SECTION 1

COAL LIQUEFACTION

EFFECT OF COAL PROPERTIES ON EDS ECONOMICS

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ABSTRACT

This paper discusses the effects that coal properties (as-received moisture, ash level, elemental composition) and other items such as liquid yield, plant investment, location factor, and coal price can have on the relative economics of an EDS plant. EDS is a direct coal liquefaction process which has been developed to a state of readiness for future commercial application.

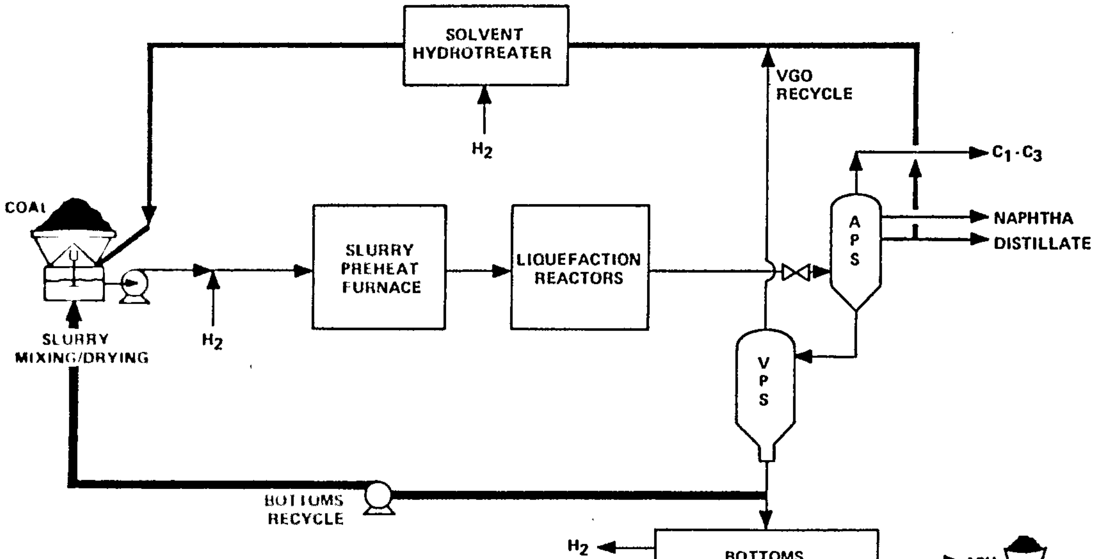
Results reported here are based on a consistent set of EDS plant simulations with the EDS Process Alternatives Model (PAM) for five different coals. The broad range of coals included bituminous (Illinois No. 6 and Pittsburgh No. 8), subbituminous (Wyodak and Wandoan from Queensland, Australia) and Texas lignite. All the coals have been run in EDS pilot plants. The simulations were for balanced, self-sufficient plant operations at various conversion levels and with different options to provide plant hydrogen, fuel, and steam.

Review of EDS Process

For a quick review, Figure 1 depicts a simplified flow plan of the EDS process. Feed coal is mixed and dried to about 4% moisture with a recycled hydrocarbon solvent; pumped to a pressure of about 2500 psi; heated to over 800°F; and fed as a slurry to a liquefaction reactor. The coal/solvent slurry moves upward through the reactor together with gaseous hydrogen. The coal is liquefied by reaction with molecular hydrogen and hydrogen donated by the solvent. The reactor effluent is separated into products using conventional petroleum refining distillation facilities. A portion of the distillate stream is used as the recycle solvent, which is now depleted of a portion of its donor hydrogen. It is fed to a solvent hydrogenation unit where it is rehydrogenated, and then recycled to the slurry mixer. The use of a separate reactor for hydrogenation of the recycled solvent is a distinctive feature of the EDS process; however, it does utilize conventional petroleum technology for hydrogenating the solvent.

FIGURE 1

EDS COAL LIQUEFACTION PROCESS


SOLVENT HYDROTREATER
H_2
VGO RECYCLE
C_1-C_3
COAL
NAPHTHA
DISTILLATE
SLURRY PREHEAT FURNACE
LIQUEFACTION REACTORS
A P S
SLURRY MIXING/DRYING
H_2
V P S
BOTTOMS RECYCLE
H_2
FUEL GAS
BOTTOMS PROCESSING
ASH
FUEL

The EDS process is a direct coal liquefaction process which has been brought to a state of commercial readiness for a broad range of coals. This paper describes the effects of coal properties and other items on EDS economics. It is based on work carried out during the EDS Consolidation Program Economic Studies, which is described more fully elsewhere (1).

Some of the items which may affect the cost to produce liquids from direct coal liquefaction are listed in Table 1. These items will affect the economics of not only the EDS process, but any other coal liquefaction process, as well. The first part of the paper describes the procedures which were used to develop an economic evaluation of the EDS process with different coals. The second part presents an interpretation of the findings of this study and illustrates how each of the items affect EDS economics.

Table 1
ITEMS WHICH AFFECT THE COST OF PRODUCING LIQUIDS FROM COAL

- **Liquid Yield**
- **Investment**
  - **+ Direct Costs** }
  - **+ Indirects** } **TEC Factor**
  - **+ Infrastructure** }
  - **+ Owner's Costs**
- **Coal Price**
- **Coal Properties**
  - **+ Ash Level**
  - **+ As-Received Moisture**
  - **+ Oxygen Content**
  - **+ Hydrogen/Carbon Ratio**
  - **+ Heteroatom Content**

A portion of the bottoms from the vacuum pipestill is typically recycled back to liquefaction in order to increase overall liquid yields. Heavy vacuum gas oil (HVGO) can also be recycled to liquefaction and partially converted to lighter liquid products. Bottoms which are not recycled can be gasified to produce a synthesis gas, which can be used as fuel or upgraded to hydrogen. Bottoms could also be combusted to provide steam or process heat.

Bases for Economic Studies

In the Consolidation Program Economic Studies, we developed a consistent economic evaluation of five coals which had been run in pilot plants during the EDS Project. The coals included bituminous coals from Illinois (No. 6, Monterey mine) and West Virginia (Pittsburgh No. 8, Ireland mine), sub-bituminous coals from Wyoming (Wyodak) and Queensland, Australia (Wandoan) and lignite from Texas (Martin Lake mine).

The technique used for evaluating economics was the EDS Process Alternatives LP Model (PAM). PAM is a computerized linear programming model of the EDS process which was developed in 1976, and used extensively throughout the EDS project for process engineering screening evaluations. The model utilizes user-provided information (yields, utilities, investments and operating costs) to develop overall plant mass, energy and utility balances.

The use of PAM to simulate a "balanced" EDS plant operation was described in a paper presented two years ago at this conference (2). That earlier work was part of this same study, and it described the EDS plant configurations which we used. By a configuration we mean how the plant produced hydrogen, fuel and steam for its internal consumption. The plant itself is self-sufficient (i.e., balanced) with only coal, water and power being imported. This study used three different plant configurations. In each case, plant hydrogen was made by solidified bottoms/water slurry partial oxidation (POX), sometimes supplemented with water slurry coal POX. The three options for plant fuel included: 1) using liquefaction produced C_2^- gas as fuel (high Btu gas, HBG); 2) using a solidifed bottoms/water slurry POX to produce an intermediate Btu gas (IBG), and 3) using a solid bottoms and coal-fired hybrid boiler to supply liquefaction process heat. The hybrid boiler also supplies plant steam. These configurations are abbreviated as: POX/C_2^-, POX/POX, and POX/HB.

Along with balancing the EDS plant with different configurations, PAM also calculates total plant investment and operating costs. Investments are based on prorations from the Wyoming Coal Bottoms Recycle Study Design Addendum (3). Then, with a variety of economic assumptions, one can estimate overall economics for a plant's operation. Even though the Economics Studies report (1) presents values for the production cost of coal liquids, this paper concentrates only on relative effects. Enough things have changed in the past year or two, and will continue to change, that the reported absolute production costs are not valid any longer. However, the economic trends versus coal properties which we found in this work should continue to be valid.

Coal Composition and Development of Yields

As mentioned previously, the coals examined in this study included two bituminous coals, two sub-bituminous coals and a lignite. Table 2 shows the dry coal elemental composition and the as-received moisture level. Note that moisture ranged from 4 wt% to 31 wt%.

Table 2
COAL ANALYSES FOR EDS CONSOLIDATION STUDIES

Coal Mine	West Virginia Pittsburgh #8 Ireland	Illinois #6 Monterey	Wyoming Wyodak	Texas Lignite Martin Lake	Queensland Wandoan Austinvale
Elemental Analysis (Wt% Dry Coal)					
Carbon	74.4	69.3	70.1	65.2	70.4
Hydrogen	5.3	5.1	4.6	4.7	5.7
Oxygen (By Difference)	7.2	11.0	16.2	16.0	14.3
Nitrogen	1.1	1.3	1.0	1.3	1.0
Sulfur	4.2	4.3	0.7	0.8	0.2
Ash (SO_3-Free)	7.8	9.1	7.4	12.0	8.4
Moisture Content (Wt% As-Received)	4	16.7	31.0	30.0	10.5
Heating Value (HHV Btu/lb, Dry)	13,660	12,610	11,670	11,340	12,790
Coal Cleaning	Washed	Washed	None	Selective Mining	Heavy Medium

Coal cleaning operations were selected for each coal to reduce as-mined coal ash to reasonable levels for use in a commercial liquefaction project. The two bituminous coals, Ireland and Monterey, were cleaned before liquefaction with jigs and water-only cyclones. Wandoan coal used deep cleaning with heavy media cyclones. Wyodak needed no cleaning and Texas lignite used selective mining to achieve a relatively low ash level for a lignite of about 12 wt%. This was the ash level tested at the 250 T/D EDS Coal Liquefaction Pilot Plant (ECLP). A sensitivity case of 18% ash was also considered for the lignite.

As far as the elemental coal composition is concerned, note that the oxygen content varied from about 7 to 16 wt% and the sulfur level from less than 1% to over 4% for the bituminous coals.

The expected EDS yields from liquefaction and solvent hydrogenation were developed at several different operating conditions for each coal. Conditions were selected to portray a typical EDS operation which is termed the reference operation, a high conversion lighter slate operation and, with some coals, a high distillate-to-naphtha ratio operation.

The operating conditions for these cases cover a range in coal conversion levels between about 65 and 75 wt% on a dry ash free feed basis. This represents the region which is likely to contain the optimum economic operation as indicated by past screening studies. The actual optimum for any specific coal depends on project specific basis items, such as whether high Btu gas should be sold and the extent of onsite upgrading of products. With the basis items used in this study, the high conversion operations were the most attractive (see later discussion). The yields for the high conversion operation are shown in Table 3. Note that it may be possible to attain even higher conversions with many coals, but extra conversion tends to be C_1/C_2 hydrocarbon gas or C_3/C_4 LPG.

Table 3
LIQUEFACTION YIELDS FOR EDS CONSOLIDATION STUDIES HIGH CONVERSION OPERATION

Coal	West Virginia Pittsburgh #8	Illinois #6	Wyoming	Texas Lignite	Queensland Wandoan
Mine	Ireland	Monterey	Wyodak	Martin Lake	Austinvale
Conditions					
Temperature °F	840	840	820	820	840
Nom. Res Time, Min	100	80	100	100	100
H_2 Part. Press, Psig	2000	2000	2000	2000	2000
Solvent/Coal/Btms/HVGO	1.4/1/1/0.2	1.4/1/1/0.2	1.8/1/1/0.2	1.8/1/1/0.2	1.4/1/1/0.2
Yields, Wt% DAF					
H_2	−5.9	−5.9	−5.2	−5.2	−5.0
H_2O	7.3	10.6	14.4	12.5	11.4
CO_2	1.1	1.9	6.4	8.9	3.3
NH_3	0.9	0.9	0.8	1.2	0.8
H_2S	3.1	4.0	0.7	0.6	0.3
C_1/C_2	11.6	11.5	8.0	7.1	9.7
C_3/C_4	7.9	7.5	6.0	7.0	6.7
C_5/350°F	20.0	22.8	17.1	19.4	18.1
350°/650°F	22.1	17.0	19.3	16.3	22.2
650°F+	5.7	4.4	5.0	3.6	6.0
Vac Btms	26.2	25.3	27.5	28.6	26.6
C_3/850°F	55.7	51.7	47.4	46.3	53.0
Conversion	73.8	74.7	72.5	71.4	73.4

Liquefaction/solvent hydrogenation yields were developed using a semi-empirical coal liquefaction model (4) which is based on data from the 75 lb/D Recycle Coal Liquefaction Unit (RCLU). The RCLU-based model fit the pilot plant data very well and has high correlation coefficients for major component yields (coal conversion, C_1/C_3 gas yield, C_4/400°F naphtha yield, C_1-1000°F total organics yield and hydrogen consumption). Using the model rather than specific pilot plant data offered greater flexibility in selecting operating conditions. The expected yields for a commercial-size EDS operation were then developed by adjusting the RCLU predictions in several areas based on operating experience with the larger EDS pilot plants (1 T/D Coal Liquefaction Pilot Plant, CLPP, and 250 T/D ECLP). The adjustments are described in Reference 1.

The next several figures show how the various yield components--liquids and chemical gases--varied with different coals. Figure 2 shows C_3^+ yield for the high conversion and reference operations. For convenience, these yields are plotted as a function of the as-received coal moisture level. Note that the liquid yield ranged from 56 wt% on a DAF basis for West Virginia Ireland to 48 wt% for Wyodak and Texas lignite at the high conversion level. Water production and carbon oxides as a function of DAF oxygen content are shown on Figure 3. The water production varied from 6% on DAF feed to liquefaction to about 12%. Carbon oxides varied from less than 1% to about 8%. Figure 4 shows H_2S yield versus coal sulfur level and Figure 5 shows NH_3 versus coal nitrogen level.

