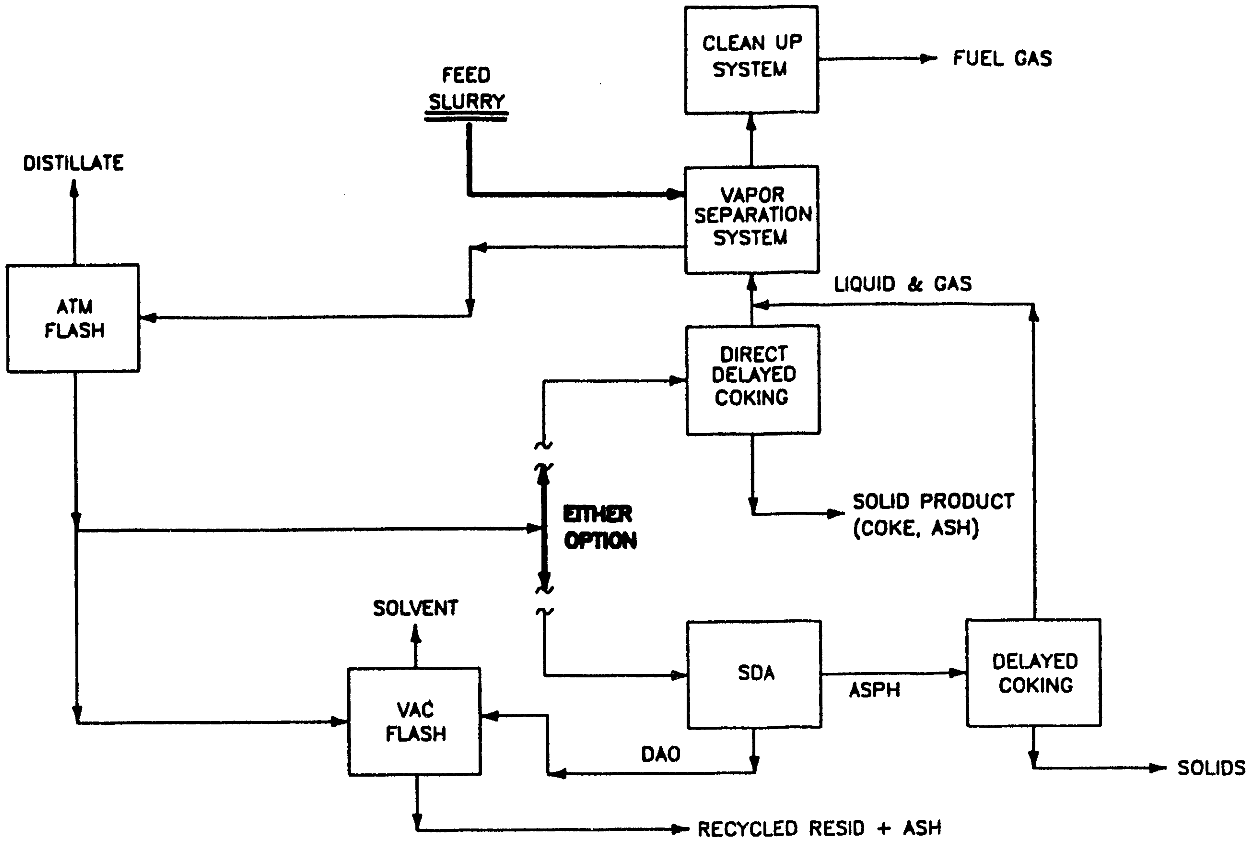
SLIDE 10

Effect of Solvent Preswelling on Pyrene Conversion



SLIDE 11

Integrating of the Ascot Process/Delayed Coking Process



CLEAN UP SYSTEM

FUEL GAS

FEED SLURRY

VAPOR SEPARATION SYSTEM

DISTILLATE

ATM FLASH

LIQUID & GAS

DIRECT DELAYED COKING

EITHER OPTION

SOLID PRODUCT (COKE, ASH)

SOLVENT

VAC FLASH

SDA

ASPH

DELAYED COKING

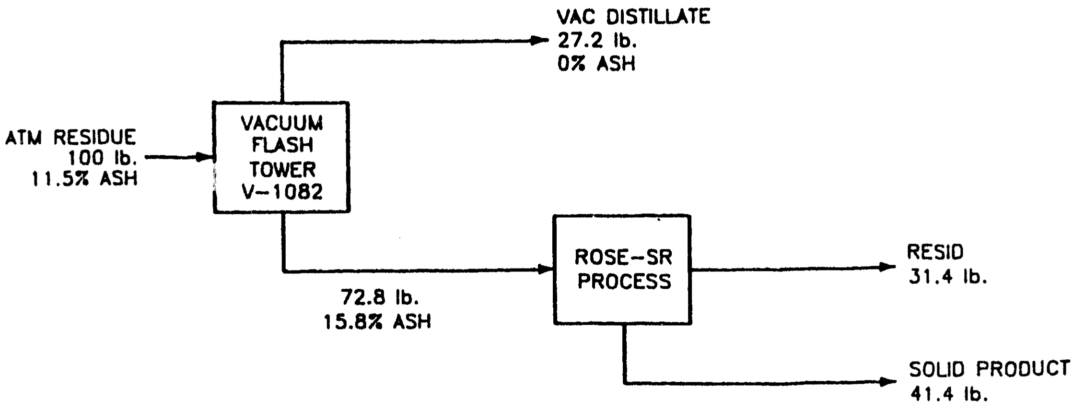
DAO

SOLIDS

RECYCLED RESID + ASH

SLIDE 12

Material Balance Around Vacuum Flash and ROSE–SR™ Units



VAC DISTILLATE
27.2 lb.
0% ASH

ATM RESIDUE
100 lb.
11.5% ASH

VACUUM FLASH TOWER V–1082

ROSE–SR PROCESS

RESID
31.4 lb.

72.8 lb.
15.8% ASH

SOLID PRODUCT
41.4 lb.

SLIDE 13

FEEDSTOCK INSPECTION:
(Wilsonville ATB)

Characteristics

Specific Gravity	1.187
Softening point, °F	124
Conradson Carbon, wt%	38.1
Toluene Insolubles, wt%	23.2
Ash, wt%	11.5
Asphaltenes, wt% (heptane)	10.9
Distillation, °F	
-10%	810
-40%	975

SLIDE 14

COMPARISON OF YIELDS FROM ATB'S

Products/Approaches	Wilsonville (VT+ROSE-SR)	Delayed Coking	ASCOT
Gas	--	2.8	1.4
Oil			
Distillate	27.2	*50.0	*23.1
Deasphalted	--	--	40.2
Resid	31.4	--	--
Solids/Coke	41.4	47.2	35.3
Total	100.0	100.0	100.0

* This includes a small resid fraction.