

## ADVANCES AND NEW DIRECTIONS IN DIRECT LIQUEFACTION

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### 1.0 INTRODUCTION

With advances in single stage processes such as H-Coal, EDS and SRC, and refining and upgrading of coal liquids by Chevron and UOP, the direct liquefaction process has continuously evolved to the present two-stage catalytic configuration, which produces the highest liquid yield and product quality of any process worldwide.

The Two Stage Liquefaction (TSL) process has been successfully applied to bituminous and subbituminous coals, overcoming problems associated with earlier processes. But, potential for additional improvement is recognized in several areas:

- o Cleaning coal prior to liquefaction.
- o Low temperature and pressure preconditioning of feed coal.
- o Novel catalysts development to arrest regressive reactions and improve hydrotreatment and cracking reactions.
- o Improvement in hydrocarbon value recovery and reduced energy rejection by alternate bottoms processing techniques.

In this paper, after discussing briefly the history of liquefaction and development of the TSL process, present potential areas for research and development are presented.

### 2.0 BACKGROUND

During the 1970's, four single stage processes (SRC-I, SRC-II, H-Coal and EDS) received substantial interest. Two of these, SRC-I and SRC-II, primarily involved thermal liquefaction and hydrogenation reactions. Others utilized catalytic reactions as well. The liquids from these processes needed substantial upgrading to obtain marketable products (1). The common features and drawbacks of these processes are:

- o 90% or better coal conversion is obtained but, reaction severity is high (820-860°F temperature, 1500-3000 psi pressure and 20-60 minutes residence time).
- o Distillate yields are about 50% of MAF coal, which are low relative to recent developments.

- o Hydrogen utilization is good but, efficiency is low due to high yields of hydrocarbon gases.

Attempts to improve the distillate yields and reduce reaction severity resulted in the development of two stage liquefaction (TSL) processes.

### 3.0 INTEGRATED TWO STAGE LIQUEFACTION (ITSL)

#### A. Early Studies

In late 1970's several thermal coal dissolution investigations concluded that coal conversion is essentially complete in an extremely short residence time of 1-2 minutes. The investigations also observed that higher hydrotreatment temperature and residence times resulted in increased yield of hydrocarbon gases. About the same time, at Wilsonville (Runs 145-146), increased importance of liquid phase hydrogen transfer in liquefaction was observed. Combining these observations Lummus developed the ITSL process.

#### B. Lummus ITSL

The Lummus ITSL process, tested in a 500 lbs per day PDU, consists of a short contact time (SCT) coal dissolution first stage followed by a LC-Fining catalytic hydrotreater as a second stage. Based on petroleum background, Lummus introduced Antisolvent Deashing (ASDA) equipment between the two stages.

The SCT reactor operated at shorter residence times (2-3 min.) and low pressures (500-1000 psi), while maintaining coal conversions above 90% MAF. The hydrocarbon gas yields were low and hydrogen utilization efficiency was high. Distillate yields were significantly better than the single stage processes. The SCT resid was reactive not only for conversion to distillate but also for heteroatom removal. The ITSL process also showed that the ashy recycle is not detrimental to catalyst activity and that a lighter and more desirable product (-650°F) can be made with little loss in hydrogen efficiency.

#### C. Wilsonville ITSL

Scale-up of the ITSL process to 6 tons/day (24 times) was performed at Wilsonville. A H-Oil ebullated bed hydrotreater (in place of the LC-Fining unit) and a Kerr-McGee Critical Solvent Deashing (CSD) unit for ash removal (in place of ASDA) were utilized. In spite of the retrogressive reactions in the CSD that lowered the coal conversion from 92 to 88% and the high organic rejection with the ash concentrate stream, a distillate yield of about 54% was obtained.

Wilsonville increased the distillate yield to 62% by placing the de-asher after the second stage (after vacuum distillation) which had no detrimental effect on the catalytic activity in the second stage reactor. With this reconfigured ITSL (RITSL) operation, retrogressive

reactions were limited and good operability with on-stream time of more than 95% was demonstrated. This RITSL operation showed that deashing prior to second-stage hydrotreatment was not necessary.

To further reduce retrogressive reactions by minimizing holding time between the reactors (first and second stage) and to eliminate pressure let down and repressuring, the two reactors were operated in a close coupled ITSL (CCITSL) mode. In this operation, all the first stage gases (CO, H<sub>2</sub>S, H<sub>2</sub>O etc.) and light oil were removed prior to second stage. There was no significant impact on catalyst activity and there was no discernable loss in performance relative to ITSL (yields, allowable space velocities, etc.). However, more rigorous analysis at a consistent set of conditions is necessary to verify the improvement of CCITSL over RITSL.

#### 4.0 CATALYTIC TWO-STAGE LIQUEFACTION (CTSL)

##### A. HRI CTSL (1984 - Present)

In CTSL, the first stage temperature was lowered to 750°F to more closely balance hydrogenation and cracking rates, and to allow the recycle solvent to be hydrogenated *in situ* to facilitate hydrogen transfer during coal dissolution. The second stage was operated at higher temperature (820-830°F) to promote resid hydrocracking and generation of an aromatic solvent, which is then hydrogenated in the first stage (see Figure 1). The lower first stage temperature provides better overall management of hydrogen consumption, with hydrocarbon gas yields reduced by about 50 percent. Higher distillate yields were attained by the reduction of resid in the rejected ash-concentrated stream and the subsequent conversion of that recovered resid to distillates.

A pressure filter reduces resid concentration in the reject stream (filter cake) below 45-50 percent. This change signalled the end of the "hydrogen balanced" process and showed that overall liquefaction economics improve if the process maximizes distillate yield and produces hydrogen by natural gas reforming or by coal gasification.

A third change by HRI was in the use of NiMo catalyst. The H-Coal process had used a cobalt-molybdenum (CoMo)-on-alumina catalyst (American Cyanamid 1442B), which is used in petroleum applications. In coal liquefaction, hydrogenation of solvent must occur first, before the aromatic molecules can thermally crack. The catalyst must hydrogenate large molecules which determine the rate at which resid is converted. The (NiMo) catalyst has a bimodal pore distribution with larger micropores, 115-125 Å, which allows easier diffusion, as opposed to 60-70 Å for H-Coal catalyst, and the nickel promoter is also more active for hydrogenation than cobalt.

The latest reported results with Illinois No. 6 coal show a 78 percent distillate yield (Table 1). Hydrogen efficiency is over 10 pounds of distillate per pound of hydrogen reacted. In addition, the two catalytic reaction stages produce a liquid with low heteroatom concentrations and a high H/C ratio.

#### B. Wilsonville CTSL (1986-Present)

The most significant differences at Wilsonville are the reactor temperatures. As in ITSL, most of the thermal cracking takes place in the first reactor and solvent hydrogenation is in the second reactor. Therefore, the first reactor is at the higher temperature (800-820°F), while the second reactor is kept slightly lower at 795°F. Other reaction conditions are similar to HRI CTSL, including the catalyst type. The distillate yields are about the same, i.e. 78% MAF Coal. Wilsonville deashes by CSD, and steady improvement has reduced organic rejection to 8-15 percent, about the same as achieved by HRI.

#### C. Evolution of Liquefaction Technology

Substantial improvements in liquefaction processes and catalysts associated with these processes have taken place. The yields and quality of liquids have improved substantially. History of process development improvements are shown in Table 1. Yields of distillates have increased from 41% to 78% (5 barrels/ton of MAF bituminous coal). Quality is comparable to or better than No. 2 Fuel Oil with good hydrogen content and very low heteroatom content.

### 5.0 FUTURE RESEARCH AND DEVELOPMENT

The overall goal of coal liquefaction R&D is to develop technology to produce marketable liquids economically (\$25/Bbl by 1995). This requires scientific and engineering knowledge based on:

- o Improved processes to provide product selectivity and quality, increased liquid yields per ton of coal and improved thermal efficiency--involves current as well as novel catalysts and processes.
- o Improved plant operability and onstream factors by process and component development.
- o Reduction of Capital and Operating costs by optimization and integration of R&D improvement.

Brief descriptions of significant areas follow:

#### A. Preconversion and Regressive Reactions

The preceding discussion placed emphasis on process improvements, principally on the coal dissolution and resid upgrading reactions. This requires a better understanding of coal conversion chemistry.

The term "first reactor" is a misnomer, because there is strong evidence that the coal has undergone considerable reaction before entering that vessel (2). Coals have been found to undergo changes at temperatures as low as 200°C. Suuberg (3) has measured the evolution of carbon dioxide from low rank coals at low temperatures and Solomon (4) has related this gas evolution to cross-linking, which reduces coal reactivity thereafter. The onset of swelling has been measured at 200°C, with completion at about 500°C (4), again an indication of cross-linking. Derbyshire has shown that soaking coal at temperatures below 400°C increases yield of toluene solubles, presumably as the result of increased hydrogen transfer from the solvent (5). Recently, with liquid-phase transfer, 85 percent conversion of sub-bituminous coal and 91 percent conversion of bituminous coal (to quinoline-solubles) in about 30 seconds at 425°C (6) was reported. These findings show that coal has already reacted in the preheater, and in all likelihood, the coal (or coal liquid), in the reactor may be less reactive and must have necessitated high severity reaction conditions to undo the damage that took place during heat-up.

More information on the mechanism of these preconversion reactions and their impact on process yields and product quality are required. The effects of time, temperature, solvent quality, and catalyst-dispersed or soluble-on the kinetics of coal dissolution below 400°C and on the structure of the liquid product must be quantified. Process developers will utilize this information to modify preheat conditions to supply a more reactive feed to the first reactor. The anticipated benefits are increased coal conversion, increased reactivity of coal liquids, smaller reactors, moderating reaction conditions and better hydrogen efficiency. A more reactive feed should also improve catalyst activity in both stages.

#### B. Hydrotreatment and Cracking Reactions

Process development has emphasized resid conversion and liquid yield, but how is conversion achieved? Unlike petroleum resid, which cracks thermally to smaller molecules, which are then hydrogenated, coal resid must first be hydrogenated before cracking can occur. Hydrogenation is catalytic, while the cracking reactions may be either thermal or catalytic. Little is known about the kinetics of these reactions, and this work has the potential to improve on current TSL performance.

Catalyst activity for conversion falls to about 20 percent of its initial value in a few days. Sandia has related most of the catalyst deactivation to carbon laydown on the catalyst and the inhibiting effects of certain nitrogen compounds in the coal liquids (7). Others point to phenols as a source of deactivation (8). The mechanism of deactivation is not understood. With additional information, improved catalysts and regeneration may be possible.

A better understanding of the kinetics of these reactions could greatly improve process economics or even cause a major modification of the process. Lummus Crest, Inc. (LCI) found that resid hydrogenation is rapid at 450°C (9) therefore, most of the second stage reactor volume is required for conversion, which might be by thermal cracking. Increasing the cracking functionality of the catalyst could significantly reduce reactor volume.

In addition to investigating the kinetics of resid hydrogenation/cracking, additional information is needed on kinetics of hydrogenating heavy distillate (650°F+), and hydrogen transfer rates from solvent to coal and from distillate to resid. This latter point is of great importance in the preheater reactions just discussed. The benefits of soaking at low temperature may be related to relative rates of thermal cracking and hydrogen transfer at 200-400°C. Therefore, this temperature range must be included in the kinetic study of hydrogenation and cracking.

### C. Integration of Coal Beneficiation and Cleaning

The quality and quantity of resid (or organic) rejected is a function of ash composition in the coal. Removal of ash by coal beneficiation has been a fairly standard practice and interest in deep cleaning to remove pyritic sulfur has increased substantially in the last decade. This has resulted in significant advances, such as:

- o Heavy media cyclone cleaning
- o Oil agglomeration
- o Microbubble flotation
- o Molten caustic cleaning

Intuitively, reduced ash content reduces organic rejection and facilitates liquefaction and hydrotreating by reduced corrosion and erosion. However, reduced pyrites and sulfur may decrease the catalytic activity. As a result, benefits of beneficiation and cleaning were uncertain and liquefaction units operated with standard coal beneficiation used for power plants (10% ash).

Recent coal agglomeration work by Consol, Alberta Research Council and PETC, and liquefaction data from PETC, HRI and Wilsonville operations have shown the advantages of deep coal cleaning (about 5% ash). Liquid yields increased by 5% and energy rejection was reduced. Corresponding economic benefits were noted by Mitre.

There are many unanswered questions:

- o What are the liquefaction characteristics of cleaned coal?
- o Can selective coal cleaning improve the process substantially.

- o Should the coal be cleaned to an ash content of 1%, 2% ash or 5%? What limits this ash content - coal cleaning process or liquefaction process?
- o How do we integrate? With bottoms? With heavy distillates?
- o What are the implications of integration on liquefaction reactions, hydrotreating reactions and coal cleaning?
- o Which coal cleaning process is more attractive economically and under what conditions?

Future R&D should provide answers to some of the above.

#### D. Alternate Liquid/Solid Separation System

The Wilsonville PDU employs the CSD developed for the SRC-1 process and HRI uses pressure filtration because the feed is lighter and less viscous than deasher feeds of just a few years ago. Both CSD and filtration achieve high recovery of resid, but are expensive to install and operate. As a result, comparative economics of alternate systems and alternate processes are required to achieve even better results at lower cost.

Recently, a fluid coking study (10) showed that over 60 percent of the toluene solubles in the deasher feed is recoverable as coker distillate. This is also expensive, but Mitre has estimated that it has economic advantages over CSD (11). Additionally, the coker distillate is highly aromatic and analyses by Consol have shown that, after hydrogenation, it is capable of effecting higher coal conversion than recycle solvents currently being used (12). Therefore, coking is being investigated, not only as a viable alternative approach to liquid/solid separation, but as a possible source of improved coal reactivity.