Figure 2
LIQUEFACTION YIELD AS A FUNCTION OF COAL MOISTURE LEVEL

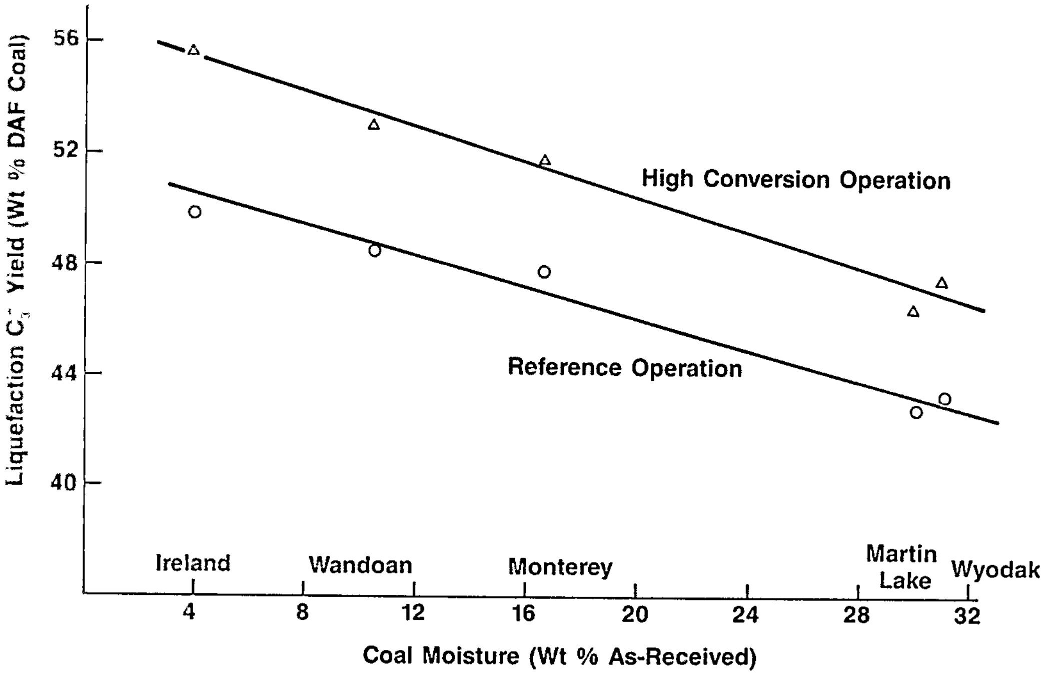


Figure 3
CHEMICAL GASES YIELD DURING LIQUEFACTION

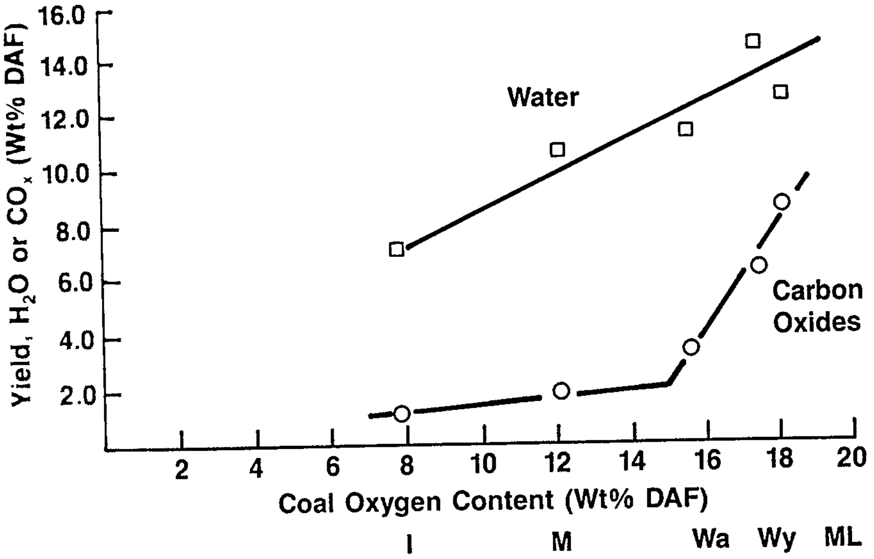


Figure 4

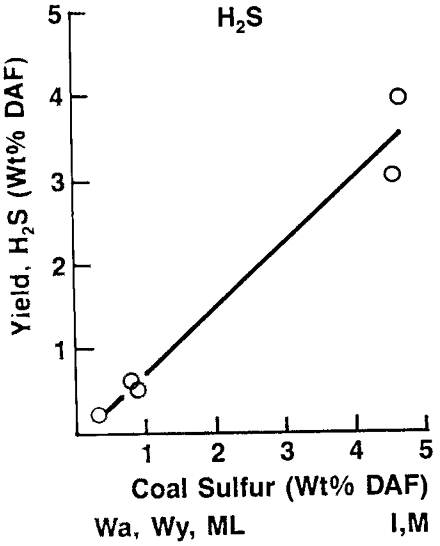
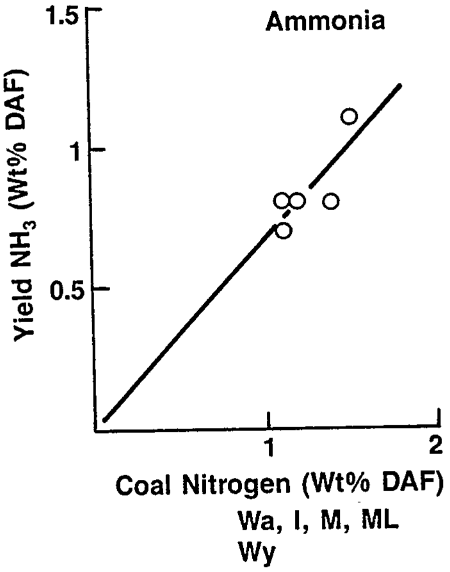


Figure 5



I = Ireland
M = Monterey
Wa = Wandoan
Wy = Wyodak
ML = Martin Lake

EDS Plant Products

EDS plant liquid products from this study include C_3 and C_4 LPG, naphtha after hydrotreating to meet catalytic reforming feed specifications, and excess hydrotreated solvent (350/850°F material). Naphtha hydrotreating is necessary to stabilize this material for shipping. The hydrotreated naphtha could be reformed to gasoline either at a refinery or onsite at the coal liquefaction plant. The $350°F^+$ material is sent through solvent hydrogenation, and is expected to be stable for shipment to a refinery for additional upgrading, or used as is. EDS products and product qualities are discussed elsewhere (5, 6).

Development of PAM Input

Input to PAM was developed from a variety of in-house tools. Product yields, as mentioned previously, were established from a semi-empirical coal liquefaction model. Next, a heat and material balance program was run to determine various component rates through the different pieces of equipment. The rates were used to determine equipment sizes and thus the investment. A reactor design program was also run to estimate the reactor exotherm and size the reactors. Another program was used to determine the heat and material balance for the water slurry bottoms feed to partial oxidation for producing plant hydrogen. The feed rate to liquefaction for each coal was set at 25 k ST/SD of dry coal, which was the same rate as the Wyoming Study Design (3). Supplemental coal was used, if necessary, to balance the plant in either boilers or coal POX.

Economics for Producing Coal Liquids

The EDS Project has used the concept of Required Initial Selling Price (RISP) as a measure of a plant's economics. RISP is the price per barrel at which the plant's products must be sold in the first year of the plant's operation to life of the plant. Calculating a RISP requires making numerous assumptions about the course of future events. Rather than enumerate the ones which were used several years ago in the Wyoming Study Design work--and are out of date--this paper presents results on a normalized basis. For those interested in absolute numbers for RISPs, see References 1 and 3.

The calculation procedure for RISP is shown in Table 4. Note that there is a cost term in the numerator, while the denominator is the total number of barrels of product. There is also an adjustment for possible HBG sales on a fuel oil equivalent barrel basis. Let's review the liquid production rate term first and compare the relative quantity of liquids produced with each coal.

Table 4
REQUIRED INITIAL SELLING PRICE (RISP) FOR COAL LIQUIDS

$$\text{RISP} = \frac{\text{Total Cost of Production}}{\text{Barrels of Product}}$$

Cost (k\$/SD) = Capital Recovery + Operating Costs -- By-Product Credits

Operating Costs = Coal + Power + Water + Cat/Chem + Salaries + Repair

$$\text{Barrels (B/SD)} = \left(C_3 + \frac{\text{kB}}{\text{SD}}\right) \frac{\left(C_1 + \frac{\text{kFOEB}}{\text{SD}}\right)}{\left(C_3 + \frac{\text{kFOEB}}{\text{SD}}\right)}$$

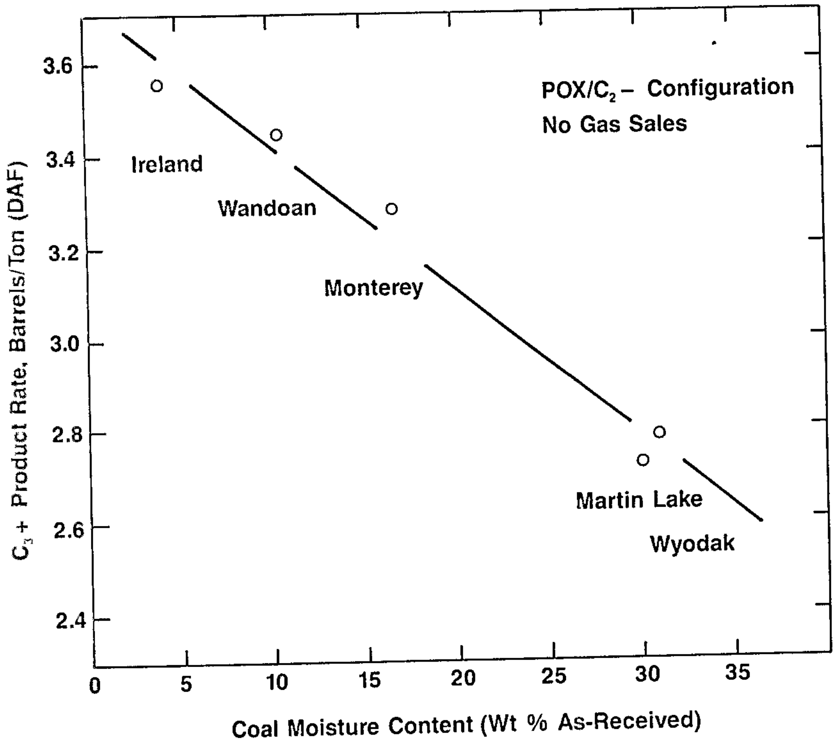
Adjustment for Gas Sales

FOEB = Fuel Oil Equivalent Barrel

Balanced Plant Yield Varies With Coal Moisture Level

One of the most interesting findings from this study is shown in Figure 6. This figure is a plot of the number of C_3+ barrels produced in a balanced EDS plant per ton of total dry ash-free coal used. The total coal includes both coal to liquefaction and coal to a boiler or to partial oxidation. In this particular figure, each coal used a POX/C_2^- configuration with no HBG gas sales.

Figure 6
EDS BALANCED PLANT YIELDS
CORRELATE WITH COAL MOISTURE



The relationship wherein liquids decrease with increasing moisture results from the prediction of liquefaction yields discussed earlier. In Figure 2, the high moisture coals, Wyodak and Texas lignite, produced about 16% less C_3+ on a weight basis than West Virginia Ireland when the plant was driven to about the same conversion level. Why were less liquids made? One important factor is that the high moisture coals also have a high oxygen content. These are younger coals, in the ground for less time, and the as-mined moisture level tends to go hand-in-hand with the oxygen content. When a coal has a high oxygen content, this means that most of the oxygen will be driven off during liquefaction as either H_2O or carbon oxides. Ireland produces only about 8 wt% H_2O plus CO_x during liquefaction, whereas Wyodak and Texas lignite each produce about 21 wt%. This difference of 13 wt% results in less hydrocarbon liquids being formed.

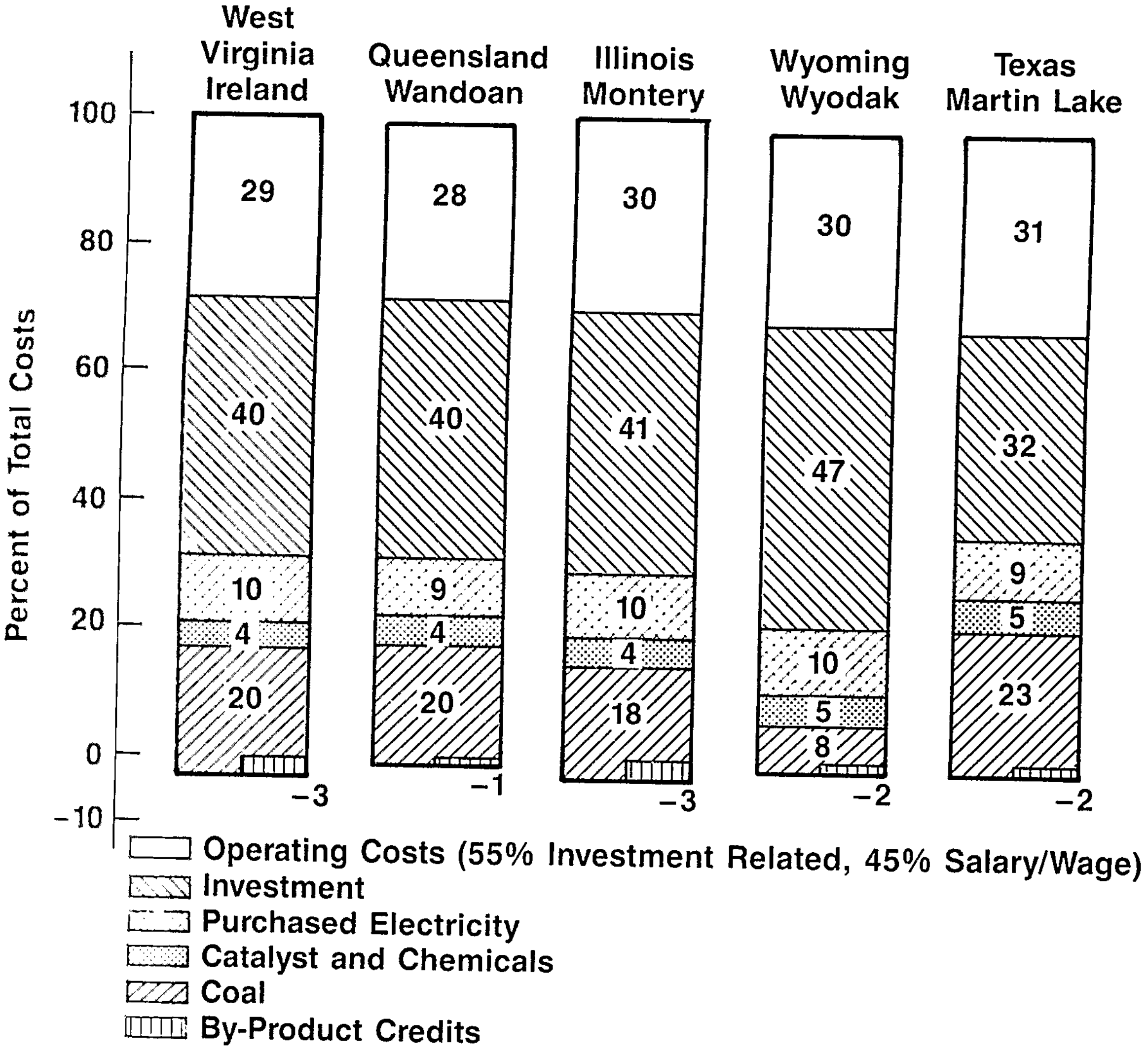
The other feature which affects the downward slope of the line from Ireland to Wyodak is the needed energy for drying the coal before feeding to liquefaction. Coal drying is accomplished in slurry driers where the energy for vaporizing coal moisture is supplied by hot recycle bottoms, hot solvent or condensing steam. The steam is raised in coal-fired boilers and this affects the slope of the yield versus moisture line. The three coals with moisture levels less than 20 wt% have their drying needs supplied by recycle bottoms and solvent. Only Wyodak and Texas lignite need supplemental coal to boilers.

Costs to Produce Coal Liquids

Returning now to the other half of the RISP equation from Table 4, let's consider the costs associated with producing liquids. Figure 7 shows the breakdown of RISP component costs for the different coals on a percentage basis for the POX/C_2- cases at high conversion and with no gas sales. These costs have been normalized to the total costs for the case with the lowest (i.e., best) RISP; the West Virginia Ireland case. Note that the cost of the coal contributes about 20%

Figure 7
BREAKDOWN OF RISP COMPONENTS

Reference is Ireland
High Conversion Case
POX/C_2–, No Gas Sales



to overall costs for Ireland. By-product credits for sulfur and ammonia reduce costs by about 3%. Other costs include catalyst and chemicals (4%), electricity (10%), capital charges (40%), and operating costs (29%).

For the other coals, it turns out that the total costs are essentially the same for this plant configuration, but the relative size of various components can be quite different. The relative total erected cost (TEC) factors for different locations are 1.0 for West Virginia and Illinois, 1.08 for Queensland, Australia and Wyoming and 0.81 for East Texas. These factors were developed at Exxon Research and Engineering and reflect a 1981 timeframe for material and labor costs at each location, and our judgment of indirect costs such as labor burden, field labor overheads, other field indirects and detailed engineering. Costs for construction camps, worker transportation, incentives, and other location specific items were also included. It should be noted, however, that the TEC location factors exclude infrastructure allowances and owner's costs. These latter items, which may include water supply, power supply, access roads, product pipelines, terminals, permanent housing, etc., could generally increase the costs for the more remote Wyoming or Australian locations.

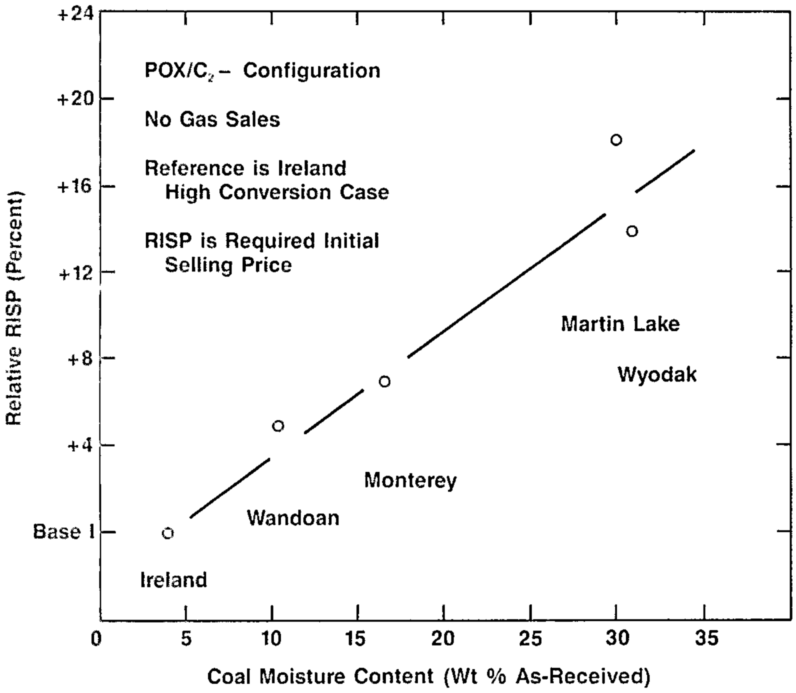
Let's compare the Texas and Wyoming cases. The capital charges for the lignite are much lower than the Wyoming case because of the relative TEC factors. However, Wyoming coal is much lower priced, and the result is that the capital plus coal costs are equal for both Texas and Wyoming. Note that Texas lignite is not generally traded on the open market and its "price" is essentially set by the competing price of rail transport of Wyoming coal to Texas.

The comparison between the Ireland and Wandoan cases is also worth mentioning. The capital charges are essentially equal even though Wandoan has an 8% higher TEC factor. Here is an example where coal properties favor Wandoan. Wandoan has lower sulfur than Ireland (<1 wt% versus >4 wt%), and a higher hydrogen/carbon ratio. There are, therefore, lower investment and operating costs for acid gas cleanup and hydrogen generation with Wandoan and this balances the higher TEC multiplying factor.

Relative RISP's For Different Coals

Figure 8 shows what happens when the product liquid yields and the costs to produce those products are put together. This figure is a plot of the relative RISP's for the different coals; again plotted for convenience versus coal moisture. West Virginia Ireland was selected as the base because it has the lowest RISP. These results indicate EDS plants with Wandoan or Monterey coals would need to sell their products at about a 6% higher price to achieve the same rate of return on investment as the Ireland plant. Wyodak has a 14% higher RISP

Figure 8
RELATIVE COST OF EDS LIQUIDS CORRELATES WITH COAL MOISTURE

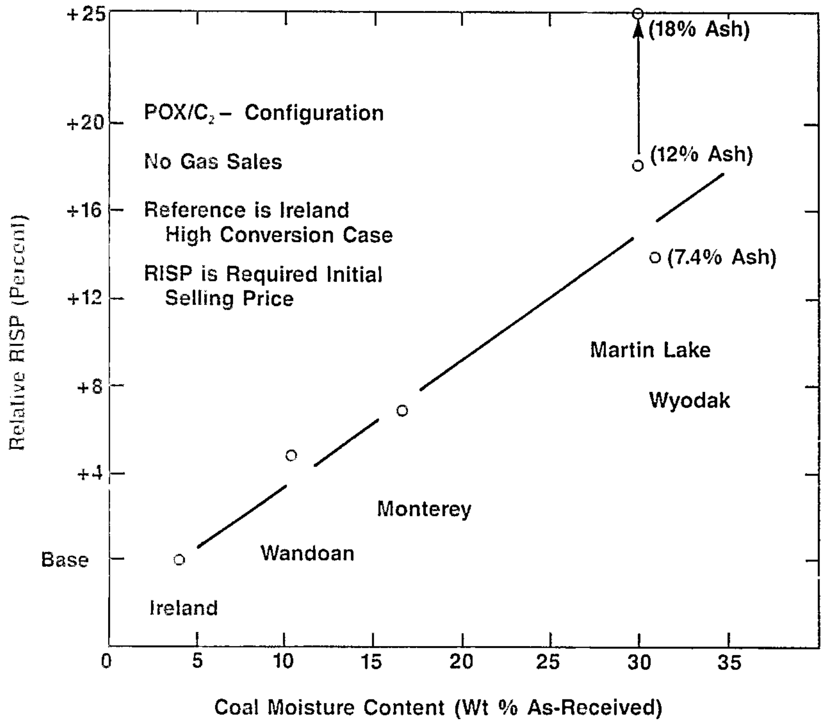


nearly constant for these coals, these results essentially reflect the yield differences for the coals in a balanced plant. Obviously, this figure is not meant to be a general correlation for all coals, because the cost components in the RISP equation could move any particular coal up or down. For example, if the TEC location factor in Wyoming was the same as in East Texas (0.81 instead of 1.08) and the coal price was still low, the Wyodak RISP would be about the same as the Ireland RISP.

Effect of Coal Ash on RISP

Let's look in more detail at Martin Lake versus Wyodak. It has already been shown that the coal costs and location factors balance each other for these coals. However, Texas lignite has a higher ash level. In fact, all the coals except Martin Lake have a dry ash level between 7.4 and 9 wt%. Figure 9 shows a high ash sensitivity case for Martin Lake which has 18% ash on a dry coal basis compared with the base case at 12% ash. Note the relative RISP now moves up to about 25% greater than the Ireland case, whereas the base Martin Lake case was 18% higher. However, if the Texas lignite ash level had been as low as Wyodak (7.4 wt%), its relative RISP would move down to about +13%; that is, essentially equivalent to the Wyodak case.

Figure 9
RELATIVE COST OF EDS LIQUIDS INCREASES WITH COAL ASH CONTENT

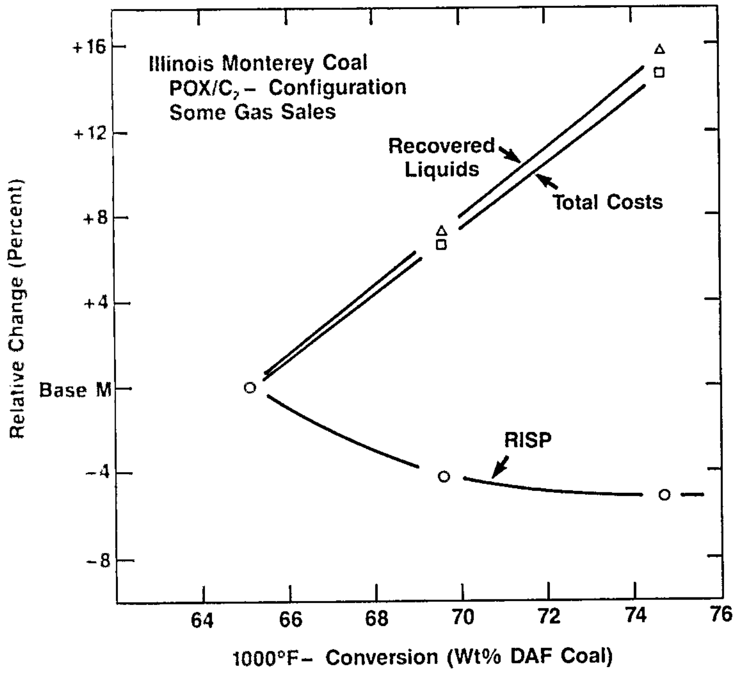


Effect of Conversion on RISP

It has been shown that liquid yield is a very important factor affecting EDS economics with different coals. A question is, how does conversion level, which was held approximately constant for the high conversion comparison cases, affect liquid yield and RISP?

In this study, the selected liquefaction operating conditions led to conversion levels between 65 and 75%. Past studies had shown that this is likely to be the range for optimum economical operation (2). As liquefaction severity is increased, i.e., higher temperature or longer residence time, liquid production increases, but so does gas production and overall costs. Figure 10 shows typical results from one of the coals in this study, Illinois Monterey, as conversion level was increased from 65% to about 75%. This figure is for the POX/ C_2^- configuration with some HBG sales at Btu parity with coal liquids. These cases were used because the no gas sales case at the lowest conversion level was out of plant balance with excess bottoms. The bottoms went to boilers to raise steam which, in turn, was sent to condensing turbines. Note that liquid yield increased by about 15% with the change in conversion, but so did the overall costs. The bottom curve shows that the relative RISP did improve somewhat; and this was primarily related to the HBG sales and the value of the gas. If gas were valued at only 50% of Btu parity with liquids, the RISP improvement would be 3% at the highest conversion level instead of the 5% improvement shown in the figure.

Figure 10
ECONOMICS SHOW SMALL IMPROVEMENT WITH CONVERSION



With the Wyodak and Martin Lake coals in a POX/C_2^- configuration with no gas sales, the RISP changed by only about 2% as conversion level was increased from 65 to 72%. Again, the increased liquids were essentially balanced by increased costs. Overall, these cases indicate there is a pretty broad range where the economics of coal liquefaction do not change very much. There is, therefore, only a minor incentive to increase conversion much beyond 70% to 75%, if the costs increase at the same rate as liquid recovery.

Summary

To summarize, the EDS Process Alternatives LP Model was used to develop a set of consistent comparisons for EDS operations with a wide range of coals, plant configurations and conversion levels. When the case results are examined, they show the effects that different items have on the economics of producing coal liquids with EDS. These items include liquid yield, plant investment and relative TEC location factors, coal price, and coal properties. The coal properties include ash level, as-received moisture level, oxygen content, hydrogen/carbon ratio, and the sulfur and nitrogen heteroatom contents.

Acknowledgement

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MULTISTAGED CATALYTIC PROCESS DEVELOPMENT FOR COAL LIQUEFACTION

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ABSTRACT

Catalytic coal liquefaction experiments have been conducted on a once-through pilot plant using Wilsonville process-derived solvent. Net liquefaction yields compare very well with the fully-integrated process yields observed at Wilsonville. AMOCAT™-1A was found to be very active initially as a first-stage catalyst, leading to large improvements in resid and asphaltene conversion and in distillate selectivity. The catalytic/catalytic close-coupled configuration results in lined-out distillate yields comparable to those from a thermal/catalytic configuration, but at a significantly lower first-stage temperature. The aged first-stage catalyst is deactivated by carbonaceous deposits, metals (Ti and Ca), and sintering of the cobalt function. Both fresh and aged catalysts have been used to improve the liquefaction yields by adding the catalyst directly to the feed in the form of ground fines.

INTRODUCTION

This joint three year research project between Amoco and EPRI is designed to complement the development and implementation of advanced coal liquefaction technology at the Wilsonville pilot plant, through the use of improved catalysts and application of these catalysts to multistaged hydroprocessing of coal slurries. The research is performed with experimental facilities located at the Amoco Research Center in Naperville, Illinois, using solvents and in part, catalysts obtained from Wilsonville.

The project is divided into 6 functional work tasks as follows:

- Establish a correlation between the Amoco and Wilsonville facilities for Thermal/Catalytic 2-stage performance.
- Test two likely Catalytic/Catalytic 2-stage configurations for use at Wilsonville:
  1) AMOCAT™-1A/AMOCAT™-1C
  2) AMOCAT™-1A/SHELL-324

- Expand the database on Catalytic/Catalytic 2-stage processing by conducting additional experiments with commercially available catalysts, and test the concept of catalyst recycle.
- Determine the effect of a solvent hydrotreating stage (3rd stage) on the coal liquefaction process.
- Develop improved catalysts for the coal dissolution stage (1st-stage).
- Develop improved catalysts for the upgrading stage (2nd stage).

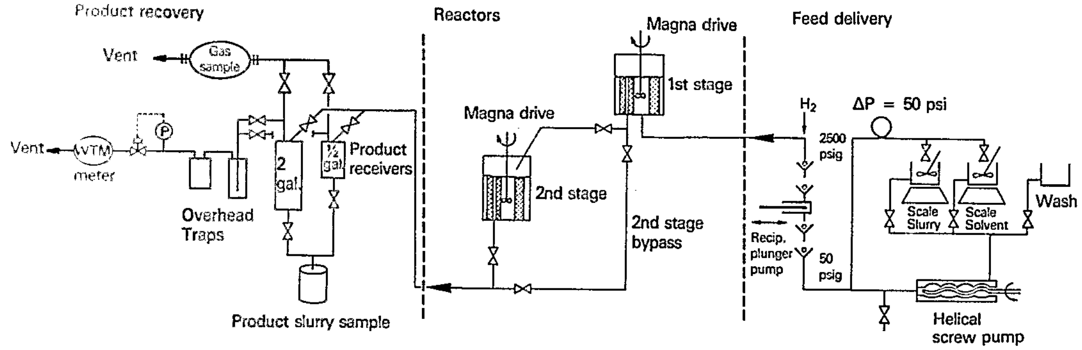
In this paper, we present some of the major findings from the first three tasks.

EXPERIMENTAL BACKGROUND

A simplified flow diagram of the continuous-feed once-through coal liquefaction pilot plant is shown in Figure 1. The pilot plant, AU-51, includes a H_2 delivery system, a coal slurry delivery system, two close-coupled stirred autoclave reactors in series, with an optional by-pass around the second reactor, two liquid product receivers in parallel, product gas scrubbers, and a wet test meter. Each reactor can be operated as a thermal stage by removing the stationary catalyst basket, or as a catalytic stage by loading the basket with appropriate catalysts. Either 300 or 1000cc autoclaves are used with catalyst loadings of up to 200cc. The slurry feedrate is typically around 200gm/hr.