Should deep cleaning of coal become an integral step of direct liquefaction, the solids rejected will be only about 9 percent of MAF coal, and solids removal by vacuum distillation may become attractive. Total organics rejected in the vacuum tower bottoms would be only about 11 percent (less than 15 percent by CSD). Most of the bottoms will be recycled to the solvent tank and a small purge stream will remove ash, possibly by coal beneficiation. This alternate liquid/solid separation scheme is dependent on improvements elsewhere in the process and corresponding follow-up R&D, process integration and economic evaluation are required.

#### E. Systems Integration Schemes

Research to improve direct liquefaction technology must take into account the integrated nature of the process. A change made in any component in the process will impact others. Therefore, the entire

system, its technical viability and overall economics, must be considered as process improvements occur. For example, the alternative liquid/solid separation discussed earlier (Figure 2) uses a vacuum tower as the means of liquid/solid separation and may result in many process changes:

- o The composition of the recycle solvent will be changed (ratio of solvent/resid/solids);
- o The vacuum tower bottom may be fed to coal beneficiation to recover more organics;
- o The vacuum tower overhead may be the agglomerating oil for beneficiation;
- o The vacuum tower bottoms may be fed to a coker to recover coker distillate, and the coker distillate may be hydrogenated in the second stage.
- o The hydrogenated coker distillate may leave as product or may be recycled as solvent. Its effect on solvent quality is, as yet, unknown.

Similarly, the investigation of preconversion reactions may well result in changes that may effect the entire process and a similar systems approach will be necessary. Even changes in catalyst or reaction conditions must be viewed in terms of its impact on overall operability and economics of the process. Coordinated R&D with systems integration schemes are required.

#### F. Integration and Optimization

The direct liquefaction section is part of a larger plant. Some of the other areas that must be considered include:

- o Hydrogen production and purification
- o Coal preparation and handling
- o Waste processing and disposal
- o Refining and upgrading of coal liquids to marketable products

The first three areas constitute a large fraction of the cost of a liquefaction plant and R&D to improve these operations could greatly improve the overall economics of liquefaction.

Hydrogen production is always a potentially fruitful topic for research because of the cost of the hydrogen plant. Should hydrogen be made by gasification of CSD or vacuum tower bottoms, or by gasification of coal, or by reforming of natural gas? Whichever is selected will effect the entire plant. The effect of carbon monoxide on cata-

lyst activity is still not clear. Research is needed in that area. If CO has no inhibiting effect on catalyst activity, the hydrogen plant can be simplified. Conversely, the economic incentive of a less expensive hydrogen plant may be the impetus to develop such a CO-resistant hydrotreating catalyst. What are the requirements for recycle gas purification? How can they be integrated and optimized?

Similarly, it is to be expected that the use of coals different than those tested to date may require process modifications to achieve optimum yields. These coals may require different liquefaction processing or coal preparation. Weathering and oxidation effects on reactivity may have to be investigated.

The refining of coal liquids has received relatively little attention, even though this is the step that makes the marketable products that are the ultimate goal of the plant. Chevron (1) has already shown that a heavy distillable coal liquid is difficult to refine. This finding directed efforts to the production of a lighter (-650°F) coal liquid, which has been achieved successfully. However, further integration with the utilities and refiners may lead to other process modifications in order to make coal liquids more valuable, either as a refinery feed or as marketable products.

## 6.0 CONCLUSIONS AND RECOMMENDATIONS

The current CTSL process is the best direct liquefaction process in the world. It produces the highest yield of liquid product, having the highest quality-- and it does this at a lower cost per barrel than previous processes. Significant improvements, however, are attainable and are needed to be competitive with crude oil prices (\$25/bbl). These will come from research on the fundamentals of coal liquefaction and on process modifications. All research must be performed with an understanding of the effect it will have on the entire process. The most promising areas for future research are in preconversion chemistry and retrograde reactions, hydrogenation and cracking reactions, coal preparation, and solids rejection. Many of these programs are already in progress. The results are expected to provide a better understanding of liquefaction and foster a new generation of more economic and efficient direct liquefaction technology.

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**Table 1. CTSL DEMONSTRATION RUN COMPARISON WITH H-COAL  
(ILLINOIS NO. 6 COAL)**

Process	H-Coal (PDU-5)	CTSL Run No.	
		(227-20)	(227-47)
<b>YIELDS, Wt% MAF</b>			
C <sub>1</sub> -C <sub>4</sub>	11.3	6.6	8.6
C <sub>5</sub> -390°F	22.3	18.2	19.7
390-650°F	20.5	32.6	36.0
650-975°F	8.2	16.4	22.2 <sup>1</sup>
975°F+ Oil	20.8	12.6	2.7 <sup>1</sup>
<b>HYDROGEN CONSUMPTION</b>	6.1	6.3	7.3
<b>COAL CONVERSION, Wt% MAF</b>	93.7	94.8	96.8
<b>975°F+ CONVERSION, Wt% MAF</b>	72.9	82.2	94. <sup>1</sup>
<b>C<sub>5</sub>-975°F, Wt% MAF</b>	51.0	67.2	77.9 <sup>1, 2</sup>
<b>HYDROGEN EFFICIENCY</b>	8.4	10.7	10.7
<b>C<sub>5</sub>- DISTILLATE PRODUCT QUALITY</b>			
EP, °F	975	975	750
°API	20.2	23.5	27.6
% Hydrogen	10.63	11.19	11.73
% Nitrogen	0.49	0.33	0.25
% Sulfur	0.2	0.05	0.01
<b>BBL/TON</b>	3.3	4.1	5.0

<sup>1</sup>750°F Distillate end point.

<sup>2</sup>Coal contained 5.8% ash.

NOTE: All data at catalyst age representative of typical commercial replacement rates.

**Table 2 HISTORY OF PROCESS DEVELOPMENT AND PERFORMANCE  
FOR BITUMINOUS COAL LIQUEFACTION**

Process	Configuration	Distillate (wt% MAF coal)	Yield (bbt/t MAF coal)	Distillate Quality (gravity °API)	Nonhydrocarbon (wt%)		
					S	O	N
SRC II (1982)	One-stage, noncatalytic	41	2.4	12.3	0.33	2.33	1.0
H-Coal (1982)	One-stage, catalytic	52	3.3	20.2*	0.20	1.0	0.50
Wilsonville (1985), RITSLS	Integrated two-stage, thermal-catalytic	62	3.8	20.2**	0.23	1.9	0.25
Wilsonville (1986), CTSL	Integrated close- coupled two-stage catalytic-catalytic	70	4.5	26.8**	0.11	<1	0.16
Wilsonville (1987), CTSL	Integrated close- coupled two-stage low-ash coal	78	5.0	+	+	+	+
HRI, CTSL (1987)	Catalytic-catalytic	78	5.0	27.6	0.01	-	0.25

\*Light product distribution, with over 30% of product in gasoline boiling range; less than heavy turbine fuel.

\*\*Higher boiling point distribution, with 20% of product in gasoline fraction and over 40% turbine fuel range.

\*API and elemental analysis data unavailable at this time.

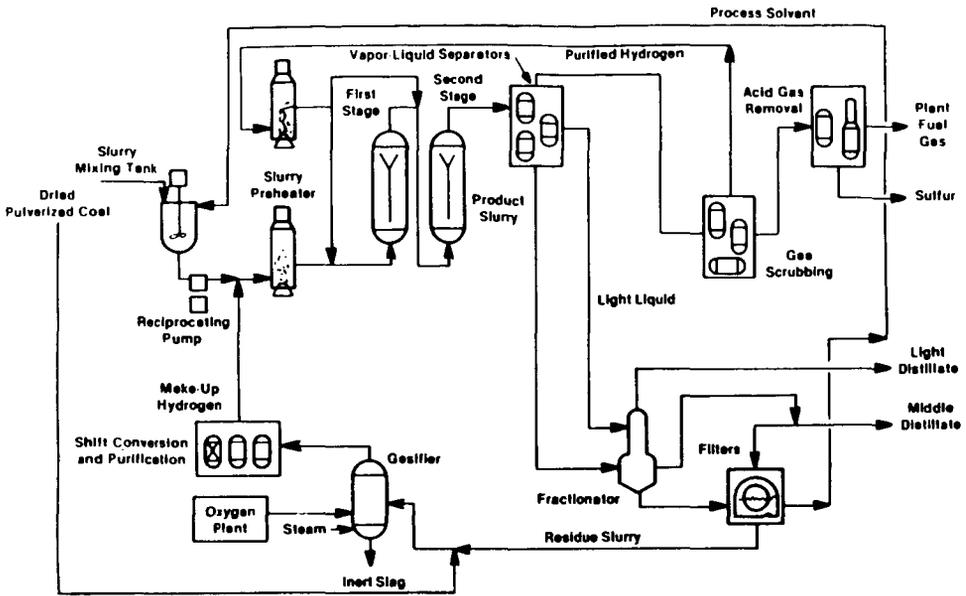


FIGURE 1. HRI CATALYTIC TWO-STAGE LIQUEFACTION

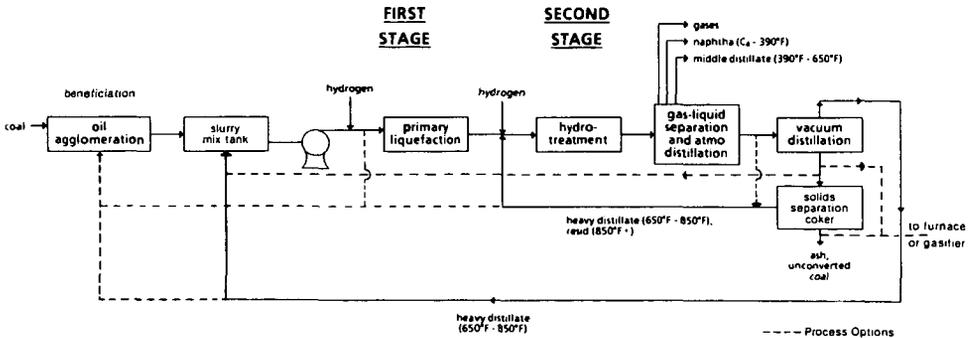


Figure 2. Process Options with Beneficiation and Coking.

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## TWO-STAGE COAL LIQUEFACTION PROCESS DEVELOPMENTS AT WILSONVILLE

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### INTRODUCTION

The Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama has been operating for over 14 years to develop alternate technologies for producing low cost fuels. A recently completed close-coupled integrated (CC-ITSL) processing mode was an important development in the Wilsonville program for making clean distillate fuels. In the CC-ITSL mode the two reactors were directly coupled without any pressure letdown. Interstage cooling was done only to the extent required to control the second reactor temperature. Such close-coupled operation should offer several process benefits such as increased overall thermal efficiency, reduced potential for retrogressive reactions which may take place in the absence of hydrogen at longer residence times, and improved product quality.

This paper is focused on two-stage coal liquefaction process performance with close-coupled reactors. Results are presented for two runs: Run 253 and Run 254. Run 253 processed high ash Illinois No. 6 coal and used Shell 317 1/20" trilobe bimodal catalyst in both reactors. Product yield and product quality data are discussed. Catalyst performance comparisons for Shell 317 (Run 253) and Amocat 1A and 1C (Run 251-I and Run 252) are made in terms of distillate yields, catalyst deactivation and catalyst replacement rates.

Run 254 processed low ash Ohio No. 6 coal and used Shell 317 1/20" trilobe bimodal catalyst in both reactors. The effects on process performance of the low ash feed coal, high resid recycle, high second stage reaction temperature and high space velocity are presented. The effect of the coal type on the distillate yield is discussed in comparisons of Illinois No. 6 and Ohio No. 6 coals. The first stage catalyst equilibrium activity level is discussed. Catalyst performance data at different second stage reaction temperatures are presented in terms of catalyst deactivation and catalyst replacement rates. Optimum and cascading catalyst requirements are discussed.

Catalyst properties used in the close-coupled integrated runs (Run 250-254) are listed in Table 1. Catalyst performance in the close-coupled configuration has been extensively studied and reported in the previous EPRI and DOE contractors' conferences (1,2,3,4). Relative process economics evaluations (5), configuration effects on process performance (6) and developments of ITSL models (7) were reported elsewhere.

## PROCESS DESCRIPTION

A block flow diagram of the catalytic-catalytic CC-ITSL process is shown in Figure 1. The process consists of a slurry preparation step and two catalytic reaction stages followed by hydrotreated solvent recovery and critical solvent deashing systems. The system was integrated by the recycle of CSO (Critical Solvent Deashing) resid, hydrotreated solvent, and low-pressure flash bottoms containing ash, unconverted coal, hydrotreated resid, and hydrotreated solvent. Solids recycle allowed an increased concentration of solids in the CSD feed and hence a lower CSD feed rate. The solvent recovery system consists of atmospheric flash and vacuum flash equipment. The recycle distillate was fractionated in a vacuum tower to reduce the light ends (650°F- fraction) in the recycle solvent.

## RUN 253 RESULTS

### Catalyst Activity and Deactivation

Run 253 was the first CC-ITSL run with a significantly extended operation of catalyst addition to the first stage (2 lb/ton MF coal). The operation time with the catalyst addition was about 27 days. The impact of the catalyst addition was very significant. The C<sub>4</sub>+ distillate yield is approximately higher by 21 wt % MAF coal at 3000 lb resid + CI/lb catalyst of the second stage catalyst age, compared to the yield linearly extrapolated from the batch deactivation data.

A slight decline of the slope indicates that 2 lb/ton addition is not sufficient at 385 MF lb/hr coal feed rate to maintain catalyst activity to achieve the "all-distillate" product slate with 69 wt % MAF C<sub>4</sub>+ distillate. This observation is further substantiated in the catalyst requirement data for the resid extinction mode. Using the estimated catalyst activity data approximately 4.0 lb/ton catalyst addition is projected for the "all-distillate" product slate with a 69 wt % distillate yield. At 480 MF lb/hr high coal feed rate, the catalyst requirement is doubled to 8.1 lb/ton (Table 2).