Figure 1

Simplified flow diagram of the continuous aging unit


Product recovery
Reactors
Feed delivery
Vent
Gas sample
Vent
VTM
meter
P
Overhead Traps
2 gal.
½ gal
Product receivers
Product slurry sample
Magna drive
Magna drive
1st stage
2nd stage
2nd stage bypass
H_2
2500 psig
ΔP = 50 psi
Recip. plunger pump
50 psig
Scale Slurry
Scale Solvent
Wash
Helical screw pump

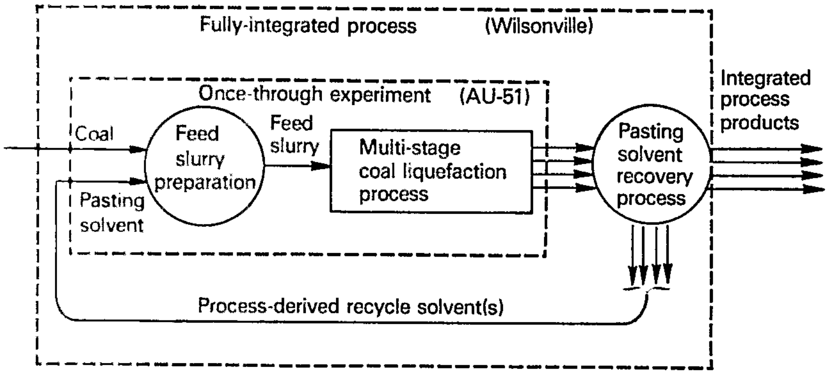
Coal conversion is defined as the percentage of coal-derived product soluble in tetrahydrofuran (THF). The percentage of coal-derived product soluble in hexane (oils), and in toluene (oils + asphaltenes) are routinely determined. The elemental composition of the THF insoluble product, and the boiling point distribution, elemental composition, and at times, the solvent quality of the THF soluble product are also determined.

Solvent qualities for liquefaction products are obtained on a shaking-autoclave apparatus. The test procedure is to combine 2gm solvent and 1gm Illinois #6 coal under 500 psig H_2, and heat the mixture to 750°F for 30 min with shaking, followed by rapid quenching. The solvent quality is defined as the wt% of coal converted to THF soluble products.

Pasting solvents were obtained from, and are representative of, the Wilsonville pilot plant. Net product yields are calculated by subtracting the pasting solvent out of the once-through products. The concept is illustrated in Figure 2. Calculations are performed on a component mass flow rate basis with results reported in terms of the wt% of moisture-and-ash-free (MAF) coal in the feed.

Figure 2

Conceptual illustration of the interrelation of once-through experiments and the fully-integrated process


Fully-integrated process (Wilsonville)
Once-through experiment (AU-51)
Coal
Feed slurry preparation
Feed slurry
Multi-stage coal liquefaction process
Pasting solvent
Pasting solvent recovery process
Integrated process products
Process-derived recycle solvent(s)

The calculations assume regeneration (and recycle) of a constant quality and boiling range pasting solvent. In actuality, because of the mode of operation (i.e. high initial catalyst activity is not compensated for with a low start-of-run temperature), the high initial catalyst activity results in overconversion of the pasting solvent, leading to negative calculated yields for some of the product components. The point of solvent balance is generally achieved within a few days at constant operating conditions after the catalyst activity has been moderated by deactivation. Yield decay curves, although at times involving calculated negative yields, are still valid for comparative catalytic activities.

TWO-STAGE PILOT PLANT RESULTS

Results for three cases, a thermal/catalytic base case, a catalytic/catalytic case, and an additional two-stage case in which catalyst fines were added to the base feed of a thermal/catalytic configuration are presented. For all three cases, the base feed consisted of 1 part Illinois #6 coal (Table I) and 2 parts Wilsonville ITSL process solvent (Table II), by weight. The thermal/catalytic work was conducted at 2500 psig with first-stage conditions of 810°F and 30 min space time, and second-stage conditions of 720°F and 0.5 LHSV. These conditions were chosen to mimic Wilsonville's ITSL run 244. The catalytic/catalytic work was conducted at the same pressure and second-stage conditions, but the first-stage conditions were 765°F and 0.5 LHSV.

TABLE I

ELEMENTAL COMPOSITION OF THE ILLINOIS #6 BURNING STAR MINE BITUMINOIS COAL

	Analysis, wt%
Moisture	6.36
Ash	9.67
C	65.85
H	5.20
N	1.25
S	2.83
O (by difference)	8.84

Thermal/Catalytic (T/C) base case

The catalyst used in the second stage of this thermal/catalytic experiment was an aged SHELL-324 obtained from Wilsonville, run 245. The yield structure after 100 hours-on-stream (50 lb coal/lb catalyst) is compared to Wilsonville's in Table III.

The net yields from the once-through pilot plant are very similar to the fully-integrated yields of Wilsonville. The slight (3%) shift in distillate/resid selectivity can be attributed to the close-coupled mode of

TABLE II

COMPOSITION OF THE WILSONVILLE-PROCESS-DERIVED PASTING SOLVENT

ELEMENTAL ANALYSES	
C, wt%	89.08
H, wt%	8.75
N, wt%	0.65
S, wt%	0.19
O, wt%	1.73
Fe, ppm	253.
Ti, ppm	2.0
Na, ppm	2.3
Ca, ppm	51.
Mg, ppm	4.0
V, ppm	0.1
PHYSICAL CHARACTERIZATION	
Moisture (KF water)	0.16
Ash	0.0
THF insoluble	0.80
Toluene insoluble	1.30
Hexane insoluble	23.1
API Gravity	0.7
Specific Gravity, 20/20	1.076
Viscosity, cs, at 40 C	6380.
100 C	41.4
135 C	11.2
Solvent Quality	81.2
THF-SOLUBLE DISTILLATION	
Atmospheric Distillate, wt%	20.4
Vacuum Distillate, wt%	42.1
Resid, wt%	37.5
RESID ANALYSES	
C, wt%	90.02
H, wt%	7.31
N, wt%	0.970
S, wt%	0.22
O, wt%	1.77

operation used. Wilsonville achieved close to 60% distillate yield in both the RITSL mode with post-second-stage deashing (Run 247), and the CCITSL mode with the two reactors close-coupled (Run 250) using the SHELL catalyst. The gas yields for our apparatus are somewhat less reliable, as gas sampling is performed downstream of the large product receivers. These vessels are drained and repressurized with clean H_2 daily, making it difficult to obtain an undiluted representative gas sample.

The data in Table III indicate a one-to-one correlation between our 'net' yields and those of Wilsonville provided the solvent is properly chosen. Thus, with the baseline well-established and tied to Wilsonville's data base, performance improvements due to either catalyst selection or process configuration observed on our pilot plant should be attainable in similar operations at Wilsonville.

TABLE III

COMPARISON OF BASE CASE THERMAL/CATALYTIC PILOT PLANT YIELDS WITH WILSONVILLE'S YIELDS UNDER THE SAME PROCESS CONDITIONS

Product Yields (wt% MAF coal)	Pilot Plant Once-Through Calculated net yields	Wilsonville Fully Integrated ITSL-Run 244 yields
C_1-C_4	3.4	7.0
CO-CO_2	0.5	1.4
H_2O	12.3	9.0
H_2S	2.8	2.5
NH_3	0.9	1.2
Total Distillate	60.5	56.0
Resid + U.C.	24.3	27.5
Hydrogen	-4.8	-4.6

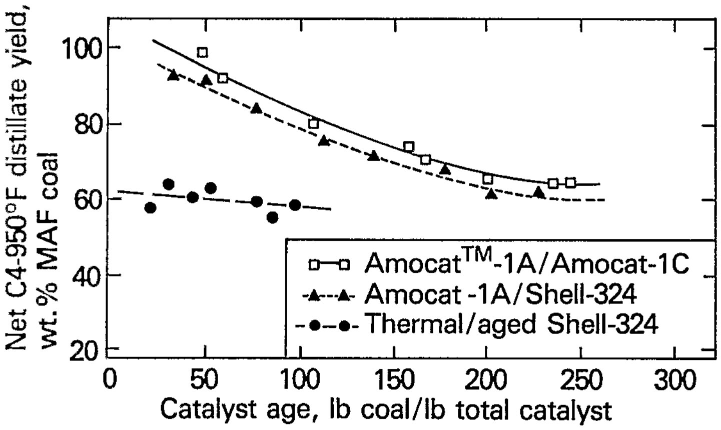
Catalytic/Catalytic (C/C) cases

Two likely catalyst combinations for use at the Wilsonville pilot plant have been tested: AMOCAT™-1A/AMOCAT™-1C, and AMOCAT™-1A/SHELL-324. Yield data indicate that either catalyst combination results in superior performance, especially for resid conversion, compared to the thermal/catalytic base case. This was achieved with a first-stage catalytic temperature 45°F lower than the first-stage thermal temperature.

The calculated net distillate yields for the three cases are shown in Figure 3. The very high initial net yields for the two C/C cases are, in part, the result of extensive overconversion of solvent resid due to high initial catalyst activities. None-the-less the high C/C yields relative to the T/C case illustrate a selectivity advantage for the C/C configuration.

Figure 3

Comparison of the C_4-950°F distillate yield.
For various 2-stage configurations: thermal/catalytic, and catalytic/catalytic with two different second-stage catalysts.



Throughout the range of catalyst age studied, use of the AMOCAT™-1C as a second-stage catalyst yields about 5 wt% more distillable liquids than SHELL-324.

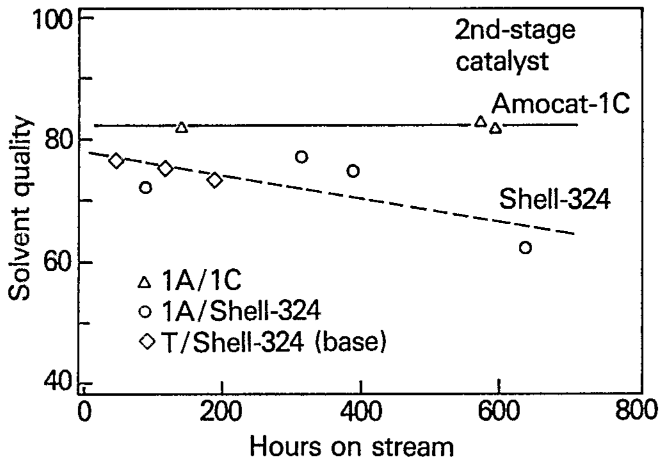
The observed initial deactivation for the first-stage Amocat™-1A catalyst appears typical for the H-COAL-like first-stage environment. The result is a decay in process performance such that, by about 100-150 lb coal/lb catalyst age, a near-solvent-balanced operation with a C_4-950°F distillate yield of 70-80 wt% MAF coal is observed. The performance continues to decline with additional catalyst age, and appears to be leveling-off at about 60-65% distillate yield after about 250 lb coal/lb catalyst.

It is not clear why we observe the deactivation trend for the T/C case in Figure 3. The aged SHELL-324 second-stage catalyst from Wilsonville (Run 245) had been used to process 1500 lb thermal resid/lb catalyst. We anticipated the catalyst would have been sufficiently 'lined-out' that no significant performance losses would be observed in the time scale of our experiments. However, we do observe a loss as shown in Figure 3, and the loss is even more apparent in the hydrogen consumption which drops from 5.2% to 3.9% over the course of the experiment (100 lb coal/lb catalyst). These losses in catalyst performance may be due to the unique close-coupled environment, noting that the catalyst had lined-out in the non-close-coupled ITSL configuration. We have observed in other work that unimodal catalysts are not ideally suited for the close-coupled mode-of-operation.

The bimodal AMOCAT™-1C catalyst is more effective than the unimodal SHELL-324 at maintaining solvent quality. Figure 4 shows the solvent quality of the THF soluble liquid product for the three cases presented in Figure 3. The noteable observation is that with SHELL-324 in the second-stage, solvent quality drops with time-on-stream, regardless of whether the first-stage is thermal or catalytic. This is further evidence that the unimodal catalyst is deactivating in a close-coupled environment after being lined-out in a non-close-coupled second-stage environment. With AMOCAT™-1C in the second-stage, solvent quality can be maintained at the same value as the original pasting solvent.

Figure 4

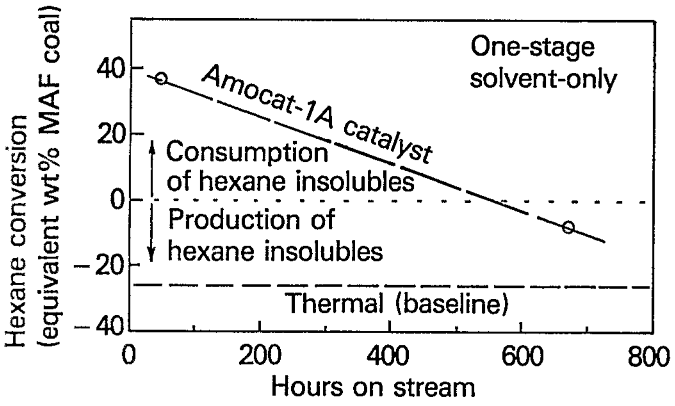
Comparison of the solvent quality of various 2-stage products: thermal/catalytic, and catalytic/catalytic with two different second-stage catalysts



The loss of first-stage catalyst activity is illustrated by the conversion of hexane insolubles in single-stage catalytic processing of the neat pasting solvent (Figure 5). The conversion data are presented in terms of the 'equivalent MAF coal conversion', i.e. the amount of coal that would have to be converted in order to observe the same quantity of hexane soluble oils produced. The data clearly show that in the absence of a 1st-stage catalyst, the first-stage (thermal only) is a net producer of hexane insolubles from the solvent alone. Fresh AMOCAT™-1A initially reduces the hexane insolubles being fed to the second stage by 60 wt% MAF coal, compared to the thermal case. The reduction is still positive at about 20 wt% MAF coal after 700 hours on stream.

Figure 5

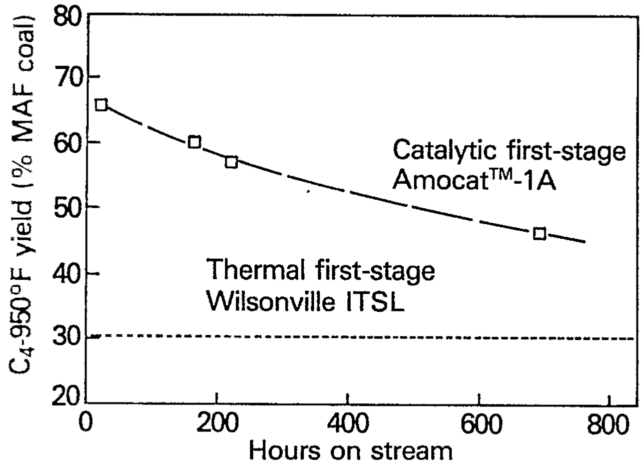
Comparison of catalytic versus thermal single-stage conversion of the hexane-insoluble organic matter
in a neat solvent feed on the basis of the equivalent MAF coal conversion.



The lower asphaltene content of the feed to the C/C second-stage versus the T/C second-stage should markedly improve the lifetime of a second-stage catalyst. Similarly, the catalytic first-stage greatly contributes to resid conversion. In Figure 6, we compare our catalytic one-stage distillate yield to Wilsonville's ITSL distillate yield for the dissolver alone. In this case, we observe a fresh catalyst incentive of about 35 wt% MAF coal and a end-of-run incentive of about 16 wt% additional resid conversion to distillable products.

Figure 6

Comparison of catalytic versus thermal single-stage distillate yield.



Thermal/Catalytic case with catalyst fines addition

Several experiments were conducted in which the feed to the coal liquefaction process was spiked with 0.1 to 1.0 wt% catalyst fines (-325 mesh). Catalyst fines addition relates to the concept of used catalyst recycle and the potential of advantageous use of catalyst-interior activity. Results from one experiment with 0.5% fines addition and the thermal/catalytic base case are tabulated in Table IV. The catalyst-fines experiment was performed at the end of the T/C experiment in Figure 3. The base-case data in Table IV are the end-of-run data which differ from the data in Table III because of second-stage catalyst deactivation. Basically, the effect is a shift in the yields of about 9 wt% from the 950°F+ resid product to mostly vacuum distillate product, accompanied by a selective increase in the hydrogenation of the liquid products. In addition, the asphaltenes and pre-asphaltenes in the two-stage product are greatly reduced by the addition of fresh .5 wt% AMOCAT™-1A to the feed in the thermal/catalytic case. Distillate yields are intermediate between the T/C and C/C cases as shown in Figure 7. Thus yield and quality benefits can be achieved either by loading catalyst extrudes in the reactor, or by adding catalyst fines to the feed. We observe similar effects even if the catalyst fines are aged rather than fresh.

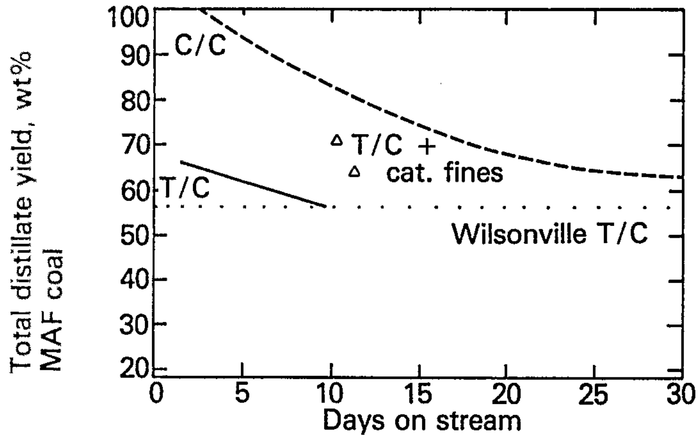
TABLE IV

TWO-STAGE COAL LIQUEFACTION RESULTS
THERMAL/CATALYTIC OPERATION WITH CATALYST FINES IN FEED

	2-Stage Base Case	2-Stage Base Case + .5% AMOCAT™-1A
'Net' Yields, wt% MAF Coal		
C_1-C_4	3.8	4.1
C_5-650°F	48.4	50.1
650°F-950°F	6.1	14.1
950°F+	25.1	16.0
U.C	4.3	4.4
Hydrogen	-3.9	-5.9
H_2 by liquid prod.	-1.4	-3.3
H_2 by other	-2.5	-2.6
Insoluble Conversion, wt% MAF Coal (wt% Total Insolubles)		
THF	95.7(93.9)	95.6(93.8)
Toluene	74.9(71.5)	90.8(86.6)
Hexane	53.6(34.4)	93.4(59.8)

Figure 7

Effect of adding 0.5 wt% Fresh Amocat^{TM}-1A to the feed of the two-stage thermal/catalytic base case on the distillate yield, as compared to the thermal/catalytic base case and the catalytic/catalytic case with Amocat^{TM}-1C in the second stage.



POST-MORTEM CATALYST EXAMINATIONS

As an aid in gaining a better understanding of the mechanism for catalyst deactivation, some aged first-stage catalysts have been analyzed by surface techniques, combined with bulk chemical and physical analyses. The more pertinent results are summarized in Table V. Note that these first-stage catalysts have been used at 765°F vs. the nominal 825°F H-Coal operating temperature. Two noticeable features are the high carbon and titanium levels, which are typical of spent H-Coal catalysts.

Examination of the effects of carbon deposition by N_2 desorption and Hg porosimetry indicates that carbon fills the catalyst pores uniformly in the radial direction. The porosity loss in the BET pores is such that the median pore diameter, as measured by N_2 desorption, remains constant at ~90Å over the range of 8-25 wt% carbon. This is typical of other AMOCAT^{TM} catalysts used in the H-Coal type process (Figure 8). At 25 wt% Carbon these catalyst have lost about 80% of their BET pore volume. Over the same range of carbon content (8-25%), the APD as determined by Hg porosimetry increased from 145Å to 185Å, indicating a preferential filling of the BET pores relative to the macro-pores (>1000°A).

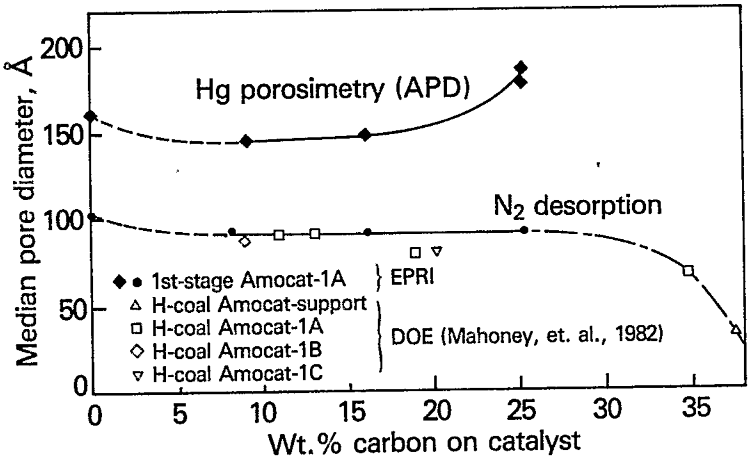
TABLE V

CHARACTERIZATION OF THREE AGED AMOCAT^{TM}-1A CATALYST SPECIMENS

Run #	175	176	177
Start-Up Feed	slurry	solvent	wash-oil
Mixing Speed, RPM	1500	1500	3000
Days-on-Stream with,			
wash-oil feed	0	0	1
solvent feed	6	6	0
slurry feed	23	25	10
total	29	31	10
Elemental Analysis, wt%			
C, THF extracted	25.3	16.1	8.2
H, THF extract	1.41	1.02	1.22
S, THF extract	4.1	4.7	5.0
Mo, Calcined at 1000°F for 2hrs	7.4	8.8	9.5
Co, Calcined at 1000°F for 2hrs	1.8	2.2	2.4
Ti, Calcined at 1000°F for 2hrs	1.30	1.51	1.33
V, Calcined at 1000°F for 2hrs	0.054	0.055	0.075
Fe, Calcined at 1000°F for 2hrs	0.60	0.53	0.41
Na, Calcined at 1000°F for 2hrs	0.231	0.151	0.097
BET surface area M^2/g	38	87	136

Figure 8

Effect of carbon deposition on the median pore diameter of the Amocat^{TM}-1A first-stage catalyst
as determined by N_2 digisorb (BET method) and Hg porosimetry (APD = 4.PV/SA).



Microscopic examination of the aged catalyst specimen from run 176 revealed discrete 5-10 micron particles of sintered CoS on the interior surface of the catalyst and very large filament-like crystals throughout the catalyst, but predominantly within 50 microns of the exterior surface of the extrudate. The crystals averaged about 2 x 10 micron in size, and appear to be a calcium salt with close to a 1:1 stoichiometric amount of Ca:S. In addition, an extreme preference for titanium to deposit at the exterior surface of the extrudate was observed. This well-defined outer-skin, approximately 1 micron wide, is composed of 2 titanium atoms per molybdenum atom. The layer is also deficient in sulfur, as there is less than half of the sulfur anticipated for the Co and Mo levels.

From these preliminary results it is not clear which of these changes in catalyst composition contribute to the loss of activity. Ways of avoiding, minimizing, or reversing these changes in catalyst composition are being investigated.

Additionally, the data in Table V suggest that pre-conditioning the catalyst with a vacuum-distillate solvent for 24 hours, prior to processing coal/solvent slurries, greatly reduces the level of carbon deposition for a given age. The reduction in carbon deposition however had no apparent effect on performance. This and other findings lead us to believe that no single mechanism of deactivation is responsible for the entire activity loss.

CONCLUSIONS

We have demonstrated nearly a one-to-one correspondence between our base-case T/C experiment and Wilsonville. Solvent selection is one of the keys towards obtaining meaningful process-development data from once-through pilot plants like AU-51. An improved selectivity towards distillable hexane soluble oils in the two-stage C/C process is observed, compared to the T/C process. The magnitude this improvement is difficult to determine due to the relatively short run durations and because of solvent-imbalanced operation at the start of the C/C experiments. The first-stage AMOCAT™-1A catalyst undergoes typical H-Coal-like activity loss during the 30-day experiments. This loss in activity appears to be the result of more than one deactivation mechanism.

ACKNOWLEDGEMENTS

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TWO-STAGE COAL LIQUEFACTION PROCESS PERFORMANCE WITH CLOSE COUPLED REACTORS IN WILSONVILLE

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and

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Southern Company Services

ABSTRACT

An integrated run has recently been completed at Wilsonville with direct coupling of the thermal and catalytic reactors using Illinois No. 6 coal. Product yield and product quality data are presented. Comparisons are made to previous ITSL data. Also, a broad comparison of the performance and stability of Shell 324 and Amocat 1C catalysts is made in terms of rate constants for resid and preasphaltene conversion, catalyst analyses, and model compound activities. The effect of higher system space velocity on process performance and the impact of solids recycle are discussed. Finally, catalyst replacement rates for "all-distillate" product slate are projected as a function of hydrotreater temperature and system space rate.

The operability of the close-coupled scheme was good. The yields were similar to the previous ITSL yields. The major effect of close-coupled operation without interstage separation was an increased hydrogen consumption with correspondingly higher product quality. "All-distillate" operation was demonstrated at approximately double the system space velocity used in the previous ITSL runs. The projected catalyst replacements rates for Amocat 1C in the close-coupled mode are reduced by a factor of 3 to 4 when compared to Shell 324 in the ITSL mode of operation. The results from solids recycle were in the right direction to reduce the cost of distillate fuels from coal. Extended research in the areas of reaction selectivity, throughput improvements, and catalyst management can result in further cost reductions.

INTRODUCTION

The Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama has been operating for over 12 years developing alternate technologies for producing low cost synthetic fuels. A recently completed close-coupled and integrated (CC-ITSL) scheme was an important development in the Wilsonville program for making high quality distillate fuels. Slide 1 shows the Wilsonville project organization. The U. S. Department of Energy and the Electric Power Research Institute are the primary sponsors. Since its inception, the facility has been operated by Catalytic, Inc., under the management of Southern Company Services, Inc. Amoco Oil Corporation became a sponsor in 1984 through an agreement with EPRI. Kerr-McGee Corporation and Hydrocarbon Research, Inc. have participated by providing Critical Solvent Deashing (CSD) technology and H-OIL ebullated-bed hydrotreater design, respectively.

Slide 2 summarizes the salient features of the individual units with relevance to the Wilsonville CC-ITSL run. The TLU dissolver is identical to the hydrotreater except that it is not provided with catalyst addition-withdrawal capability. The dissolver has multiple take-offs so that the residence time can be varied.

The current CC-ITSL process option has evolved from the ITSL operation. Reconfigured ITSL (RITSL) was an intermediate step between the ITSL and CC-ITSL process developments. Slide 3 summarizes the key differences among the three configurations. ITSL employed TLU, CSD, and HTR units in series while RITSL and CC-ITSL employed TLU, HTR, and CSD units in series. Accordingly, the hydrotreating catalyst was exposed to ash-, UC-, and preasphaltene-rich environment in the RITSL and CC-ITSL configurations. As the name implies, in the CC-ITSL configuration, the two reactors were direct coupled without any pressure letdown. The interreactor cooling was done only to the extent necessary 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. Product yield and product quality data are discussed. Appropriate comparisons of catalysts, and configurations are made in terms of product yields. The effect of higher system space velocity and the impact of solids recycle are discussed. A comparison of Shell 324 and Amocat 1C is made in terms of process derived deactivation trends, model compound activity trends, pore size distributions, and contaminant deposit levels. Finally, the batch deactivation rate data were used to project the catalyst replacement rates as a function of key process variables.

PROCESS DESCRIPTION

A block flow diagram of the CC-ITSL process is shown in Slide 4. The process consists of a slurry preparation step, a thermal reaction stage, and a catalytic reaction stage followed by hydrotreated solvent recovery and critical solvent deashing systems. The system was integrated by the recycle of hydrotreated resid and hydrotreated solvent. The solvent recovery system consists of atmospheric flash and vacuum flash equipment. The process flow diagram is shown in Slide 5. Note that an interstage vapor separator was installed between the two reactors. About half of the 450°F+ distillate recovered from the interstage separator overheads was fed to the hydrotreater.

A variation of the CC-ITSL configuration, known as CC-ITSL with solids recycle, was investigated near the end of the CC-ITSL Run 250. The process flow chart is shown in Slide 6. In this mode, the low pressure flash bottoms containing ash, unconverted coal, hydrotreated resid, and hydrotreated solvent were recycled to the liquefaction solvent blend tank. A higher solids content vacuum bottoms stream was deashed in the CSD unit. The objective was to reduce the feed rate to the CSD unit, and thereby decrease the size of the CSD unit.

RUN 250 STUDIES

A brief chronology of Run 250 operations is shown in Slide 7. Illinois No. 6 bituminous coal from the Burning Star mine was processed in Run 250. At the beginning of the run, a brief baseline test was conducted using aged Shell 324 to broadly assess CC-ITSL performance relative to the ITSL. No interstage vapor separation was utilized during the baseline test period. The major part of the run was devoted to evaluating the close-coupled ITSL with interstage separation using a bimodal nickel-molybdenum catalyst, Amocat 1C. During this portion of the run, higher system space velocities were explored by increasing coal feed rates. Near the conclusion of Run 250, the concept of solids recycle was tested. During the coal space rate as well as the solids recycle studies, compensatory changes in the reactor temperatures were made with the goal of producing "all-distillate" yield slates.

ITSL vs CC-ITSL COMPARISON

The Run 250 results with the aged Shell 324 catalyst are compared to previous ITSL Run 244 in Slides 8 and 9. Reactor temperatures and space velocities compare closely in both the periods. The catalyst was slightly younger in the ITSL period. The main difference in the operating conditions is the inlet hydrogen partial pressure. Since the interstage separator was not used during the Shell 324 catalyst portion of Run 250, the inlet hydrogen partial pressure to the TLU had to be increased in order to maintain a "normal level" of inlet hydrogen partial pressure to the HTR unit.

From Slide 9 it is seen that the majority of the yields were similar for the ITSL and CC-ITSL periods under comparison. The CC-ITSL distillate yield was 61%, compared to 57% in the ITSL mode. However, the sum of the distillate yield and resid yield was roughly the same in both the configurations. The major effect of the close-coupled operation was an increase in the hydrogen consumption. Since there was no change in the C_1-C_3 and water yields, the excess hydrogen consumption should result in improved product quality. This was indeed found to be true as will be discussed in the product quality section. A question arises as to whether the increased hydrogen consumption in the CC-ITSL operation was due to the higher inlet hydrogen partial pressure. The data from Run 244 studies showed the inlet hydrogen partial pressure had a relatively small effect on hydrogen consumption when the partial pressure was reduced by a factor of about two (1). It appears that the higher hydrogen consumption in Run 250B was mostly due to the close coupling of the reactors.