These higher catalyst requirements for Run 253 with Shell 317 catalyst (approximately 2 to 3 times higher than those for Run 251-I and 252 with Amocat 1A and 1C catalysts) (Tables 2 and 3) were attributed to less catalyst charges in both reactors by 12 wt % and lower TSL catalyst activity as compared in Figures 2 and 3. Shell 317 catalysts for Run 253B showed a lower C<sub>4</sub>+ distillate yield by 10 wt % MAF coal at a similar catalyst volume basis and by 3 wt % MAF at the same catalyst weight basis (Figure 2), compared to Amocat 1A/1C catalysts used in Run 251-IC. In addition, Amocat 1C/1C catalysts for Run 252B showed a higher C<sub>4</sub>+ distillate yield by 5 wt % MAF coal at a similar catalyst volume and the same catalyst weight basis, compared to Amocat 1A/1C catalysts used in Run 251-ID and IE (Figure 3).

Each stage catalyst activity was much different from TSL catalyst activity trends discussed before; Run 253 Shell 317 catalyst activity was lower in the first stage and higher in the second stage reactor, compared to Run 251-I and 252 Amocat 1A and 1C catalysts. Run 253 Shell 317 catalyst deactivation rates for both reactors appeared to be very similar to those for Runs 251-I and 252 Amocat 1A and 1C catalysts (2,3).

Catalyst selectivities in TSL hydrogenation and heteroatom removal were discussed and compared in Run 253 Report (8). Selectivities were studied with relation to TSL hydrogen consumption, which is an indication of TSL process severity. Run 253 with Shell 317 and Run 252 with Amocat 1C catalyst showed slightly higher selectivities for the potential liquid yield (C<sub>4</sub>+ resid) production by 1 to 3 wt % MAF coal, compared to Run 251-I with Amocat 1A and 1C catalysts. This was primarily attributed to less C<sub>1</sub>-C<sub>3</sub> gas make. Overall heteroatom (N, S, O) removal was similar for all three runs. However, Run 253 with Shell 317 and Run 252 with Amocat 1C catalyst showed higher nitrogen removal activity. Analyses of aged Shell 317 catalysts used for Run 253 indicated the first stage as a guard bed by removing catalyst deactivation and poison material before going to the second stage. The second stage aged catalyst showed lower carbon deposits by 6 wt % of catalyst than the first stage and a higher hydrogenation activity value by 50 (m moles of hydrogen consumed) in hydrogenation of naphthalene. This guard bed effect was also commonly observed with other catalysts such as Amocat 1A and 1C used for Run 251-I and Run 252 (2,3).

#### Product Quality

Run 253 product quality data are listed in Table 4. During Run 253 the recycle distillate was fractionated in a vacuum column to reduce the light ends in the recycle solvent. The naphtha and distillate yields were about the same in all the periods (C, E and F). The gas-oil yield was the lowest in the concentrated coal slurry test. Other than this there were no major differences in product quality among various Run 253 tests. Preliminary laboratory analyses of distillate products indicated a significant reduction of the distillate product end point, by 30 to 80°F. This was achieved by increasing the recycle of 650°F+ by 8 wt % in the recycle process solvent (from 89 to 97 wt %).

#### RUN 254 RESULTS

Run 254 processed low ash Ohio No. 6 coal in a catalytic-catalytic close-coupled configuration. Unwashed high ash Ohio coal with about 10-12 wt % ash was used for the startup process solvent equilibration at 500 MF lb/hr coal feed rate. Low ash Ohio coal with 6 wt % ash was prepared by washing the run-of-the-mine coal with heavy media. During the operation with 40 wt % resid level, the "all-distillate" product slate could not be achieved because of high potential distillate (C<sub>4</sub>+ resid) yields, 76-78 wt % MAF coal, and high excess resid yields, 8-10 wt % MAF processing the low ash Ohio No. 6 coal. In order to achieve one of the run objectives of the resid extinction, it was recognized that a higher catalyst activity level is required, since Ohio No. 6 coal apparently has lower resid conversion activity than Illinois No. 6 coal. The higher level of resid recycle could also improve significantly resid conversion, as observed in the previous runs (8,9), that is, 0.3 wt % MAF coal distillate yield increase per 1 wt % resid content increase in the recycle process solvent.

#### Low Ash Ohio No. 6 Coal

Advantages of the low ash Ohio No. 6 coal with 6 wt % as opposed to the high ash with 10 wt % are threefold as shown in Tables 5 and 6; (1) an increase of the potential liquid yield (C<sub>4</sub>+ resid) by 6 wt % MAF coal, (2) an increase of coal conversion by 3 wt % MAF coal, and (3) a decrease of organic rejection by 8 wt % MAF coal. The increase of coal conversion is probably due to removal of less reactive

coal components such as inertinites by cleaning with heavy media (10). The low UC yield with the low ash coal reduced the organic rejection and consequently increased the potential liquid yield. The ratio of the organic rejection to the UC yield was 2.68, same for both periods, which indicates that the UC yield is a primary variable affecting the organic rejection.

#### Effect of Second Stage Reaction Temperature

The effect of the second stage reaction temperature change from 760°F to 790°F was studied during periods 254C-D and 254F-G. The observed C<sub>4</sub>+ distillate yield increase due to the temperature increase was very significant, about 11 wt % MAF coal during 254C-D. The hydrogen consumption was also increased in a relatively small degree from 6.1 to 6.7 wt % MAF, which gives a significantly better hydrogen efficiency at 790°F (10.3 vs 9.5 lb C<sub>4</sub>+ dist/lb H<sub>2</sub> consumed). C<sub>1</sub>-C<sub>3</sub> gas make and organic rejection were similar for both periods. The C<sub>4</sub>+ distillate yield response during 254F-G due to the second stage reaction temperature change from 760°F to 790°F was 8 to 9 wt % MAF coal, which is slightly lower than that during 254C-D.

Activation energy for the second stage catalyst was calculated based on the C<sub>4</sub>+ distillate response during 254C-D. The activation energy was approximately 43,300-53,750 Btu/lb mole for the second stage reaction temperature range of 760°F to 790°F. A similar value of 47,800 Btu/lb-mole was also observed during 254F-G for the periods at a higher level of resid recycle about 50 wt %. This activation energy processing Ohio No. 6 coal is slightly higher than that processing Illinois No. 6 coal (42,300 Btu/lb mole for the temperature range of 720°F to 770°F) (11).

The effect of the second stage reaction temperature change from 790°F to 810°F was studied during period 254J-K. The estimated C<sub>4</sub>+ distillate response due to the second stage reaction temperature change by 20°F was 6 wt % MAF coal, which corresponds to the activation energy 69,000 Btu/lb mole for the temperature range of 790°F to 810°F. This activation energy is much higher than that observed for the temperature range of 760°F to 790°F (47,800 Btu/lb mole).

The high second stage reaction temperature at 810°F (254K) lowers hydrogen efficiency and distillate selectivity by producing more C<sub>1</sub>-C<sub>3</sub> gas make (2 wt % MAF coal), compared to at 790°F (254J).

#### Effect of High Resid Recycle

Very careful experimentation for periods 254G-H was conducted to evaluate the effect of 50 wt % resid recycle in the recycle process solvent on process performance. Period 254D was selected for comparisons with 40 wt % resid recycle. Significant advantages of the 50 wt % high resid recycle are found in process performance improvements; (1) 6 wt % MAF coal increase in the C<sub>4</sub>+ distillate yield and (2) a higher hydrogen efficiency (11.1 vs 10.3 lb C<sub>4</sub>+ dist/lb H<sub>2</sub> consumed). C<sub>1</sub>-C<sub>3</sub> gas make and organic rejection were similar for both periods. The "all-distillate" product slate became possible for period 254G-H with more resid conversion through higher recycle of the reactive resid. The C<sub>4</sub>+ distillate increase was slightly higher than the projected (5 wt % MAF). The economic impact in the commercial plant design will be slightly compensated due to the higher resid recycle by 40% and the higher slurry rate by 10%, although the production rate of the distillate is increased by about 9%.

During period 254G the C<sub>4</sub>+ distillate yield was 78 wt % MAF coal, the highest ever observed at Wilsonville, the lowest organic rejection 7 wt % MAF (254I), and the highest coal conversion 97 wt % MAF. The hydrogen efficiency was very high, 11.3 lb C<sub>4</sub>+ dist/lb H<sub>2</sub> consumed. This highly improved distillate production can be achieved by a moderate catalyst addition below 5 lb/ton of MF coal. Three main reasons can be attributed to these excellent process achievements; (1) high coal conversion activity of the low ash Ohio coal, (2) high distillate selectivity at 790°F of the second stage reaction temperature, and (3) high recycle of the reactive resid.

#### Effect of Space Velocity

Three different coal feed rates, 440, 365 and 300 MF lb/hr were studied during periods 254H, I and J. The first stage catalyst ages were similar approaching the equilibrium catalyst age of 610 lb MF coal/lb catalyst due to the catalyst addition at 3 lb/ton of MF coal, while the second stage catalyst ages were different, gradually increasing, due to the batch mode of operation. The C<sub>4</sub>+ distillate yield was 72 wt % MAF coal at 365 MF lb/hr coal feed rate (254H) and increased to 76 wt % MAF at 300 MF lb/hr (254I) and then significantly decreased to 64 wt % MAF at 440 MF lb/hr (254J). The response for 300 MF lb/hr (254I) was relatively smaller than the expected (4 wt % vs 8 wt %). This was due to the catalyst activity decline in the second stage at a low coal feed rate. Similar observations were made during Run 253 processing Illinois No. 6 coal. Catalyst requirements for 440 MF lb/hr will be high, not desirably for the practical operation, more than 5 lb/ton of MF coal, which is suggesting the operation at a higher second stage temperature than 790°F.

The effect of the coal feed rate decrease from 440 to 375 MF lb/hr at 810°F of the second stage reaction temperature was studied during period 254K-L. The estimated C<sub>4</sub>+ distillate response due to the coal feed rate change was 8 wt % MAF coal. C<sub>1</sub>-C<sub>3</sub> gas make and organic rejection were similar for both periods. Catalyst requirements for 440 MF lb/hr is estimated to be below 5 lb/ton of MF coal (Table 7), much less than at 790°F of the second stage reaction temperature. This was due to the high second stage catalyst activity at 810°F (Figure 6).

#### Catalyst Activity and Deactivation

Two-stage catalyst activity was compared in Figure 4, based on C<sub>4</sub>+ distillate yield trend data. Ohio No. 6 coal with both high (254B) and low (254C) ash contents significantly reduced the C<sub>4</sub>+ distillate yield by 7 wt % MAF coal in the batch mode of operation, compared to Illinois No. 6 coal with a high ash content (253D). In addition, in comparisons of 254D and 253EFG Ohio No. 6 coal required a higher catalyst addition (3 vs 2 lb/ton of MF coal) and a higher second stage reaction temperature (790°F vs 760°F) for a similar C<sub>4</sub>+ distillate yield (70 wt % MAF coal). These indicate that Ohio No. 6 coal has lower resid conversion activity than Illinois No. 6 coal. Run 254B in the batch operation processing Ohio No. 6 coal showed a similar two-stage catalyst deactivation rate to that for Run 253D processing Illinois No. 6 coal.

Catalyst activity trends for Run 254 operation with a high level of resid recycle (50 wt %) were analyzed for the two-stage system, first stage and second stage, based on two-stage resid make and resid + UC conversion. The first stage equilibrium activity level with 3 lb/ton of MF coal catalyst addition was achieved at the catalyst age near to 550 lb MF coal/lb catalyst (calculated equilibrium age = 610 lb MF coal/lb catalyst), as illustrated in Figure 5. The first stage catalyst ages,

550 and 610 lb MF coal/lb catalyst, are corresponding to the second stage catalyst ages, 2000 and 3000 lb resid + CI/lb catalyst, respectively. In Figure 5 the measured first stage catalyst activity values with the catalyst addition are very close to the theoretically calculated by using the estimated batch deactivation data, which confirms that the first stage batch catalyst activity data in Figure 6 are reasonable for further catalyst requirement calculations.

Because of the continuous catalyst addition in the first stage, the two-stage catalyst deactivation rate was gradually decreased and became primarily dependent on the second stage deactivation rate. Figure 6 shows a graphical presentation of differences in the second stage catalyst activity at different reaction temperatures, 760°F, 790°F and 810°F. Second stage reaction temperature increases from 760°F to 790°F, and further to 810°F significantly increased catalyst activity levels, although the second stage deactivation rate for 810°F was significantly higher (but for 790°F, slightly higher) than for 760°F. At the same reactor temperature of 810°F for both stages, the second stage catalyst activity was higher than that of the first stage and the second stage catalyst deactivation rate was lower. These observations at 810°F of the second stage reaction temperature need to be substantiated because of limited data points at high catalyst ages (1600-2100 lb MF coal/lb catalyst of second stage catalyst ages).

Catalyst requirements at 790°F of the second stage reaction temperature were 3.1 to 4.6 lb/ton of MF coal to achieve the "all-distillate" product slate (77 wt % MAF coal C<sub>4</sub>+ distillate yield) for 300 to 370 MF lb/hr coal feed rates (Table 7). Effects of the 810°F of the high second stage reaction temperature on catalyst performance were very substantial (Table 7 and Figure 7): (1) increased coal throughput, (2) increased catalyst activity, (3) lower catalyst requirements and (4) lower distillate selectivity (C<sub>4</sub>+ distillate yield decreased to 74 wt % MAF coal because of a high C<sub>1</sub>-C<sub>3</sub> gas make) (Figure 8).