CATALYST COMPARISON

After the initial baseline study with the aged Shell 324 catalyst, Amocat 1C, a bimodal nickel-molybdenum catalyst, was used in the rest of the run. The Run 250C results with the Amocat 1C are compared to the Run 250B results with the Shell 324 catalyst in Slides 10 and 11. Interstage separator was in service throughout the operation with the Amocat 1C catalyst. The catalyst age, and correspondingly the hydrotreater temperature, were lower in Run 250C. "All-distillate" operation was maintained at both sets of conditions under comparison. The distillate and hydrocarbon gas yields were similar. The hydrogen consumption was 0.8% lower in Run 250C, so the hydrogen efficiency was higher. Interstage separation (i.e., not hydrotreating all distillate products) and/or the higher selectivity of the Amocat 1C catalyst for distillate production at lower catalyst age could be the reasons for the observed phenomenon.

The organic and energy rejections were 4% higher in Run 250C. This was a result of the CSD operation with an alternate deashing solvent to maintain stable deashing performance with the highly soluble feed generated by the relatively fresh Amocat 1C catalyst during Run 250C. Lower level of preasphaltenes in the CSD feed was one of the reasons for the higher solubility observed during Run 250C.

SPACE VELOCITY STUDIES

Increased throughput in a given size plant can lower the cost of distillate fuels. Most of the integrated runs conducted at Wilsonville with a bituminous coal were at less than 200 lb/hr of MF coal. In Run 243, ITSL system parametric studies were conducted by increasing the coal feed rate to about 250 lb/hr of coal (1). But, "all-distillate" operation was not achieved at the conditions tested. Run 250 was the first integrated run in which higher system space velocities were explored with the goal of "all-distillate" operation.

The TSL operating conditions and yield structures at three different coal space velocities are given in Slides 12 and 13, respectively. The three space velocities studied were 25 (Run 250C), 37 (Run 250D), and 45 (Run 250E) lbs MF coal/hr/ft^3 of volume above 700°F which correspond to roughly 180, 280, and 340 lb MF coal/hr, respectively. Reactor temperatures were increased to compensate for higher space velocities. The catalyst age increased from 300 lb (resid+CI)/lb catalyst at the beginning of Run 250C to about 1200 lb (resid+CI)/lb catalyst at the end of Run 250E. The other operating conditions were the same in the three periods under comparison.

The main conclusion from the yield data is that "all-distillate" yield slates were obtained at increased coal throughputs by compensatory increases in reactor temperatures. The C_4+ distillate yield was slightly lower at the highest throughput rate. But it could have easily been brought to a comparable level by small adjustments in reactor temperatures. With regard to the CSD performance, it improved from Period C to E. The feed solubility decreased as the run progressed and, as a result, alternate deashing solvents were required to maintain stable deashing performance. The decreasing trend in feed solubility was characterized by an increased trend in the feed preasphaltenes concentration.

SOLIDS RECYCLE

The concept of solids recycle was first tested in Run 249 with subbituminous coal in the RITSL mode. Solids recycle increased coal conversion by 3%. A test of CSD after run completion indicated the potential for improved CSD performance with solids recycle. An obvious benefit from solids recycle is reduced CSD feed rate and, therefore, smaller CSD plant size. This benefit together with the encouraging results from the Run 249 test had prompted the study of solids recycle near the end of Run 250 (Slide 6).

The extent of solids recycle and process solvent composition depend on the ability to pump the vacuum bottoms and coal slurry. Based on the viscosity data obtained on synthetic blends, a concentration of 30% resid in the process solvent was set as an initial guideline. But as the run progressed, the actual viscosities were significantly lower than that expected from synthetic blend data. This allowed the resid content of process solvent to increase from 30 to 40%. Based on a test conducted near the end of Run 247, it was expected that the increased resid concentration would reduce the TLU resid yield by a small amount (2-4%).

A comparison of the results with and without solids recycle are shown in Slides 14 and 15. The coal space velocity was the same in Run 250D (no solids recycle) and Run 250G (solids recycle). The solvent-to-coal ratio was increased from 1.8 to 2.0 in the solids recycle scheme. The process solvent composition was 51% solvent, 40% resid, 3% UC, and 6% ash in run 250G compared to 50% solvent and 50% resid in Run 250D. The recycle solids to coal ratio was 0.18.

"All-distillate" yield slate was achieved in Run 250G with solids recycle. Although the C_4+ distillate was about the same in both Run 250D and Run 250G, the potential for higher distillates exists in the solids recycle mode as indicated by the higher C_4+ distillate plus resid yield. A remarkable result is that lower organic rejection to the ash concentrate was demonstrated in the solids recycle mode of CC-ITSL operation. The organic rejection was 15% in Run 250G. In fact, this was the lowest organic rejection that had been demonstrated in an integrated operation in a sustained manner. As a result of lower organic rejection and the same coal conversion, extra resid recovered had to be converted in the reactors. This required 5°F more temperature in thermal unit and 8°F higher temperature in catalytic unit. Solids recycle reduced CSD feed rate by about 50% which would have significant impact on CSD plant capital requirements.

COAL CONVERSION

The impact of close-coupling on observed coal conversion is shown in Slide 16. Coal conversions across the individual units are compared for the ITSL and CC-ITSL modes. It is clearly seen that for similar coal conversions in the TLU, the two stage conversions were higher in the close coupling run. Coal conversion in the hydrotreater was 0.2 ± 0.9 which is statistically insignificant.

PRODUCT QUALITY

Product quality data were obtained on blends made by mixing product streams in the proportions of their production rates. The data are presented for the periods Run 250B and Run 250D in Slide 17. For comparison purposes, ITSL data for Run 244 are included. About 65 wt % of the liquid products were naphtha and distillate. All the fractions had low levels of heteroatoms.

In the comparison of ITSL and CC-ITSL product quality, coal space velocity, catalyst type, and catalyst age were the same in Run 244 and Run 250B. The products from Run 250B were better than those from Run 244 in every respect. For comparable fractions, the hydrogen contents are 1.2-1.6% higher, and the H/C atomic ratios are 0.17-0.23% higher, for CC-ITSL. The distillate fraction is extremely light for CC-ITSL, 47.6 vs 18.6 API gravity. Also, Run 250B products had lower levels of nitrogen, sulfur, and oxygen. As reported in the catalyst comparison section, the product quality improvements were accompanied by an increase in hydrogen consumption. In Run 250B, all the TSL product was derived from the hydrotreater, whereas in the ITSL Run 244, approximately equal amounts were derived from the thermal stage and catalytic stage. This was the reason for the higher hydrogen consumption and higher quality products in Run 250B.

The product quality did not change significantly at the higher coal space velocities. The H/C atomic ratios for the product blends were in the range of 1.54-1.58 for Run 250C, D, and E periods. A comparison of Run 244 and Run 250D data shows that products from higher space velocity CC-ITSL were superior compared to those from the lower space velocity ITSL.

SLURRY HYDROGENATION

One of the primary functions of the hydrotreater in the integrated process is to hydrogenate the "depleted" process solvent from the thermal unit so that sufficient donatable hydrogen is present in the process solvent to the thermal stage. Hydrogenation of coal derived materials occurs primarily through saturation of aromatic rings. Based on thermodynamic equilibrium and reaction kinetic models, several investigators have shown that lower reaction temperatures and lower space velocities must be employed to maximize aromatic saturation (2).

Run 250 provided an excellent opportunity to understand the effects of simultaneous changes in temperature and space velocity on slurry hydrogenation. Slide 18 shows the increase in H/C atomic ratio of the slurry ($\Delta H/C$) at different combinations of hydrotreater temperature and space velocity. It is clearly seen that the $\Delta H/C$ ratio did not change significantly as the temperature and space velocity were increased simultaneously. It appears that the dehydrogenation reactions were relatively unimportant under the hydrogen-rich conditions and with a good hydrogenation catalyst. Another reason may be that the hydrogenation reactions occurred in a kinetically controlled regime.

CATALYST PORE SIZE DISTRIBUTIONS

Run 250 was the first integrated run at Wilsonville in which a bimodal catalyst was employed in the hydrotreater. Improved stability of the bimodal catalysts, compared to the unimodal catalysts, has been shown by several investigators (3, 4). The macropores work as feeder pores to aid transport of materials, especially the heavy ends, into the catalyst interior so that the materials have more access to the small pores which have most of the surface area needed for catalytic reaction. Pore mouth plugging is one of the common causes of catalyst deactivation. Bimodal catalysts are believed to be less prone to pore mouth plugging and hence more effective over extended periods of catalyst age.

Slide 19 shows a comparison of the pore size distributions for fresh unsulfided unimodal Shell 324 and bimodal Amocat 1C. The measurements were made at HRI by mercury porosimetry method. Most of the micropores are near 100 Å for both the catalysts. The main difference between the two catalysts is in the macropore volume. Amocat 1C had about 12% of the total pore volume in pores larger than 600 Å, whereas Shell 324 had less than 1%. The macropore volume in Amocat 1C was distributed almost uniformly in the range 600 to 7000 Å.

Slide 20 compares the pore size distributions of aged Shell 324 (end of Run 247) and aged Amocat 1C (end of Run 250). For both the catalysts, the micropore peak was shifted to around 60 Å. The bimodal catalyst suffered nearly complete loss of the macropore volume. However, the average pore diameter is significantly higher for the Amocat 1C catalyst. This may be one of the reasons for the slower deactivation characteristics of the Amocat 1C relative to Shell 324. Note that the average pore diameter was calculated from the following equation:

$$\text{average pore dia.} = \frac{\int a \, dV}{\int dV}$$

where 'a' is the pore diameter in Å and dV is the differential pore volume in a narrow range of pores around diameter 'a'.

CARBON AND METAL DEPOSITS

The Amocat 1C catalyst accumulated more carbon and metals than the Shell 324 catalyst. The same trend was observed by other investigators when comparing unimodal and bimodal catalysts (4). However, it should be remembered that the Amocat 1C had more pore volume to be accessible to the fouling materials and hence the increased level of deposits was not due to the bimodal pore structure in itself. This is indicated by comparing the carbon and metal deposits on a pore volume basis. Slide 21 shows that Amocat 1C accumulated less carbon and metals per unit of fresh pore volume.

CATALYST DEACTIVATION

Catalyst deactivation trends in the Wilsonville runs are characterized by plotting normalized first order rate constants for resid conversion as a function of catalyst age (5). Such a plot is shown in Slide 22 for the ITSL/Shell 324 and CC-ITSL/Amocat 1C operations. Catalyst deactivation was rapid initially due to coke deposition. This was followed by slower deactivation rates. The catalyst performance in the CC-ITSL run was outstanding as can be seen from the nearly flat decay line after a catalyst age of 100 lb (resid+UC+ash)/lb catalyst. Higher resid conversion rate constants were maintained in the CC-ITSL mode using Amocat 1C catalyst.

Slide 23 is an Arrhenius plot of the resid conversion rate constants for the ITSL/Shell 324 combination and the CC-ITSL/Amocat 1C combination at approximately 500 lb (resid+CI)/lb catalyst age. The temperature sensitivity of the resid conversion was about the same for both combinations as indicated by the roughly equal values for the apparent activation energies. However, the actual values of the rate constants were higher for the CC-ITSL/Amocat 1C combination.

The activity characteristics of the Shell 3234/RITSL and Amocat 1C/CC-ITSL were determined using naphthalene hydrogenation reaction as a probe (Slide 24). The initial activity of the Amocat 1C catalyst was about 70% of the Shell 324 activity. However, after the initial decay over the first 100-200 lb catalyst age, the lined out activities were approximately the same for Amocat 1C and Shell 324 catalysts.

The preasphaltene conversion rate constants are compared as a function of catalyst age for Shell 324/Run 247 and Amocat 1C/Run 250 in Slide 25. Again, the deactivation rate was lower for the Amocat 1C/CC-ITSL combination. This resulted in higher preasphaltene conversion rate constants after about 400 lb catalyst age for Amocat 1C/CC-ITSL. One of the process implications of this result is more stable viscosity of the recycle process solvent, particularly at lower solvent-to-coal ratios, since preasphaltenes are relatively high in viscosity.

CATALYST REPLACEMENT RATES

Batch deactivation kinetic equations can be coupled with the age distribution function for the catalyst in the hydrotreater in order to project catalyst requirements to maintain "all-distillate" product slate. The usefulness of this approach had been demonstrated in the Wilsonville Run 245 (6).

The catalyst replacement rate as a function of hydrotreater temperature is shown in Slide 26 for ITSL/Run 245, RITSL/Run 247, and CC-ITSL/Run 250 modes. The curves were generated under the actual operating conditions used in the respective runs except for the hydrotreater temperature which is, of course, a variable in the interrelationship plot. The coal feed rate was set at 180 lb/hr MF coal. A comparison of the catalyst replacement rates shows that under the Run 250 conditions the catalyst requirements are substantially lower than the others. For example, at a hydrotreater temperature of 730°F, ITSL and RITSL configurations with Shell 324 require about 1 pound per ton of coal whereas CC-ITSL with Amocat 1C requires only about one-fourth pound per ton of coal.

The catalyst replacement rates under high space velocity conditions of Run 250 C, D, and E periods are shown in Slide 27. At a given hydrotreater temperature, the catalyst replacement rates were significantly increased at higher space velocities. There were several reasons for these results. First, the hydrotreater space velocity increased with increased coal space velocity. Second, the TLU resid yield increased with increased space velocity. Third, the CSD resid recovery improved in Run 250E. Slide 28 shows catalyst replacement rates after adjusting for a constant TLU resid yield of about 46% MAF.

RUN 250 SUMMARY

- The operability of CC-ITSL mode using bimodal Amocat 1C catalyst in Run 250 was good.
- Run 250 process yields were similar to the previous ITSL runs in several respects.
- Higher hydrogen consumption, with correspondingly better product quality, was the major effect of close-coupled operation without interstage separation.
- At the same coal feed rate, product yields were similar with Shell 324 and Amocat 1C catalysts in the close-coupled operation. The lower hydrogen consumption observed with the Amocat 1C can be attributed to the effect of interstage separation and/or to the higher selectivity of the catalyst for distillate production.
- CC-ITSL products had lower levels of nitrogen, sulfur, and oxygen, higher levels of hydrogen, H/C atomic ratio, and API gravity, compared to ITSL products. The above improvements were accompanied by an increased hydrogen consumption.
- Higher system space velocities to produce "all-distillate" product slate were demonstrated by compensatory increases in reactor temperatures.
- The increase in slurry H/C atomic ratio across the hydrotreater did not change significantly with simultaneous increases in hydrotreater temperature and space velocity.
- Product quality did not change significantly at the higher system space velocities. Products from high space velocity CC-ITSL were of better quality than those from low space velocity ITSL.
- In solids recycle operation, resid concentrations as high as 40% were achieved in the process solvent without any pumping problems.
- In the solids recycle operation, the CSD feed rate was reduced by a factor of 2. Moreover, the organic rejection to the ash concentrate was lowered significantly in a sustained manner. The lowest value demonstrated was 15% MAF.
- Coal conversion measured around the overall system was 3% higher in CC-ITSL compared to the ITSL run.
- The resid conversion and preasphaltene conversion stability of the Amocat 1C catalyst in the close-coupled run was better than that of the Shell 324 in the ITSL and RITSL runs.
- The resid in CC-ITSL/Amocat 1C operation was more reactive than in ITSL/Shell 324 operations.
- Amocat 1C catalyst lost nearly all of its macropore volume during aging up to 1200 lb catalyst age. However, the average pore diameter of Amocat 1C was significantly higher than that of Shell 324 at comparable ages.

- Carbon and metal depositions on pore volume basis were lower for Amocat 1C in the close-coupled run compared for Shell 324 in the RITSL run.
- From naphthalene tests, the initial hydrogenation activity was lower for Amocat 1C relative to Shell 324. But, after the initial decay, the activities were similar.
- Under Run 250C conditions, Amocat 1C catalyst replacement rate was projected to be one-fourth pound per ton of MF coal at an operating temperature of 730°F in the hydrotreater. This rate is less than that for ITSL and RITSL modes by a factor of 4.
- The projected catalyst replacement rates increased significantly at higher system space rates.

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project organization

sponsors	participants
■ U.S. Department of Energy	■ Catalytic, Inc.
■ Electric Power Research Institute	■ Kerr-McGee Corporation
■ Amoco Corporation	■ Hydrocarbon Research, Inc.
■ Southern Company Services, Inc.	

CATALYTIC

CC-ITSL process units

unit	salient features
thermal liquefaction unit (TLU)	■ forced backmixed dissolver ■ disposable catalyst may be utilized ■ 90-95% coal conversion (cresol solubles) ■ commercial supported—catalyst may be utilized
hydrotreating (HTR) unit	■ ebullated-bed reactor ■ commercial supported—catalyst utilized ■ catalyst addition/withdrawal capability
critical solvent deashing (CSD) unit	■ proprietary extraction process ■ conditions near critical point of deashing solvent ■ capable of fractionating coal extract ■ efficient deashing

9220-17

CATALYTIC

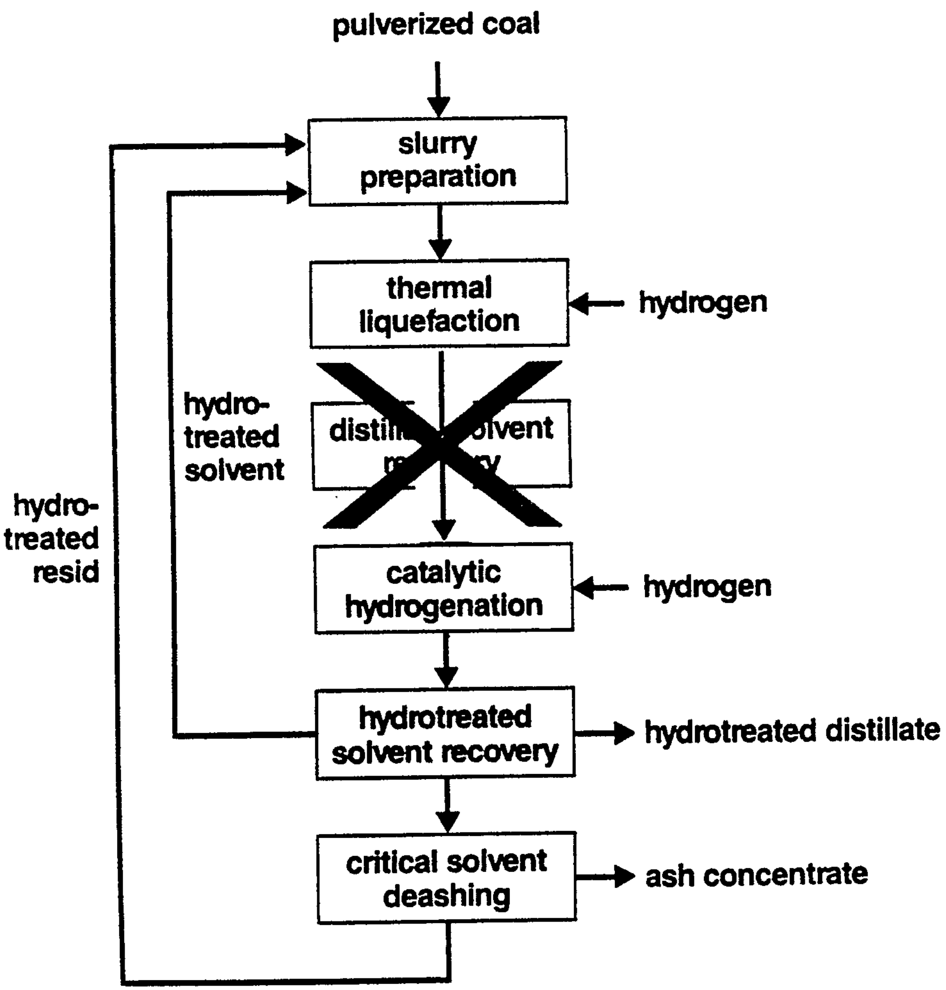
CC-ITSL evolution

	ITSL ►	RITSL ►	CC-ITSL
■ runs	242-245, 248	247, 249	250
■ deashing after hydrotreating	no	yes	yes
■ interreactor cooling and reheating	yes	yes	no
■ interreactor pressure reduction and repressurization	yes	yes	no

9219-71

CATALYTIC

CC-ITSL
two-stage liquefaction close-coupled integrated mode


pulverized coal
slurry preparation
thermal liquefaction
hydrogen
hydro-treated solvent
distil
lvent
catalytic hydrogenation
hydrogen
hydro-treated resid
hydrotreated solvent recovery
hydrotreated distillate
critical solvent deashing
ash concentrate

9174-71

CATALYTIC

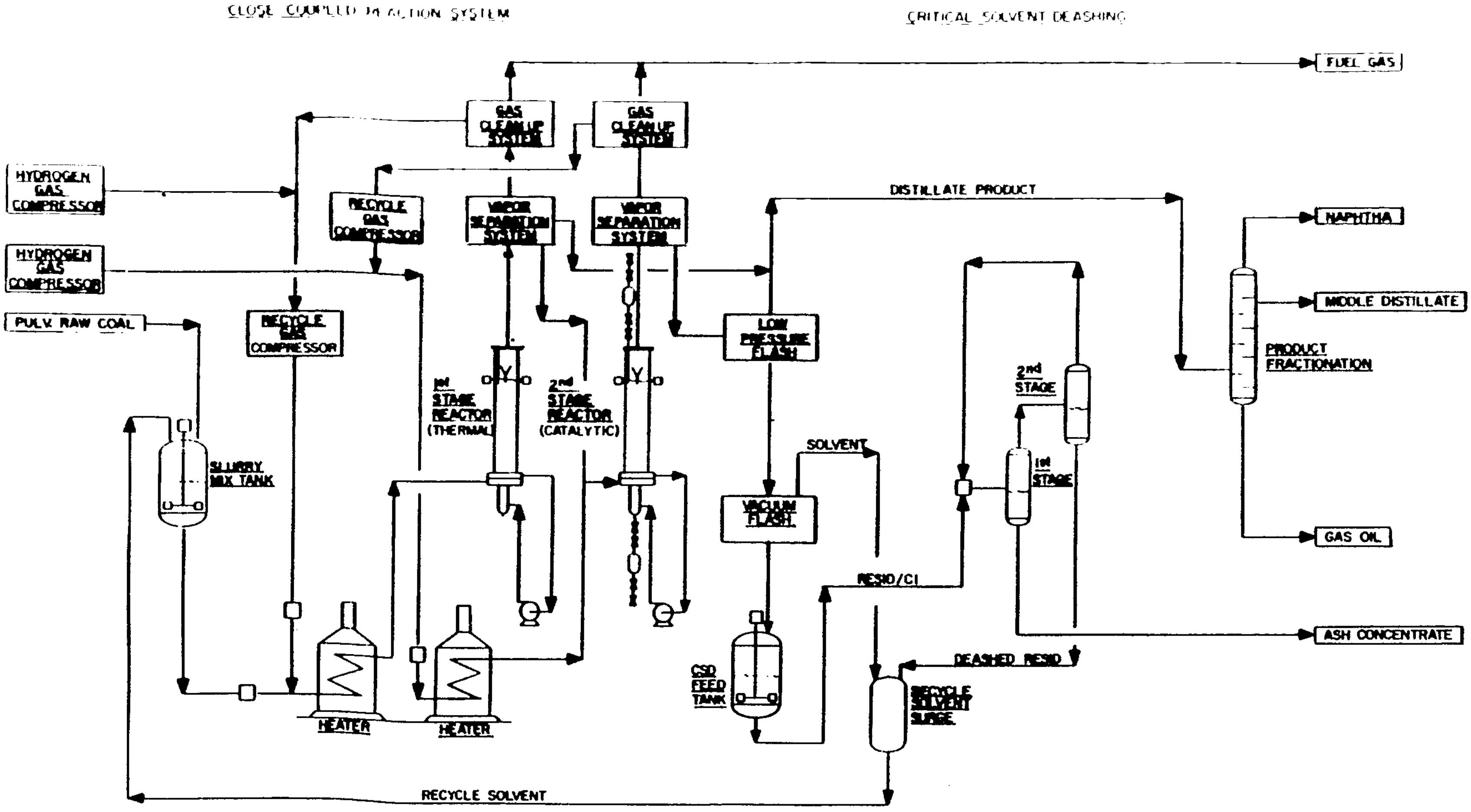
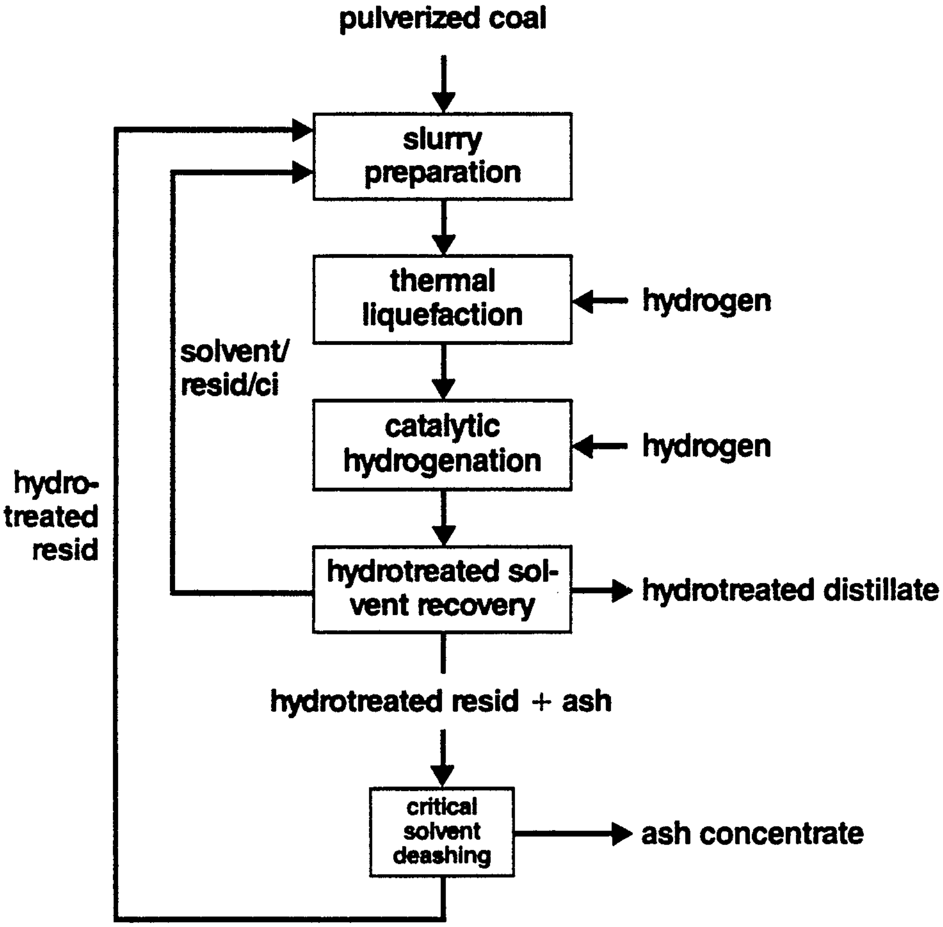

CLOSE COUPLED REACTION SYSTEM
CRITICAL SOLVENT DEASHING
FUEL GAS
GAS CLEAN UP SYSTEM
GAS CLEAN UP SYSTEM
HYDROGEN GAS COMPRESSOR
HYDROGEN GAS COMPRESSOR
RECYCLE GAS COMPRESSOR
RECYCLE GAS COMPRESSOR
VAPOR SEPARATION SYSTEM
VAPOR SEPARATION SYSTEM
PULV. RAW COAL
DISTILLATE PRODUCT
NAPHTHA
MIDDLE DISTILLATE
PRODUCT FRACTIONATION
GAS OIL
LOW PRESSURE FLASH
1st STAGE REACTOR (THERMAL)
2nd STAGE REACTOR (CATALYTIC)
SLURRY MIX TANK
2nd STAGE
1st STAGE
SOLVENT
VACUUM FLASH
RESID/CI
ASH CONCENTRATE
DEASHED RESID
CSD FEED TANK
RECYCLE SOLVENT SURGE
HEATER
HEATER
RECYCLE SOLVENT

FIGURE 2: CLOSE COUPLED INTEGRATED TWO STAGE LIQUEFACTION SYSTEM THERMAL-CATALYTIC WITH INTER-STAGE VAPOR SEPARATION

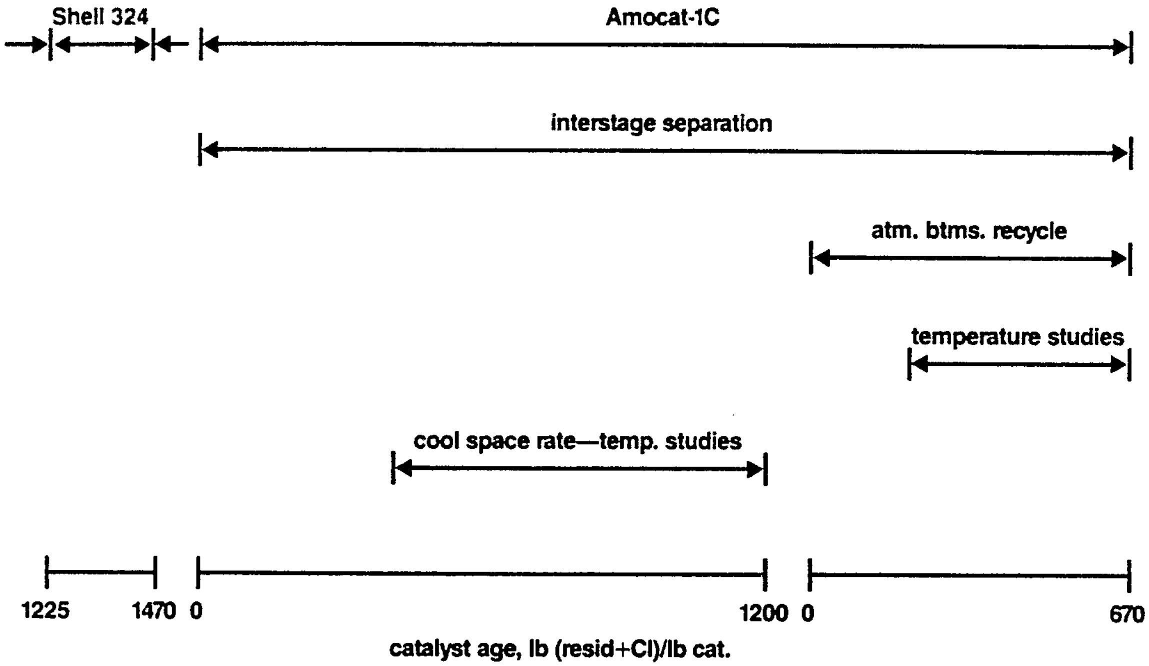
CC-ITSL with ash recycle two-stage liquefaction close-coupled mode


pulverized coal
slurry preparation
thermal liquefaction
hydrogen
solvent/ resid/ci
catalytic hydrogenation
hydrogen
hydro-treated resid
hydrotreated solvent recovery
hydrotreated distillate
hydrotreated resid + ash
critical solvent deashing
ash concentrate

9175-71

CATALYTIC

CC-ITSL process studies (run 250)


Shell 324
Amocat-1C
interstage separation
atm. btms. recycle
temperature studies
cool space rate—temp. studies
1225
1470
0
1200
0
670
catalyst age, lb (resid+Cl)/lb cat.