#### Optimum Catalyst Requirements and Cascading

Catalyst replacement rates reported in Table 7 and Figure 7 were calculated, assuming to achieve each stage performance experimentally measured at the Wilsonville pilot plant. Considering the significant differences in each stage catalyst activity due to different reaction temperatures employed for CC-ITSL configuration studies, one might visualize that there would be an optimum catalyst requirement for a fixed coal feed rate with resid extinction only by shifting each stage catalyst requirement loading. For instance, Figure 9 presents graphically optimum catalyst requirements for 300 and 370 MF lb/hr coal feed rates. The variable selected as X-coordinate is the first stage resid + UC conversion. The plots are simply showing that the optimum catalyst requirement is not only a function of the coal feed rate but also of the first stage resid + UC conversion. In addition the operation range for the optimum is very narrow within 1 to 3 wt % variation of the first stage resid + UC conversion. Data in Figure 9 were generated without considering catalyst residual activities and based on 77 wt % C<sub>4</sub>+ distillate yield with resid extinction. Organic rejection was assumed to be 8 wt % MAF coal. Operating conditions were 810°F first stage temperature, 790°F second stage temperature, 2.3 solvent/coal ratio, 50 wt % resid and 12 wt % CI in the recycle process solvent.

Other interesting points can be made from plots in Figure 9, that is, (1) catalyst cascading is practically possible with a possible reduction of catalyst addition about 1 to 2 lb/ton of MF coal (this saving can be considered as maximum) and (2) Wilsonville plant experimentations were conducted at operating conditions of optimum catalyst requirements (Run 254I and GH).

Four different cases were studied for optimum catalyst requirements and cascading possibility. Results were generated with considering catalyst residual activities and are summarized below. The catalyst addition for the cascading is listed for the range of interest. The actual amount is dependent on the cascading catalyst activity, which needs to be experimentally determined. The upper limit has only theoretical meaning for an equal amount of the catalyst addition for both stages with zero cascading catalyst activity. This upper limit shows a higher catalyst addition than the optimum.

Case	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Base data	<u>254I</u>	<u>254GH</u>	<u>254L</u>	<u>254K</u>
Coal feed, MF lb/hr	300	370	375	440
Second stage T, °F	790	790	810	810
C <sub>4</sub> + dist with resid extinction wt % MAF coal	77	77	74	73
<u>Catalyst addition</u> lb/ton of MF coal				
<u>experimentally measured</u>				
<u>first stage</u>	2.4	3.3	3.3	3.8
<u>second stage</u>	0.7	1.3	0.2	0.7
<u>total</u>	<u>3.1</u>	<u>4.6</u>	<u>3.5</u>	<u>4.5</u>
<u>optimum</u>				
<u>first stage</u>	2.4	3.3	0.3	1.1
<u>second stage</u>	0.5	1.0	1.2	1.8
<u>total</u>	<u>2.9</u>	<u>4.3</u>	<u>1.5</u>	<u>2.9</u>
<u>cascading</u>				
<u>first stage</u>	1.8	2.6	0.9	1.6
<u>second stage</u>	1.8	2.6	0.9	1.6
<u>total</u>	<u>1.8-3.6</u>	<u>2.6-5.2</u>	<u>0.9-1.8</u>	<u>1.6-3.2</u>

As already pointed out, in Cases 1 and 2 at 790°F of the second stage reaction temperature, optimum catalyst requirements only improve slightly about 0.2-0.3 lb/ton of MF coal, since Wilsonville pilot plant data were generated near at the optimum operating conditions. Another significant improvement can be made by doing cascading from the second stage to the first stage reactor, potentially reducing the catalyst requirement by 1.1 to 1.7 lb/ton of MF coal.

Very unusual striking results were revealed for the operation at 810°F of the second stage reaction temperature. Optimum calculations are suggesting that Wilsonville plant experimentations were not conducted at operating conditions of

optimum catalyst requirements (Run 254L and K) and therefore, if operated at optimum, catalyst savings will be about 1.6 to 2.0 lb/ton of MF coal. Additional reduction of catalyst addition can be made by 0.6 to 1.3 lb/ton of MF coal by doing catalyst cascading (this can be considered as a maximum potential). These observations need to be substantiated by further experiments at young catalyst ages, which data are not available at the present time. The assumption made for the second stage catalyst activity at 810°F should be further investigated and experimentally proved, before making definite conclusions of significant process performance achievements at 810°F of the second stage reaction temperature.

A significant advantage of 810°F of the second stage reaction temperature as opposed to 790°F lies in an increase of the coal throughput by 47% and the C<sub>4</sub>+ distillate production rate by 40% (Cases 1 and 4). Optimum catalyst requirements for both Case 1 and 4 were same, 2.9 lb/ton of MF coal. These process performance improvements will impact tremendously the process economic valuation for commercialization and reduce significantly the selling price of the distillate product, if other critical variables in the economic evaluation are similarly affecting the results for both cases.

#### SUMMARY

Several noteworthy accomplishments in 1987/88 are listed below:

- (1) Successful operations processing Illinois No. 6 and Ohio No. 6 coals were demonstrated by using Shell 317 catalyst in the close-coupled ITSL catalytic-catalytic configuration.
- (2) Interstage separation was eliminated, resulting in significant reduction in capital costs.
- (3) Best process performance was achieved processing low ash Ohio No. 6 coal with 78 wt % MAF coal distillate yield, 97 wt % coal conversion and 7 wt % organic rejection.
- (4) High second stage reaction temperatures, 790°F and 810°F, were investigated, resulting in significantly increased coal throughput and distillate production due to high catalyst activity and low catalyst requirements.
- (5) The increased reactive resid recycle improved the distillate production.
- (6) The increased gas-oil recycle produced lighter and better quality distillates.
- (7) The close-coupled ITSL process data-base was significantly expanded for processing bituminous coals.
- (8) The process economics was significantly improved for future commercialization of the coal liquefaction process.

#### ACKNOWLEDGEMENTS

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Table 1

**Wilsonville CC-ITSL catalyst properties**

catalyst RUN(s)	Shell 324 250,251	Amocat 1C 250-252	Amocat 1A 251	Shell 317 253,264
shape	( ----- cylindrical ----- )			trilobe
size	1/32"	( ----- 1/16" ----- )		1/20"
Ni (wt %)	2.7	2.3		2.7
Co			2.5	
Mo	13.2	10.4	9.8	11.6
surface area, m <sup>2</sup> /g	185	190	235	235
pore volume, cc/g	0.48	0.85	0.80	0.75
pore size distribution	unimodal	( ----- bimodal ----- )		
compactd bulk density, lb/ft <sup>3</sup>	54	42	41	36

Table 2. Shell 317 Trilobe Catalyst Replacement Rates

run no.	253D	253B
coal feed (mf lb/hr)	385	480
WHSV (hr <sup>-1</sup> )	3.9	5.1
second stage reactor temperature (°F)	760	760
TSL C4+ distillate (% maf coal)	69	68
catalyst addition (lb/ton mf coal)	4.0	8.1

Table 3. Amocat 1A and 1C Catalyst Replacement Rates

run no.	251-IE	251-ID	251-1C	252C
catalyst (1st/2nd stage)	1A/1C	1A/1C	1A/1C	1C/1C
coal feed (mf lb/hr)	300	385	480	385
WHSV (hr <sup>-1</sup> )	2.7	3.4	4.2	3.5
second stage reactor temperature (°F)	760	760	760	760
TSL C4+ distillate (% maf coal)	70	70	70	70
catalyst addition (lb/ton mf coal)	0.9	1.6	3.0	1.2

Table 4. Run 253 - Distillate Product Properties

distillation cut	%MAF <sup>1</sup>	elemental (wt%)					*API
		C	H	N <sup>2</sup>	S	O (diff)	
<b>Run 253C (40% coal slurry)</b>							
naphtha (IBP-350°F)	19.9	84.80	14.94	0.02	0.06	0.18	46.7
distillate (350-650°F)	27.3	87.74	12.03	0.11	0.01	0.11	18.9
gas oil (650°F+)	18.2	88.84	10.83	0.29	0.01	0.23	5.6
<b>Run 253E (no separator)</b>							
naphtha (IBP-350°F)	14.6	85.35	14.45	0.04	0.07	0.00	44.1
distillate (350-650°F)	26.2	87.97	11.61	0.15	0.05	0.02	17.5
gas oil (650°F+)	27.0	89.57	9.97	0.37	0.02	0.10	2.9
<b>Run 253F (ground catalyst &amp; no separator)</b>							
naphtha (IBP-350°F)	14.7	85.58	14.21	0.03	0.02	0.16	43.8
distillate (350-650°F)	22.4	87.83	11.71	0.13	0.01	0.32	18.1
gas oil (650°F+)	28.5	89.54	10.07	0.34	0.02	0.03	3.8

<sup>1</sup>by simulated distillation on GC

\*nitrogen by Kjeldahl

Table 5

run no.	TSL operating conditions	
	254B	254CD
<b>first stage</b>		
catalyst replacement (lb/ton MF coal)	none	3
average reactor temperature (°F)	(-----810-----)	(-----)
inlet hydrogen partial pressure (psf)	(-----2600-----)	(-----)
coal feed rate (lb/hr MF)	385	370
space velocity (lb feed/hr-lb cat)	(-----3.9-----)	(-----)
solvent-to-coal ratio	(-----2.0-----)	(-----)
solvent resid content (wt%)	(-----40-----)	(-----)
solvent Cl content (wt%)	(-----12-----)	(-----)
catalyst age [lb (resid + Cl)/lb cat]	850-1300	1150-1200
(lb MF coal/lb cat)	400-650	550-800
<b>second stage</b>		
average reactor temperature (°F)	760	760/790
space velocity (lb feed/hr-lb cat)	(-----3.7-----)	(-----)
feed resid content (wt%)	(-----41-----)	(-----)
catalyst age [lb (resid + Cl)/lb cat]	600-900	1100-1450
(lb MF coal/lb cat)	400-600	700-950

Table 6

run no.	TSL yield structures	
	254B	254CD
<b>10% vs 6% coal ash</b>		
<b>potential liquid yield</b>		
C <sub>4</sub> + resid (% maf coal)	70	76
coal conversion (% maf coal)	94	97
energy content of feed coal rejected to ash conc. (%)	18	9
organics rejected to ash conc. (% maf coal)	18	8

Table 7. Shell 317 Trilobe Catalyst Replacement Rates

run no.	254I	254GH	254L	254K
coal feed (mf lb/hr)	300	370	375	440
WHSV (hr <sup>-1</sup> )	3.5	4.3	4.3	5.1
second stage reactor temperature (°F)	790	790	810	810
TSL C4+ distillate (% mf coal)	77	77	74	73
catalyst addition (lb/ton mf coal)	3.1	4.6	3.5	4.5

Figure 1

**CC-ITSL with solids recycle  
catalytic-catalytic  
close-coupled mode**

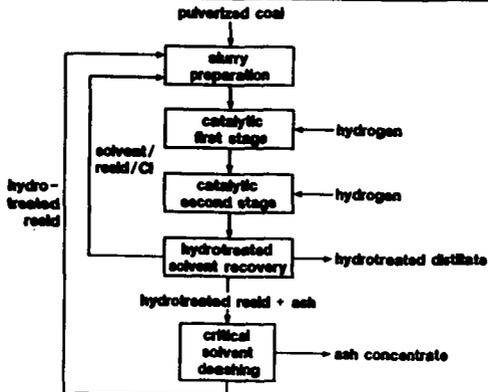


Figure 2. Amocat 1A/1C vs Shell 317 Catalyst

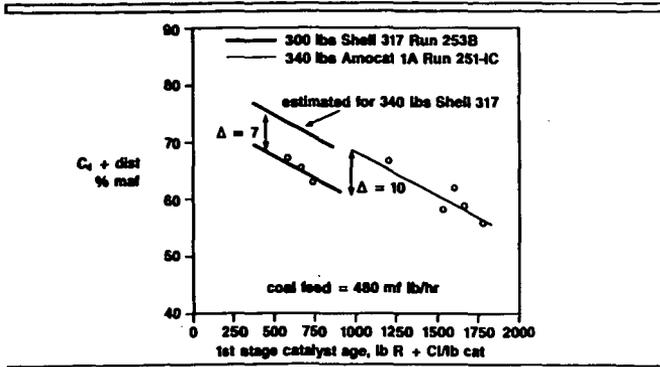


Figure 3. Amocat 1A/1C vs Amocat 1C/1C Catalyst

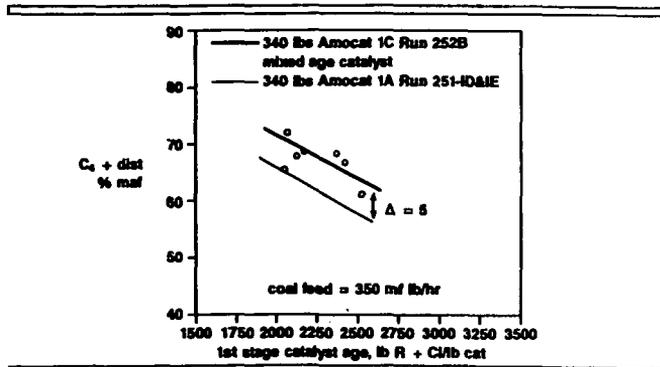


Figure 4. Illinois No. 6 vs Ohio No. 6 Coal

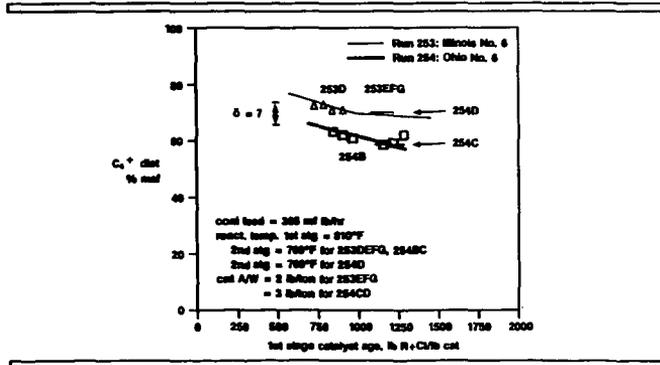
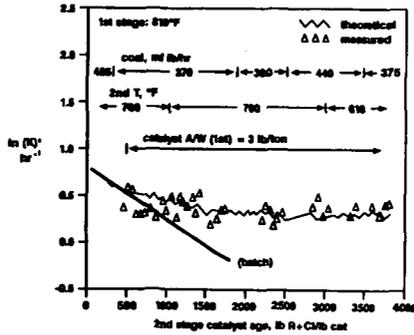


Figure 5

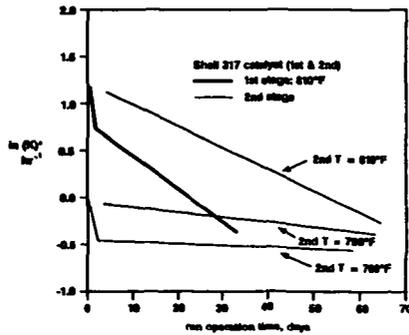
**RUN 254 first stage Shell 317 aging with catalyst addition**



\* (meald + UC) conversion rate constant

Figure 6

**catalyst aging - RUN 254**



\* (meald + UC) conversion rate constant

Figure 7. Run 254 - Catalyst Replacement vs 2nd Stage Temperature

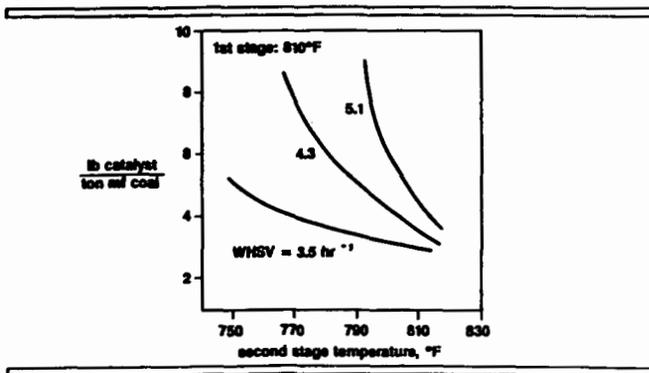


Figure 8. Run 254 - Distillate Selectivity vs 2nd Stage Temperature

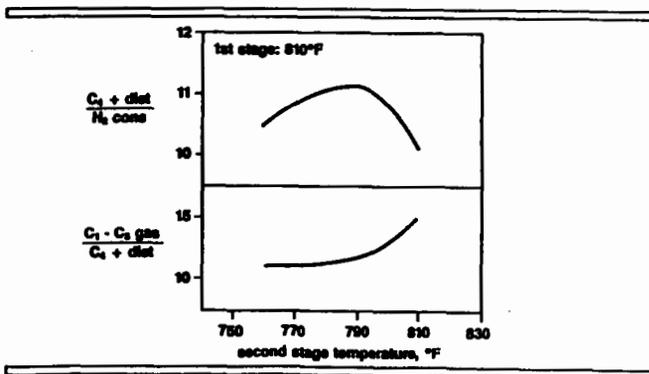
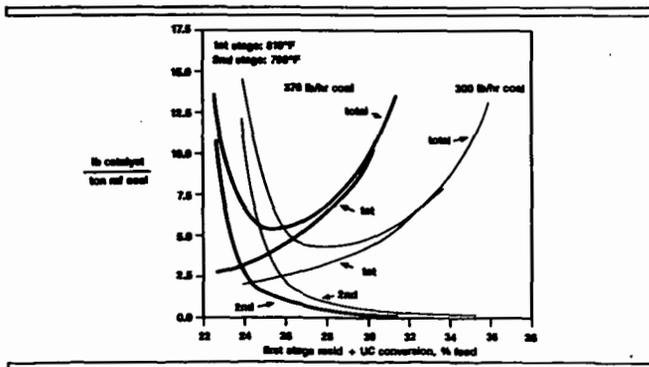


Figure 9. Run 254 - Optimum Catalyst Replacement Rate



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**PROGRESS IN DIRECT COAL LIQUEFACTION:  
THE ECONOMIC PERSPECTIVE**

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**ABSTRACT**

The economic impact of demonstrated and projected improvements in two-stage direct coal liquefaction processes are evaluated. The computerized methodology employed estimates the quantity and quality of products from a 30,000 ton/day commercial scale plant, based on input test data. Steam, hydrogen and fuel gas balances are determined. Capital and operating costs are then estimated, and the required selling price of raw liquid products is determined by conventional discounted cash flow (DCF) analysis. Product quality is quantified by computing the cost of upgrading the raw products to motor gasoline.

Improvements in two-stage processing since the early demonstration of the Lummus Integrated Two-stage (ITSL) process in 1980 are shown to reduce the required initial selling price (RISP) of gasoline from coal liquids by about 16 percent. Further process improvements, which offer the potential for an additional 16 percent RISP reduction, are identified.

This report also compares the economics of two-stage processing with earlier studies of the H-Coal, Exxon Donor Solvent and Lummus ITSL processes. The high costs of coal liquids found in these earlier studies are explained and revised costs for these earlier plants using a common financial and technical basis are determined.

**INTRODUCTION**

Two-stage coal liquefaction research and development efforts have yielded significant increases in distillate quantity and quality over the last few years. The Lummus Integrated Two-stage Liquefaction (ITSL) process experience<sup>(1)</sup> showed that high yields of good quality coal liquids can be produced from bituminous coals using a combination of short contact time (SCT) thermal processing, anti-solvent deashing and LC-Fining\* of deashed coal extract. Since then the concept has undergone several modifications.

At the Wilsonville Advanced Coal Liquefaction R&D Facility<sup>(2)</sup>, both the thermal processing and the hydrotreating have generally been of longer duration than at Lummus. The critical solvent deashing system<sup>(3)</sup> has been more efficient at recovering coal extract and has thus rejected less soluble material than the Lummus anti-solvent process.<sup>(4)</sup> The ITSL concept itself, where the thermal first stage and catalytic second stage have been separated by the deashing step, has been modified so that the topped thermal effluent is hydrotreated before deashing. This configuration is called the Reconfigured ITSL (RITSL) mode of operation.<sup>(5)</sup> More recently the RITSL mode has been modified so that the first and second stage reactors are directly coupled together and the entire thermal effluent is

\* Registered Trade Mark of Lummus-Cities Service hydrorefining process.

hydrotreated. This is the close-coupled operation (CC-ITSL). A vent separator is often used between the two-stages to let down the first stage products. In even more recent tests a portion of the ash-containing effluent from the hydrotreater is recycled to the first stage, the so called ash-recycle mode.<sup>(8)</sup> Catalytic-catalytic configurations have also been tested at Wilsonville.<sup>(6)</sup>

The overall objective of these modifications in two-stage processing is to increase the yield of high quality distillate while reducing the cost of production.

Sandia National Laboratories, which is supported by the U.S. Department of Energy under contract DE-AC04-76DP00789, has contracted MITRE to develop a method to quantify the impact of these modifications on the cost of coal liquids. In response, MITRE has developed a computerized coal liquefaction cost model that simulates the technical and economic performances of conceptual commercial scale coal liquefaction plants that incorporate the research and development improvements under study at Wilsonville.

## METHODOLOGY

### Introduction

The analysis methodology employed in the coal liquefaction cost model has been developed over the past several years. The objective of the methodology is to estimate the outputs and required selling price of products from a conceptual commercial scale plant. During 1986, the methodology was refined and computerized to permit rapid evaluation of the impact of variations in process performance on the required selling price of product liquids. The model is programmed in LOTUS 1-2-3 (Issue 2) and can be readily modified and expanded as refinements in the analysis methodology are developed. The paragraphs below present a brief overview of the analysis methodology. A more complete description may be found in reference (7).

### Commercial Plant Output

Product outputs, product quality, and the flows to primary process units in the liquefaction plant are determined from experimental test data. The data may be directly scaled to the selected commercial size based on moisture ash free (MAF) coal throughput. (Postulated results may of course be substituted for test data in order to determine the potential economic impact of speculative process improvements.) The model is designed to make certain data adjustments if desired. In most runs, the data are adjusted to reflect operation with no net output of resid (+850°F residual material). When this adjustment is made in the model, the space velocity (hence capacity) of the hydrotreater is adjusted to the level required to achieve the desired resid conversion.

The resid adjustment provision of the program is also used when there are changes in the resid available to be converted because of assumed changes in the quantity of resid rejected with process solids (for example variations in deasher performance). The conversion factors for the resid are averages of several actual sets of data obtained during the Wilsonville operations.

### Auxiliary Processes

The bottoms rejected from the liquefaction plant are gasified to produce

hydrogen. Additional coal is gasified when bottoms are not adequate to meet hydrogen requirements. Texaco gasification is assumed. Steam driven air separation equipment is used to produce oxygen for gasification. The model performs preliminary steam and fuel gas balances in order to obtain a thermally balanced plant and to determine the required capacities for auxiliary equipment. A coal fired steam plant with flue gas desulfurization is used to superheat steam produced from in-plant heat recovery, and to produce and superheat any additional steam required.

#### Cost Analyses

Preliminary designs of commercial plants employing two-stage liquefaction were prepared by UOP/SDC in 1981 under DOE contract<sup>(8,9)</sup>. These designs are used as the baseline for estimating capital and operating costs in the MITRE model. The UOP/SDC studies considered both Non-integrated Two-stage Liquefaction (NTSL)<sup>(8)</sup>, and Integrated Two-stage Liquefaction (ITSL)<sup>(9)</sup> configurations, and thus encompassed the major process elements of a wide variety of two-stage plant configurations.

The total erected costs (TEC) of process equipment required in the plant being analyzed are estimated by comparing the capacity required to the capacity of similar units in the baseline design. A 0.7 scale factor is used. Thus

$$\text{TEC (unit)} = \text{TEC baseline unit} \times \left( \frac{\text{unit capacity}}{\text{baseline capacity}} \right)^{0.7} \times \text{INF}^*$$

#### Analyses of Required Selling Prices

The required selling price per barrel of raw product is computed by dividing the annual costs by the annual output in barrels. Annual costs are the sum of net operating costs and capital recovery costs. The program computes capital recovery costs by multiplying the required capital by an input capital recovery factor. The capital recovery factor for any specific set of financial assumptions is calculated by discounted cash flow (DCF) analysis in a separate program. The baseline economic assumptions used in the study are 25% equity, 15% DCF, 3% inflation, 34% tax rate, 8% interest on debt, and a 5 year construction period. These assumptions result in a capital recovery factor of 0.167.

There are substantial differences in the quality of products produced by direct liquefaction processes in terms of boiling range, hydrogen content and heteroatoms. These characteristics necessarily influence the degree to which the product must be further processed to produce specification fuels. We have accounted for differences in product quality by estimating the cost of additional processing required to produce a standard heteroatom free 40 API gravity product (e.g., "hydrotreated product") or unleaded motor gasoline.

The value of the syncrude relative to petroleum crude (equivalent crude value) is determined by computing the cost of crude that would permit gasoline to be processed and sold at the same price as the gasoline from syncrude.

#### **RESULTS AND DISCUSSION**

Table 1 summarizes the results of using the coal liquefaction cost model. The table shows economic and technical data for four conceptual commercial \* INF accounts for inflation between the year the UOP/SDC design was developed and the year 1986 (INF = 1.125).

two-stage plants processing Illinois #6 coal. The baseline plant (Lummus ITSL) can produce raw liquid product for \$41.52/barrel (1986 dollars), which is equivalent to crude selling for \$35.82/barrel. Wilsonville run 244-B data, which was obtained using the integrated two-stage liquefaction configuration, can produce product at an equivalent crude value of \$35.36/barrel, i.e. very similar to the Lummus results. However, the close-coupled configuration run 250-D shows a significant reduction in product cost. The final column in Table 1 shows results obtained using data from Wilsonville run 250-G, which is a close-coupled run with ash-recycle. Again this shows a further decrease in product cost. Raw product cost reductions of about 16 percent have been realized in going from Lummus ITSL to the ash-recycle close-coupled Wilsonville configuration. This product cost decrease is brought about by the combination of a significant yield improvement (26 percent increase on a raw product basis) and only a slight increase in capital required to obtain that gain (about 5 percent capital increase). Therefore, it is estimated that raw coal liquids could be produced for approximately \$35/barrel; this is equivalent to crude oil at about \$30/barrel.

As an R&D guidance tool, the model can also be used to estimate potential savings in required selling prices that could be realized if certain potential process improvements were incorporated into the system. Potential improvements include using cleaned coal and eliminating the deashing system, increasing coal slurry concentration, and improving catalyst activity, selectivity and life. The model predicts that an additional cumulative reduction in required selling price of products of approximately 16 percent is possible by incorporating all of the above improvements into the current ash-recycle Wilsonville two-stage configuration processing Illinois #6 coal. Table 2 shows that these additional cost reductions result in production of coal liquids for about \$29/barrel, which is equivalent to crude at about \$25/barrel.

Table 3 summarizes earlier direct coal liquefaction economic studies undertaken by Bechtel<sup>(10)</sup>, Exxon<sup>(11)</sup> and UOP/SDC<sup>(8,9)</sup> for the H-Coal, Exxon Donor Solvent and Lummus ITSL processes respectively. Direct comparisons are not meaningful, however, because of the differences in plant scale, economic factors, and other assumptions. The earlier studies were made during a period of high inflation and high capital return expectations, and the analysts assumed a continuation of high inflation through the construction period. In order to separate the impact of improved technology from the overriding impact of changes in economic conditions, the earlier technologies were re-evaluated using the our model. The required selling prices computed by the model thus reflect the same costing methodology, plant scale and economic assumptions used in the analysis of the advanced two-stage system.

The results are shown in Table 4. Required selling prices are shown for raw liquefaction products, and for products after hydrotreatment to a consistent standard of quality. The latter prices are more meaningful for comparative purposes, since they reflect the large differences in the quality of the single and two-stage products. On this basis, required selling prices have been reduced from about \$49 to about \$36.60 per barrel, which represents a savings of about 25%.

#### CONCLUSIONS

Over the past decade continued research in the production of liquid fuels from coal has substantially increased both the quantity and the quality of distillate from a ton of coal. This increase of distillate, which amounts to approximately 35 percent, has resulted in a significant real decrease in the cost of liquid products

from coal of about 25%. Continued research is expected to further reduce the cost of coal liquids.

#### ACKNOWLEDGEMENT

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TABLE 1  
 CONCEPTUAL COMMERCIAL PLANT SUMMARY DATA  
 FOR ILLINOIS #6 COAL FEEDSTOCK

	<u>LUNMUS ITSL</u>	<u>244-B ITSL</u>	<u>250-D CC-RITSL</u>	<u>250-G-RAR</u>
<u>Economic Data (Million \$)</u>				
Plant Capital Cost	4,418	4,859	4,670	4,658
Coal Cost	271	290	314	330
Other Operating Cost	337	389	380	374
Byproduct Credit	79	69	126	150
Hydrotreating Cost	227	330	190	209
Total Operating Cost	756	939	758	762
<u>Plant Coal Requirements TPD (AR)</u>				
Coal to Liquefaction	33,232	33,232	33,232	33,232
Coal to Steam Plant	2,564	1,980	2,433	2,626
Coal to Gasification Plant	371	3,441	6,276	8,162
Total Coal to Plant	36,166	38,652	41,941	44,019
<u>Plant Product Outputs (BPD)</u>				
Raw Product	92,400	106,900	112,200	116,900
Hydrotreated Product	103,800	122,800	124,400	127,700
Gasoline	111,100	131,400	133,100	136,600
<u>Required Selling Price (\$/Bbl)</u>				
Raw Product	41.52	40.27	36.40	34.52
Hydrotreated Product	43.61	43.21	37.46	36.56
Gasoline	45.75	45.26	40.07	39.30
<u>Equivalent Crude Value (\$/Bbl)</u>	35.82	35.36	30.40	29.66

TABLE 2  
 CUMULATIVE POTENTIAL IMPROVEMENTS SUMMARY FOR CONCEPTUAL  
 COMMERCIAL PLANTS PROCESSING ILLINOIS #6 COAL

Economic Data (Million \$)	BASE CASE		CATALYST		CATALYST		CLEAN COAL NO DEASHER	SLURRY COAL 36 PERCENT
	250 G	DOUBLED	ACTIVITY DOUBLED	SELECTIVITY IMPROVED	LIFE DOUBLED	36 PERCENT		
<u>Plant Coal Requirements TPD (AR)</u>								
Coal to Liquefaction	33,232	33,232	33,232	33,232	33,232	33,232	33,596	35,596
Coal to Steam Plant	2,630	2,630	2,630	2,630	2,630	2,630	3,075	3,075
Coal to Gasification Plant	8,162	8,162	8,162	8,162	8,162	8,162	11,574	11,576
Total Coal to Plant	44,023	44,023	44,023	44,023	44,023	44,023	50,245	50,245
<u>Plant Product Outputs (BPD)</u>								
Raw Product	116,851	116,851	116,851	128,672	128,672	128,672	147,663	147,663
Hydrotreated Product	127,663	127,663	127,663	135,270	135,270	135,270	155,500	155,500
Gasoline	136,599	136,599	136,599	144,739	144,739	144,739	166,385	166,385
<u>Required Selling Price (\$/Bbl)</u>								
Raw Product	34.52	33.81	33.81	32.83	32.83	32.34	29.85	29.14
Hydrotreated Product	36.56	35.91	35.91	34.57	34.57	34.10	31.73	31.07
Gasoline	39.30	38.69	38.69	37.64	37.64	37.20	34.98	34.36
<u>Equivalent Crude Value (\$/Bbl)</u>								
	29.66	29.08	29.08	28.07	28.07	27.66	25.53	24.94

**TABLE 3**  
**REQUIRED SELLING PRICES FROM PUBLISHED STUDY DESIGNS**

PROCESS	H-COAL	H-COAL	EDS	ITSL
DATA SOURCE	BECHTEL	BECHTEL	EXXON	UOP/SDC
DEBT/EQUITY RATIO	0/100	52/48	0/100	75/25
<u>Required Selling Price</u>				
<u>(\$/Barrel)</u>				
1981 Dollars	\$ 57	\$ 36	\$ 53	\$ 43
Start-Up Year Dollars	\$ 90	\$ 57	\$121	\$ 69
(Year)	(1988)	(1988)	(1993)	(1986)
<u>Financial Assumptions</u>				
Return on equity	15.0%	15.0%	15.0%	26.0%
Interest Rate	NA	10.8%	NA	17.0%
<u>Inflation Rates</u>				
Construction costs	8.5%	8.5%	7.5%	10.0%
Operating Costs	6.0%	6.0%	7.0%	10.0%
Product Value	6.7%	6.7%	9.0%	10.0%

**TABLE 4**  
**REQUIRED SELLING PRICE OF PRODUCTS \$/BARREL (\$1986)**  
**(ILLINOIS #6 COAL)**

	<u>SINGLE-STAGE</u>		<u>TWO-STAGE</u>	
	<u>PROCESSES</u>		<u>PROCESSES</u>	
	EDS	H-COAL	ITSL	CURRENT
Raw Product	\$43.58	\$42.35	\$41.52	\$34.52
Hydrotreated Product	\$49.18	\$48.80	\$43.61	\$36.56

## RECYCLE OILS FROM FLUID COKING OF COAL LIQUEFACTION BOTTOMS

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### ABSTRACT

A series of nine fluid-coker tars, produced by Lummus-Crest, Inc., from coal liquefaction vacuum bottoms, was characterized to evaluate their use as liquefaction recycle oils. The primary variables in the coking tests were temperature (1000 to 1200°F) and coker feedstock source. The properties of the tars are principally influenced by the coking temperature. Those produced at higher temperature are more aromatic and contain less hydrogen, and are principally unsubstituted and methyl-substituted condensed aromatic compounds. The tars produced at 1000°F are expected to be poor hydrogen donor solvents, whereas those produced at 1200°F are not expected to be hydrogen donor solvents. However, a 1200°F tar was readily hydrotreated to produce a good to excellent donor solvent. Based on these results, it would appear that tars produced from fluid coking of liquefaction vacuum bottoms can be recycled to a catalytic liquefaction reactor to produce additional liquids without adversely affecting process performance.

### INTRODUCTION

In the development of processes for the direct liquefaction of coal, the efficient removal of solids from the product has proven to be particularly difficult. Many techniques have been tested and used, including filtration, hydrocyclones, vacuum distillation, Critical Solvent Deashing and antisolvent deashing; however, no truly satisfactory means has been developed. All suffer from high product rejection, high cost or serious engineering difficulties. An alternate method, fluid coking of vacuum bottoms, is being explored by Lummus-Crest, Inc., under subcontract to Burns and Roe Services Corp. through U.S. DOE Contract DE-AC22-84PC72571. The recently completed Lummus experimental program included ten tests in which five different samples of coal liquefaction vacuum bottoms were coked in a 20g/hr (nominal) continuous stirred coking unit (CSCU). The CSCU was used to simulate true fluid coking. The range of operating conditions used in the CSCU tests was chosen based on earlier tests (1,2) with a batch coker. Operating conditions for the CSCU tests are shown in Table 1, as reported by Lummus (3). Ranges of product yields (3) from the ten tests (on a wt % of total product basis) were as follows: gases, 5 to 18; coker distillate, 30 to 81; coke plus ash, 14 to 59. On an ash-free product basis, coke yields (3) ranged from 11 to 52 wt %. Details of the coker tests, the equipment and product yields appear elsewhere (3). The vacuum bottoms that were coked were originally produced in the Advanced Coal Liquefaction Test Facility at Wilsonville, Alabama, and at the Catalytic Two-Stage Liquefaction (CTSL) continuous bench unit, which is operated by Hydrocarbon Research Inc. (HRI) in Lawrenceville, New Jersey. The vacuum bottoms were produced from

Ohio 6, Illinois 6 and Wyodak coals. In the conceptual integration of liquefaction and fluid coking, the coker tars would be processed in the liquefaction plant, ultimately to produce additional distillate products. The tars could be introduced to the liquefaction plant as part of the recycle solvent or as a second stream entering a second-stage reactor. The coke would be gasified to produce hydrogen, burned for power or landfilled.

The coker tars may be quite dissimilar to typical liquefaction oils. If used as a significant part of the recycle oil, the donor-solvent quality of that stream could be altered. Moreover, the ease with which the coker tars can be hydrotreated to finished products is unknown. The objectives of the work reported here are: 1) to characterize the coker tars, 2) to evaluate their properties as donor solvents, and 3) to explore the potential of hydrotreating to improve their characteristics as products and as donor solvents.

## EXPERIMENTAL

### MATERIAL

Nine coker "distillates" were obtained from Lummus. Lummus uses the term "coker distillate" to describe these materials; however, since they are largely non-distillable, the term "coker tar" will be used here. The feedstock and operating conditions used to produce each of the coker tars are shown in Table 1 (3). Lummus' program consisted of ten tests, but no product was provided from Run CSCU-11. In some cases, the samples we received were total liquid products (TLP). In other cases we received the 650°F<sup>+</sup> portion from a true boiling point distillation of the TLP. Typically, the 650°F<sup>+</sup> portion accounted for about 97% of the TLP (4).

### ANALYSES

C, H, N and S were determined on the tars with Leco CHN-600 and SC-32 instruments. There was some difficulty obtaining samples containing representative quantities of ash for the CHN-600 instrument and, as a result, C, H, and N results may contain more uncertainty than usual. Ash was determined on the whole samples. The samples were filtered through Whatman #42 filter paper with freshly distilled tetrahydrofuran (THF). The filter cake was dried, weighed and ashed to determine the ash and insoluble organic matter (IOM) content, and to confirm the ash content. The filtrate was rotary evaporated to dryness to remove the THF and to determine the mass of solubles. Complete removal of THF was verified by proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy. <sup>1</sup>H-NMR spectra were obtained in CDCl<sub>3</sub> solution as previously reported (5). Spectra were obtained on each whole sample and on several of the THF-soluble portions. There was no significant difference between the spectra of the two types of samples. The <sup>1</sup>H-NMR solvent, CDCl<sub>3</sub>, dissolved almost, but not quite the entire THF-soluble sample. This did not appreciably affect the <sup>1</sup>H-NMR spectra since spectra obtained on the whole sample in C<sub>5</sub>D<sub>5</sub>N were essentially the same as the spectra of the THF solubles in CDCl<sub>3</sub>. Phenolic -OH contents were determined on the THF solubles by the previously reported Fourier-transform infrared spectroscopic method (6). Gas chromatography/mass spectrometry (GC/MS) analyses were performed by the previously reported method (7).

### HYDROTREATING

A sample of the coker tar from Run CSCU-1 (5g) was hydrotreated (750°F, 60 min) in a 45 mL shaking microautoclave in the presence of 5g of

Amocat 1A catalyst and 1600 psig H<sub>2</sub> (cold). The total H<sub>2</sub> charged was about 0.34 g. Its initial pressure at 750°F would be about 3700 psig. The micro-autoclave was agitated at 1000 half-inch strokes/min. The catalyst was supplied by Hydrocarbon Research, Inc., and was removed from the first-stage reactor early in Run O-1 of their Catalytic Two-Stage Liquefaction program. The product was freed of solids and analyzed as described above. The overall recovery of charged material (excluding gases) was 97.8 wt %. The THF-soluble hydrotreated product accounted for 88.5 wt % of the feed, or 101.9 wt % of the THF-solubles in the feed.

## DISCUSSION

### CHARACTERISTICS OF COKER TAR

The elemental analyses and ash and IOM contents of the coker tars are shown in Table 2. Table 3 shows the proton distributions of the chloroform solubles and the concentrations of phenolic -OH in the THF solubles. All the coker tars contained substantial quantities of ash and IOM. The ash appeared to be a mixture of coal ash and alumina particles that reported with the tars through entrainment. It appears that the alumina "seed" used as the bed in the coker (3) was the source of the alumina particles in the coker tar ash. The IOM in the coker tars may have also originated from entrainment, though some portion of it may derive from retrogressive reactions among the tar components.

The characteristics of the hydrocarbon portion of the tars are clearly influenced heavily by coking temperature. Averages ( $\pm$  std dev) of selected properties are shown below as a function of temperature.

Coking T, °F	wt %, ash free		Proton Types, % in CDCl <sub>3</sub> Solution		
	C	H	Aromatic	Cyclic Beta	Paraffinic
1000	91.2 $\pm$ 0.4	6.6 $\pm$ 0.5	36.8 $\pm$ 7.5	12.2 $\pm$ 2.7	25.0 $\pm$ 0.5
1100	91.8 $\pm$ 0.4	5.0 $\pm$ 0.3	53.2 $\pm$ 2.3	6.7 $\pm$ 0.8	12.4 $\pm$ 0.2
1200	94.8 $\pm$ 0.4	4.6 $\pm$ 0.1	68.0 $\pm$ 1.6	3.1 $\pm$ 0.3	4.7 $\pm$ 0.8

Aromatic protons consist of the sum of condensed and uncondensed aromatic protons. Paraffinic protons consist of the sum of alkyl beta plus gamma protons. Cyclic beta protons provide an indication of the donatable (hydroaromatic) hydrogen content. Though Lummus did not use a complete factorial experimental design, the above table clearly demonstrates that the properties of the hydrocarbon portion of the tar are most affected by coking temperature. With increasing coking temperature, the tars became much more aromatic and contained much lower concentrations of hydroaromatic, paraffinic and total hydrogen. Over the range tested, the other variables had a less significant impact on the properties of the hydrocarbon portion of the tars.

In fluid coking, material can report to the tar product through a combination of cracking and devolatilization. Additional material is carried out of the coker by simple steam distillation and entrainment. The characteristics of the tars indicate that the former mechanism is relatively more important at 1200°F and that the latter mechanisms are relatively more important at 1000°F. However, cracking reactions are important even at 1000°F, as evidenced by the proton distributions of, for example, the feedstock and tar product from CSCU Run 8. Though the exact feedstock used in Run CSCU-8 was not available for analysis, numerous other second-stage vacuum bottoms samples from Wilsonville Run 254 were analyzed (8). Ranges of their properties are shown below.

Proton Type	Proton Distributions, %	
	Vacuum Resid, Range From Wilsonville Run 254	Run CSCU-8 Coker Tar
Aromatic	22.4 - 35.4	42.1
Cyclic Beta	14.1 - 18.2	10.3
Paraffinic	20.5 - 32.6	21.4

The lower concentrations of paraffinic and cyclic beta protons in the tars produced at 1200°F indicate that pyrolysis reactions have cracked most of the alkyl substituents longer than methyl from the aromatic nuclei.

In contrast to the hydrocarbon moieties, the heteroatom contents and phenolic -OH concentrations in the tars show no clear temperature dependence and may primarily reflect the characteristics of the liquefaction bottoms used as the coker feed.

#### EVALUATION OF TARS AS DONOR SOLVENTS

Conceptually, the coker tars could be introduced to the liquefaction plant as a portion of the recycle oil. If the tars were to comprise a significant portion of the recycle oil, their properties as donor solvents could be important to the performance of the overall process.

None of the tars was directly tested for donor solvent quality. However, a previously developed correlation (5) between proton distributions and donor solvent quality was used for their evaluation. The original correlation was developed for distillate coal liquefaction recycle oils. Though the correlation was not developed for coker tars, it should provide a good indication of their donor solvent quality. The solvent quality index shown in Table 3 was calculated from Equation 4 of Reference 5. These data are summarized below by coking temperature.

Coker Temp., °F	Calculated Solvent Quality Index
1000	74.0 ±7.4
1100	67.4 ±6.9
1200	52.5 ±4.1

With increasing coker temperature, donor solvent quality is substantially reduced. Based on our experience in evaluating solvent quality, we would conclude that the tars produced at 1000°F are poor donors, those produced at 1100°F are even poorer donors and those produced at 1200°F are essentially non-donors.

In those situations in which donor solvent properties are important, for example in a non-catalytic first-stage reactor, it would be expected that the tars would deleteriously affect liquefaction performance if used as a substantial portion of the recycle oil. Of course, any deleterious effect would be reduced as the tar became a smaller portion of the recycle oil. In catalytic liquefaction, such as the H-Coal or catalytic two-stage liquefaction processes, the solvent quality of the recycle oil may be less important. If the tars can be rapidly hydrogenated to produce hydroaromatics (donors), then they may actually improve the donor solvent quality in the reactor inventory. The low concentration of alkyl groups longer than methyl would be beneficial to the donor solvent quality of the hydrogenated tars.

## HYDROTREATING OF COKER TAR

All advanced liquefaction processes being developed employ at least one catalytic reactor to maximize distillate production by converting the solubilized coal to distillable products. If fluid coking is to be successfully combined with liquefaction, it must be possible to hydroprocess the coker tars to produce suitable products and an acceptable recycle oil. If the tars are refractory to hydrotreating, coking will provide very little additional liquids yield to the liquefaction process.

One experiment was performed with a coker tar produced at 1200°F to explore the potential of hydrotreating to upgrade the coker tar. Procedural details are presented in the Experimental section. Analyses of the feed and product are presented in Table 4. The data show that even this simple batch hydrotreating was quite successful in hydrogenating the coker tar and removing heteroatoms. <sup>1</sup>H-NMR spectra of the feed coker tar and the hydrotreated product, which are shown in Figures 1A and 1B, respectively, show that a substantial portion of the aromatics were converted to hydroaromatics. The calculated solvent quality index (5) increased from 51.3 to 85.9, i.e., the tar was converted from an essentially non-donor solvent to a high quality solvent.

GC/MS analyses were performed on both materials. Only the portion boiling below about 500°C was detected by the procedure used. The only identified components in the coker tar were four-ring condensed aromatics containing 0 to 2 alkyl carbons (most alkylation was methyl and dimethyl). The hydrotreated product contained compounds with a range of from two to six rings, most of which were partially hydrogenated and contained 2 or fewer alkyl carbons. Examples include methyl tetralins, octahydrophenanthrene, decahydrophyrene and tetrahydrochrysene, all of which are good donors.

### ACKNOWLEDGMENT

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TABLE 1  
 COKER FEEDSTOCKS AND OPERATING CONDITIONS (3)

CSCU Run	Vacuum Bottoms Feedstock Source			Operating Conditions				
				T, °F	P, psig	Inject Steam to Feed, wt Ratio	Approx. Res. Time, sec.	
	Coal	Plant (Run No.)	Sample				Liquid	Vapor
8	Ohio 6	W'ville (254)	3587	1000	10	0.40	7.7	4.0
11	Ohio 6	W'ville (254)	3587	1100	10	0.40	7.9	4.3
9	Ohio 6	W'ville (254)	3587	1200	10	0.40	7.3	3.6
1	Ohio 6	W'ville (254)	3587	1200	2	0.31	8.2	5.2
2	Ill. 6	W'ville (250-D,E)	3567	1200	10	0.28	10.2	5.9
4	Ill. 6	W'ville (250-D,E)	3567	1200	10	0.33	7.8	4.6
12	Ill. 6	W'ville (253)	3584	1100	10	0.40	7.4	3.9
7	Ill. 6	HRI (1-25)	3576	1000	10	0.35	9.6	5.8
6	Ill. 6	HRI (1-25)	3576	1200	10	0.37	8.4	5.5
13	Wyodak	W'ville (251)	3566	1100	10	0.4	7.4	3.9

TABLE 2  
 ANALYSES OF COKER TARS

Sample	wt %, Ash Free					wt %, As Determined	
	C	H	N	S	O (diff)	Ash	IOM
CSCU-8, TLP	91.0	6.3	1.0	0.1	1.6	2.5	0.6
CSCU-9, TLP	92.1	4.7	1.0	0.2	2.0	4.7	4.0
CSCU-1, 650°F <sup>+</sup>	95.0	4.7	1.1	0.2	-1.0	10.7	6.9
CSCU-2, 650°F <sup>+</sup>	94.3	4.5	1.2	0.2	-0.2	9.8	8.8
CSCU-4, 650°F <sup>+</sup>	94.9	4.6	1.0	0.2	-0.7	12.7	8.2
CSCU-12, TLP	91.3	5.3	1.0	0.3	2.1	4.4	3.3
CSCU-7, 650°F <sup>+</sup>	91.5	7.0	0.6	<0.1	0.9	1.2	1.0
CSCU-6, 650°F <sup>+</sup>	95.1	4.7	0.9	0.1	-0.8	19.0	7.3
CSCU-13, TLP	92.0	4.9	1.0	0.7	1.6	26.9	13.6

TABLE 3  
 PROTON DISTRIBUTIONS AND PHENOLIC -OH CONCENTRATIONS OF COKER TARS

Sample	Proton Distributions, %							Conc. of Phenolic -OH in THF-Sols., meq/g	Calculated Solvent Quality Index
	Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma		
	CSCU-8, TLP	28.2	13.9	12.7	13.5	10.3	14.1	7.3	0.65
CSCU-9, TLP	54.7	10.9	14.9	10.7	3.5	3.5	1.8	0.60	59.3
CSCU-1, 650°F <sup>+</sup>	57.6	11.1	13.6	10.9	2.7	3.2	1.0	0.53	51.7
CSCU-2, 650°F <sup>+</sup>	54.8	12.4	12.2	11.6	3.3	3.7	2.1	0.53	49.5
CSCU-4, 650°F <sup>+</sup>	56.7	11.9	13.6	11.0	3.0	2.4	1.4	0.51	52.8
CSCU-12, TLP	41.2	10.3	16.6	12.3	7.3	7.8	4.4	0.64	72.3
CSCU-7, 650°F <sup>+</sup>	25.6	5.9	16.1	9.6	14.1	19.3	9.4	0.23	79.2
CSCU-6, 650°F <sup>+</sup>	60.0	9.9	12.9	10.3	2.8	2.8	1.4	0.30	49.1
CSCU-13, TLP	42.6	12.2	13.5	13.1	6.1	9.0	3.5	0.52	62.6

TABLE 4  
HYDROTREATING RESULTS

<u>Analysis, wt % Ash Free</u>	<u>Feed (CSCU-1) (a)</u>	<u>THF Soluble Hydro Product</u>
C	92.3	91.7
H	5.1	6.7
N	1.3	0.9
O (Diff)	1.2	0.6
S	0.2	<0.1
<u>Conc. of Phenolic -OH in THF Solubles, meq/g</u>	0.55	0.31
<u>H-Aromaticity of CDCl<sub>3</sub> Solubles, %</u>	68	41

(a) This is a different sample of the 650°F<sup>+</sup> fraction from Run CSCU-1 than appears in Tables 2 and 3. Differences in analytical data from Tables 2 and 3 may be real or may reflect uncertainty.

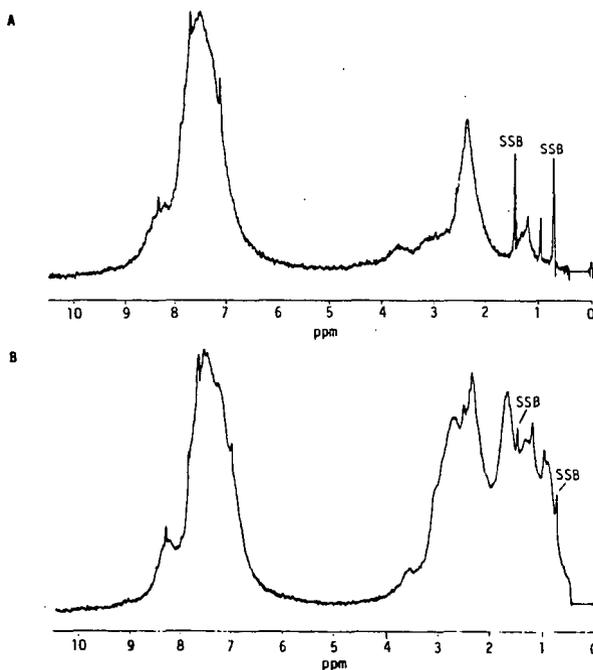


Figure 1. <sup>1</sup>H-NMR Spectra in CDCl<sub>3</sub> of A) Coker Tar from Run CSCU-1 and B) of Hydrotreated Product (SSB = Spinning Side Bands).

## CATALYSIS IN DIRECT COAL LIQUEFACTION : STATUS AND DIRECTIONS FOR RESEARCH

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The economic viability and operability of processes to convert coals to useful liquid products is contingent upon the development and application of effective catalysts. New and improved catalysts can lead to more favourable process economics by increasing the rate of conversion and the selectivity to the desired products and by allowing operation at reduced temperatures and pressures.

The processes of primary coal dissolution and coal liquids upgrading are distinguished. The status and limitations of catalysts used to promote these reactions are discussed together with approaches which could lead to the development of improved and novel catalysts.

### INTRODUCTION

The production of distillate fuels and chemicals from coal has never been economical in a free market economy. The principal factors which contribute to the high cost of coal-derived liquids are the large amounts of hydrogen which must be added to remove heteroatoms and to convert material containing about 5 wt% hydrogen to products with between 12 to 14 wt% hydrogen, the severe reaction conditions (temperature and pressure) and the relatively low rates of conversion which are experienced.

In spite of these limitations there are valid reasons for pursuing research and development in coal liquefaction. Practically every future energy scenario envisions the development of indigenous fossil fuel resources to supplement and replace materials derived from petroleum crudes. In the short term, situations could arise whereby the supplies of imported crudes to oil-poor industrialised nations are restricted and, in the long term, world petroleum reserves will be eventually be depleted.

As has occurred in the development of the petroleum processing and chemical industries, the route to significant improvements in liquefaction processing lies in the successful development and application of suitable catalyst systems. In this paper some of the more salient aspects of liquefaction catalysts are reviewed in terms of the limitations of our present understanding and approaches which could lead to improved and novel developments. Reference is made to a much more extensive critical review which the author has recently completed for the International Energy Agency under the sponsorship of the United States Department of Energy (1). A companion review on catalysis in syngas conversion has also been prepared by Alex Mills (2).

The recognition that liquefaction takes place in two loosely-defined stages, consisting of coal dissolution followed by upgrading of the solubilised products, has led to the concept of two-stage process configurations. The progression from a single, noncatalytic process to a catalytic - catalytic two stage process is summarised in Table 1 (3). The adoption of a fully catalytic process has led to increases in coal throughput and in the yield and quality of distillate products. In addition, since the construction of the first commercial-scale plants in Germany there has been appreciable progress in lowering operating severity and improving the selectivity to liquid products,

Table 2. Nevertheless there is still a pressing need for innovations which can lead to further gains in process performance and operability. The distinction between the processes of dissolution and upgrading provides a convenient division between dispersed and supported catalysts. While there are exceptions, the former have been applied primarily to promote the process of coal dissolution and the latter to upgrading the solubilised coal liquids. These catalysts cannot really be used interchangeably. It is unlikely that dispersed catalysts could realise the selectivity which is possible with supported catalysts; restricted access to the reaction surface of supported catalysts precludes their being able to directly influence the reactions of coals and high molecular weight coal derived products.

#### SUPPORTED CATALYSTS

The catalysts which have been applied to coal liquids upgrading comprise a combination of the metals Co, Ni, Mo and W, together with promotional additives, distributed over a porous support of alumina or silica-alumina. The catalysts must be sulphided in order to attain their active form. These catalysts are used extensively in petroleum refining and evolved from catalysts which were originally developed for hydroprocessing distillate coal liquids. No concerted attempts have been made to adapt them for hydroprocessing high boiling coal liquids. Research efforts have focused mainly on catalyst screening and evaluation and little attention has been given to investigating novel formulations.

One of the important conclusions emanating from a long program of research by Sullivan and co-workers at the Chevron Research Company (4, 5) is that coal liquids can be adequately hydroprocessed over conventional catalysts provided that the end-point does not exceed about 370°C. The presence of higher boiling materials is deleterious to catalyst life which is shortened by the formation of carbonaceous deposits, the adsorption of basic compounds and the deposition of metals. These effects are considerably more pronounced in the presence of non-distillable coal-derived materials. Under these conditions and during continuous processing there is a rapid and massive reduction in catalyst activity during the first 30 to 50 hours on stream, due principally to the deposition of carbonaceous materials which effect a drastic reduction in surface area. Subsequent loss in activity is more gradual and is attributed to the accumulation of metals. Other contributory causes are the loss of active metals and sintering. Substantial research has been conducted at the Sandia National Laboratories and the Pittsburgh Energy Technology Center to investigate the causes and mechanisms of deactivation (see reference 1). The deposition of carbon is generally attributed to the adsorption and reaction on catalyst acid sites of species such as polycondensed aromatics and heteroatom-containing compounds.

It is concluded that the existing generation of supported catalysts cannot adequately meet the exacting requirements for upgrading primary coal liquids. Two prospective approaches to resolving this problem are indicated. The first involves the development of new supported catalysts which are less susceptible to deactivation by the mechanisms discussed. Avenues for research are considered in reference (1). The second approach is to produce materials which are more amenable to upgrading over supported catalysts through effective catalytic control of the process of coal dissolution. While both of these strategies are considered to be important priorities for future research, the remainder of this paper will be given to a discussion of dissolution catalysis.

It is considered that successful research in this area could have an immediate impact on liquefaction process development.

#### DISSOLUTION CATALYSTS

Although many catalysts have been examined in fundamental studies, large scale investigations have been primarily concerned with two groups of catalyst materials; metal sulphides and acid catalysts. The sulphides of metals such as Mo and Fe are believed to function as hydrogenation catalysts while metal halides like  $ZnCl_2$  promote bond cleavage by an ionic mechanism. In both cases, effective control of the dissolution process requires intimate contact between the catalyst and coal. In turn, this means that the used catalyst is associated with the solid reaction products, which complicates its recovery. For this reason, low cost has been a priority in catalyst selection as it allows use on a once-through basis. This has limited the choice of candidate catalyst materials. The development of technologies for catalyst recovery could alleviate the cost constraint and have a major influence on broadening the resource base for the selection of catalysts.

It is also true to state that research on catalytic coal dissolution has been retarded by the persistent and misguided belief that catalysts cannot influence the reactions whereby the solid coal feed is converted to soluble products.

#### Sulphide Catalysts

For most metals, the thermodynamically stable form under liquefaction conditions is a sulphide or mixture of sulphides. Fortunately, a number of sulphided metals are active catalysts for coal dissolution. A water or oil-soluble catalyst precursor is normally introduced to the coal or coal-solvent slurry in a manner intended to disperse it efficiently. The sulphided catalyst is subsequently produced by the in-situ reaction of the precursor with sources of sulphur. For a given metal, the catalyst activity will be a function of its dispersion and the stoichiometry of the sulphide phase.

Dispersion is very difficult to quantify. It is always described qualitatively and inferred from experimental data. Logically, it will be dependent upon the precursor composition and the mode of its addition. There is a need to develop methods to quantitatively assess catalyst dispersion. Without this information, there is no means to distinguish effects due to differences in dispersion from those caused by changes in other parameters.

The kinetics of formation of the active phase will be determined by the dispersion and composition of the catalyst precursor and the availability of sulphur-containing species. This reaction is of some relevance since, if the rate is slow, the initial and critical reactions within the coal matrix may be thermally controlled, despite the ostensible presence of catalyst.

Increasing the partial pressure of  $H_2S$  will promote precursor conversion and can have an important influence on catalyst activity. In the presence of added pyrrhotite, increasing the  $H_2S$  partial pressure has been shown to enhance the hydrocracking of diphenylether and diphenylmethane (6). Research on upgrading petroleum feedstocks with unsupported vanadium catalysts showed that the catalyst activity passed through a maximum between 10-25 mole percent  $H_2S$  (7). Studies with supported catalysts have demonstrated that increasing the partial pressure of  $H_2S$  accelerates the rate of

hydrodenitrogenation (8-11). One explanation of these phenomena is that the H<sub>2</sub>S partial pressure serves both to maintain the catalyst in its sulphided state and to control its stoichiometry. However, it has also been found that H<sub>2</sub>S alone can promote cracking reactions and its direct participation in hydrogenolysis reactions may well contribute to the effects observed in the presence of catalysts.

Some thoughts are presented here concerning the mechanisms by which sulphide catalysts may promote coal dissolution. Indisputably, they promote hydrogenation of the coal. It is also probable that they provide several other functions although, as yet, there have been no clear indications of these.

McMillen (12-14), and earlier Vernon (15), have described a mechanism by which the addition of H-atoms to the ipso positions of linkages to aromatic systems can induce bond cleavage. Free H atoms could be made available from one of several sources including the catalytic dissociation of molecular hydrogen. However, even at high levels of dispersion, a large proportion of the catalyst centres must be distant in molecular dimensions from the bonds which are broken. The facility with which hydrogen is known to move through the structure of coals suggest that it should be able to diffuse from the sites where it is generated by a spill-over mechanism, Figure 1. Thus the catalyst can be viewed as a means to inject H-atoms into the coal or the coal-solvent mixture and thereby increase the pool of available hydrogen. This hydrogen will be available for aromatic hydrogenation, the promotion of bond cleavage reactions and radical stabilisation.

In the proposed mechanism, the catalyst does not participate directly in bond cleavage which is dependent upon the level of thermal energy input. This could explain why, for a given coal, different catalysts have been found to show evidence of liquefaction activity over the same range of temperature, Figure 2 (16). The threshold temperature will depend upon the types and distribution of connecting linkages and is expected to differ from coal to coal and to show a systematic change with coal rank.

The effectiveness of the catalyst can be strongly influenced by the presence and composition of a liquefaction solvent. While space precludes an extended discussion of this subject, it seems that those solvent characteristics which have been found to be desirable in 'thermal' liquefaction also hold for catalytic coal conversion. The solvent can provide additional routes for the transport of H-atoms produced by the catalytic dissociation of H<sub>2</sub>. The presence of polycondensed aromatics in the solvent has been found to be particularly advantageous (see reference 1).

The possibility that there exists a temperature threshold, below which hydrogenation catalysts have little effect on liquid yields places a lower limit on the temperatures required for liquefaction. However this constraint need not hinder the development of more effective catalysts.

Catalysts with higher activities for dissociating molecular hydrogen will increase the availability of hydrogen atoms and may make it possible to operate at more elevated temperatures (thereby increasing the rate of conversion) while suppressing condensation reactions. Reductions in operating pressure may also be realised. A number of single metals and metal compounds which possess the desired attributes have been excluded from research programs because of their

cost. The scope of fundamental research should not be restricted by such considerations. Until the extent of any potential benefits are determined experimentally, judgements of economic viability can only be subjective.

Although catalytic hydrogenation does not appear to significantly enhance the yield of product liquids below a certain temperature range, it has been shown that reaction at lower temperatures can effect structural modifications to the coal which are advantageous to the production of liquids upon subsequent high-temperature reaction (17,18). The influence of the catalyst can thus be augmented by reacting the coal in successive stages of increasing temperature.

Perhaps the most promising approach to the development of novel catalysts lies in research into multicomponent systems which, in comparison to work on single metals, are essentially unexplored. There are good reasons to anticipate that synergistic effects will lead to exciting discoveries. Synergism has been reported for Fe - Mo catalysts (19). It is supposed that the two metals provide complementary functions which results in non-additive behaviour. A further example of this is given below. The use of a second component could also reduce catalyst cost if the concentration of a more expensive component can be reduced.

#### Acid Catalysts

Acid catalysts can promote the cleavage of the linkages which connect coal structural units and crack the structures which comprise these units. Several of the catalysts of interest for coal dissolution are metal halides, such as  $ZnCl_2$ , which possess a low melting point and develop significant vapour pressure at sub-pyrolysis temperatures. This facilitates their penetration and dispersion in the coal matrix. Cracking reactions proceed by an ionic mechanism in which protonation of the reactants is the initial and rate - limiting step. The driving force is the strength of the acid. By using stronger acid catalysts the rate of reaction can be accelerated and the reaction temperature can be reduced.

Process development research conducted by Zielke and co-workers at the Consolidation Coal Company in the 1960s and 1970s demonstrated that it is possible to liquefy coals at fast rates of throughput and with high selectivity to gasoline-range products, using a zinc chloride catalyst. The disadvantages were (i) that the use of massive concentrations of  $ZnCl_2$  necessitated the development of techniques for catalyst recovery and (ii) that the corrosive nature of the catalyst created problems in plant construction and operation (see reference 1).

It is possible that many of these technical difficulties could be resolved. However, there is a further problem relating to the process chemistry. In general, acid catalysts do not promote hydrogenation. As a consequence of their inability to adequately stabilise the cracked products, cracking reactions are accompanied by condensation reactions leading to the production of high molecular weight materials. A possible solution is to introduce a second component which can provide a hydrogenation function, Table 3 (20). As discussed above, there are indications that research into multicomponent catalyst formulations can lead to improved control of the reaction chemistry of coal conversion. In this case, it could bring the more desirable features of acid catalysis closer to practical realisation.

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Table 1 - History of Process Development and Performance for Bituminous Coal Liquefaction

	<u>Configuration</u>			
	Single stage noncatalytic (1982)	Single stage catalytic (1982)	Two stage noncatalytic/catalytic (1985)	Two stage catalytic/catalytic (1986)
Distillate (wt% coal maf)	41	52	62	70
Distillate quality/gravity °API	12.3	20.2	20.2	26.8
Nonhydrocarbons (wt%)				
S	0.33	0.20	0.23	0.11
O	2.33	1.0	1.9	<1
N	1.0	0.50	0.25	0.16

Source: Weber and Stewart, 1987 (3)

Table 2 - Impact of Catalysis on Process Conditions and Selectivity

<u>Process</u>	<u>Temp oC</u>	<u>Pressure MPa</u>	<u>Liquid/gas ratio</u>
Single Stage			
I G Farben	480	30-70	2.4
Ruhrkohle	475	30	2.3
H-coal	450	12	4.0
Two Stage (noncatalytic/catalytic)			
British Coal	400-425	20	4.8
Lummus	410-460	18	10.8
Two Stage (catalytic/catalytic)			
HRI	400-440	17	12.0

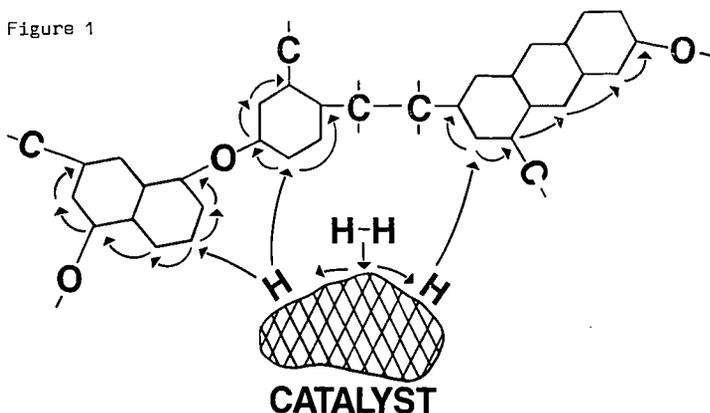
Source: various

Table 3 - Effect of hydrogenation component on ZnCl<sub>2</sub> - catalysed cracking of dibenzylther

Catalyst	% Ether Conversion	% Yield	
		Toluene	Insoluble Resin
None	3.8	1.4	-
ZnCl <sub>2</sub>	100.0	3.9	97.0
Ni	38.2	19.5	2.5
Ni+ZnCl <sub>2</sub>	96.5	65.6	6.0

Source: Mobley and Bell, 1980 (20)

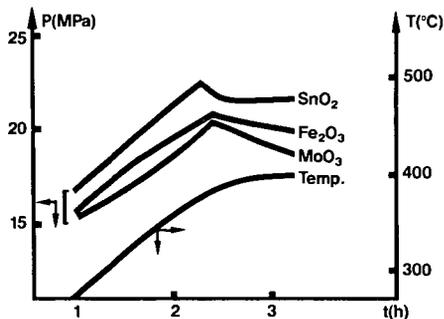
Figure 1



## DISTRIBUTION OF H-ATOMS BY HYDROGEN SPILLOVER

*Produced by catalytic dissociation of H<sub>2</sub>.  
H-Atoms induce bond cleavage and stabilise radicals.*

Figure 2



## EVIDENCE FOR EXISTENCE OF A THRESHOLD TEMPERATURE IN CATALYTIC COAL LIQUEFACTION

(BITUMINOUS COAL: TETRALIN: CATALYST =  
40: 95: 0.8; HEATING RATE 3°C/MIN)

*H. Charcosset and others (1986), Fuel Processing Technology, 12, 189-201*