9221-71

CATALYTIC

configuration comparison ITSL vs CC-ITSL (Shell 324)

TSL operating conditions

run no. configuration	244CD ITSL	250B CC-ITSL
thermal stage		
average reactor temperature (°F)	810*	809
inlet hydrogen partial pressure (psi)	2040	2800
coal space velocity [lb/hr-ft³ (>700°F)]	28	25
catalytic stage		
reactor temperature (°F)	730	725
space velocity (lb feed/hr-lb cat)	1.1	1.0
catalyst age [(lb resid)/lb cat]	943-1139	1432-1470**

*reactor outlet temperature
**based on (lb resid + UC + ash)/lb cat

9194-71

CATALYTIC

configuration comparison
ITSL vs CC-ITSL (Shell 324)

TSL yield structures

run no.	244CD	250B
configuration	ITSL	CC-ITSL
yield* (% MAF coal)		
C_1-C_3 gas (total gas)	6(11)	6(11)
water	10	10
C_4+ distillate	57	61
resid	8	6
hydrogen consumption	–5.2	–6.4
hydrogen efficiency (lb C_4+ dist/lb H_2 consumed)	11.0	9.6
distillate selectivity (lb C_1-C_3/lb C_4+ dist)	0.11	0.10
energy content of feed coal rejected to ash conc. (%)	20-22	20
organics rejected to ash conc. (% MAF coal)	19	18

*elementally balanced yield structures

8619A-71

CATALYTIC

CC-ITSL catalyst studies	TSL operating conditions	
run no.	250B	250C
catalyst	Shell 324	Amocat 1C
thermal stage		
average reactor temperature (°F)	809	809
inlet hydrogen partial pressure (psi)	2800	2500
coal space velocity [lb/hr-ft^3 (>700°F)]	25	25
solvent-to-coal ratio	1.8	1.8
solvent resid content (wt %)	49	48
catalytic stage		
reactor temperature (°F)	725	703
space velocity (lb feed/hr-lb cat)	1.0	1.3
feed resid content (wt %)	50	50
catalyst age [(lb resid) + UC + ash)/lb cat]	1432-1470	302-396

9188-71

CATALYTIC

CC-ITSL catalyst studies

TSL yield structures

run no.	250B	250C
catalyst	Shell 324	Amocat 1C
yield* (% MAF coal)		
C_1-C_3 gas (total gas)	6(11)	5(11)
water	10	10
C_4+ distillate	61	61
resid	6	2
hydrogen consumption	−6.4	−5.6
hydrogen efficiency (lb C_4+ dist/lb H_2 consumed)	9.6	10.9
distillate selectivity (lb C_1-C_3/lb C_4+ dist)	0.10	0.09
energy content of feed coal rejected to ash conc. (%)	20	24
organics rejected to ash conc. (% MAF coal)	18	22

*elementally balanced yield structures

9189-71

CATALYTIC

CC-ITSL
space velocity studies

TSL operating conditions

run no.	250C	250D	250E
thermal stage			
average reactor temperature (°F)	809	824	829
inlet hydrogen partial pressure (psi)	2500	2500	2500
coal space velocity [lb/hr-ft^3 (>700°F)]	25	37	45
solvent-to-coal ratio	1.8	1.8	1.8
solvent resid content (wt %)	48	50	49
catalytic stage			
reactor temperature (°F)	703	742	750
space velocity (lb feed/hr-lb cat)	1.3	2.1	2.6
feed resid content (wt %)	50	53	55
catalyst age [(lb resid) + UC + ash)/lb cat]	302-396	697-786	1040-1191

9190-71

CATALYTIC

CC-ITSL
space velocity studies

TSL yield structures

run no.	250C	250D	250E
yield* (% MAF coal)			
C_1-C_3 gas (total gas)	5(11)	7(12)	6(12)
water	10	10	9
C_4+ distillate	61	64	58
resid	2	−2	7
hydrogen consumption	−5.6	−6.1	−5.7
hydrogen efficiency (lb C_4+ dist/lb H_2 consumed)	10.9	10.5	10.2
distillate selectivity (lb C_1-C_3/lb C_4+ dist)	0.09	0.11	0.11
energy content of feed coal rejected to ash conc. (%)	24	23	22
organics rejected to ash conc. (% MAF coal)	22	22	19

*elementally balanced yield structures

CC-ITSL ash recycle studies

TSL operating conditions

run no.	250D	250G
ash recycle	no	yes
thermal stage		
average reactor temperature (°F)	824	829
inlet hydrogen partial pressure (psi)	2500	2500
coal space velocity [lb/hr-ft^3 (>700°F)]	37	37
solvent-to-coal ratio	1.8	2.0
solvent resid content (wt %)	50	40
catalytic stage		
reactor temperature (°F)	742	750
space velocity (lb feed/hr-lb cat)	2.1	2.2
feed resid content (wt %)	53	46
catalyst age [(lb resid) + UC + ash)/lb cat]	697-786	346-439

9192-71

CATALYTIC

CC-ITSL
ash recycle studies

TSL yield structures

run no. ash recycle	250D no	250G yes
yield* (% MAF coal)		
C_1-C_3 gas (total gas)	7(12)	8(13)
water	10	10
C_4+ distillate	64	63
resid	−2	5
hydrogen consumption	−6.1	−6.4
hydrogen efficiency (lb C_4+ dist/lb H_2 consumed)	10.5	9.8
distillate selectivity (lb C_1-C_3/lb C_4+ dist)	0.11	0.12
energy content of feed coal rejected to ash conc. (%)	23	16
organics rejected to ash conc. (% MAF coal)	22	15

*elementally balanced yield structures

9193-71

CATALYTIC

impact of close coupling on observed coal conversion*

(bituminous coal)

	ΔTLU	+	Δ HTR	+	Δ CSD	=	two-stage
ITSL (TLU-CSD-HTR)	92.5				-4.8		87.7
	(1.1)				(1.4)		(1.3)
CC-ITSL (TLU-HTR-CSD)	92.4		0.2		-1.4		91.3
	(0.9)		(0.9)		(0.8)		(0.8)

- conversion of unconverted coal in HTR statistically insignificant
- for similar TLU coal conversion, overall CC-ITSL conversion higher than ITSL

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*cresol solubles

9222-71

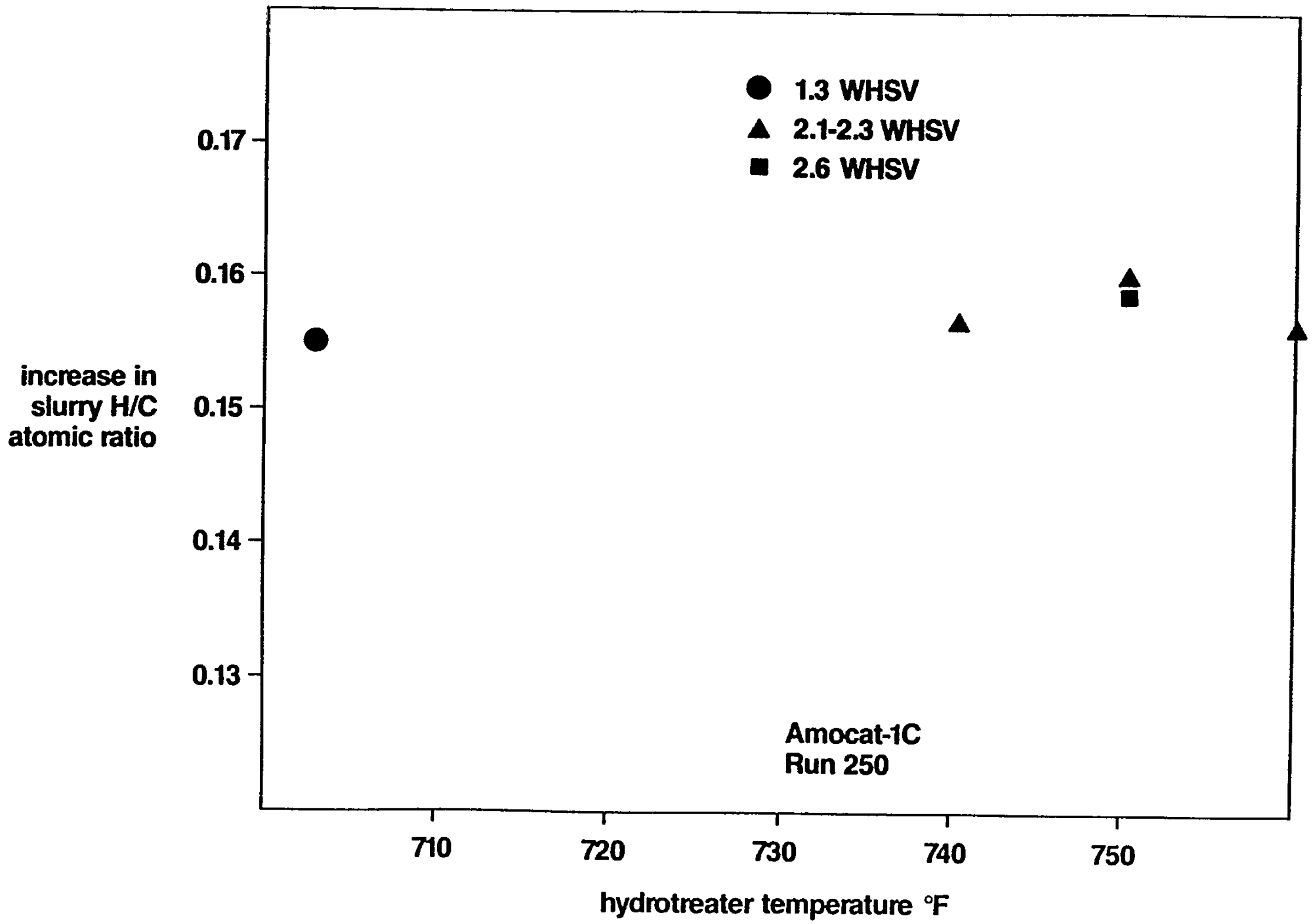
CATALYTIC

properties of distillate products

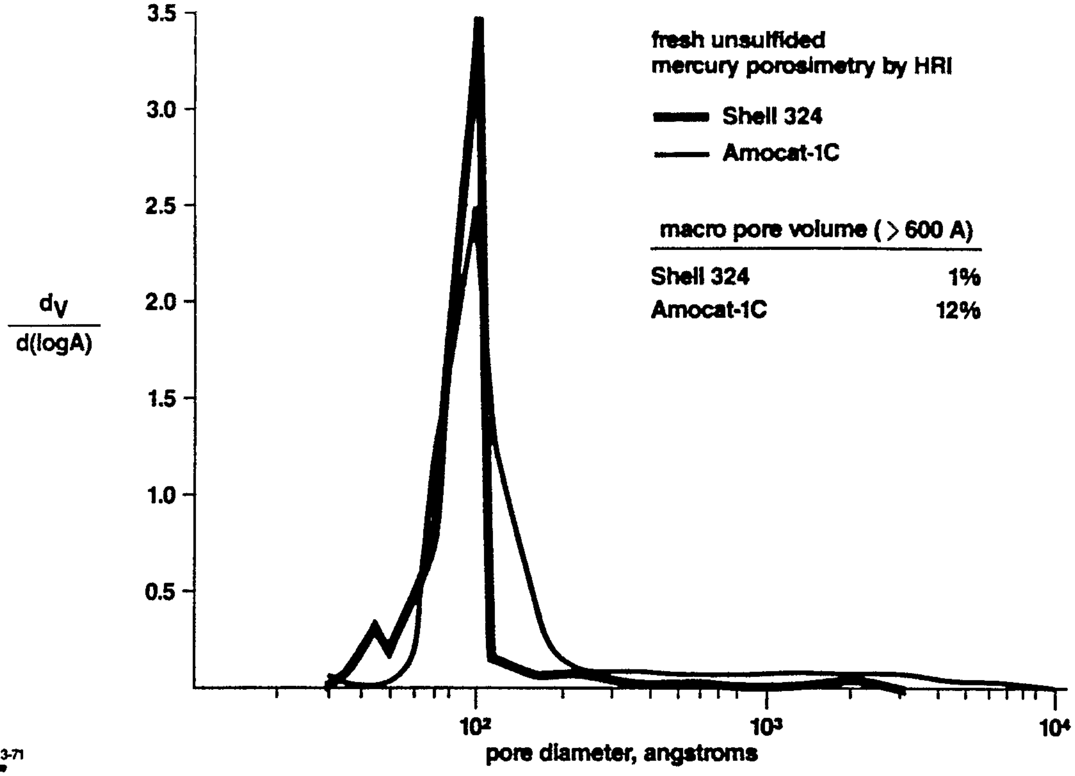
distillation cut	wt % of crude	elemental (wt %)					°API
		C	H	N	S	O (diff)	
ITSL (run 244)							
naphtha (IBP-350°F)	18.6	85.21	12.86	0.08	0.36	1.49	43.1
distillate (350-650°F)	46.1	86.34	10.73	0.23	0.22	2.48	18.6
gas oil (650°F+)	35.3	89.07	9.69	0.31	0.16	0.76	7.3
CC-ITSL (run 250B)							
naphtha (IBP-350°F)	19.0	85.31	14.51	0.02	0.01	0.15	42.5
distillate (350-650°F)	46.8	87.43	12.12	0.10	0.06	0.29	47.6
gas oil (650°F+)	34.2	88.41	10.88	0.19	0.04	0.48	10.4
CC-ITSL (run 250D)							
naphtha (IBP-350°F)	18.6	85.35	14.25	0.04	0.18	0.18	49.9
distillate (350-650°F)	45.0	87.45	11.73	0.22	0.09	0.51	42.4
gas oil (650°F+)	36.4	88.77	10.27	0.36	0.07	0.53	9.7

CATALYTIC

space velocity and temperature effects on slurry hydrogenation



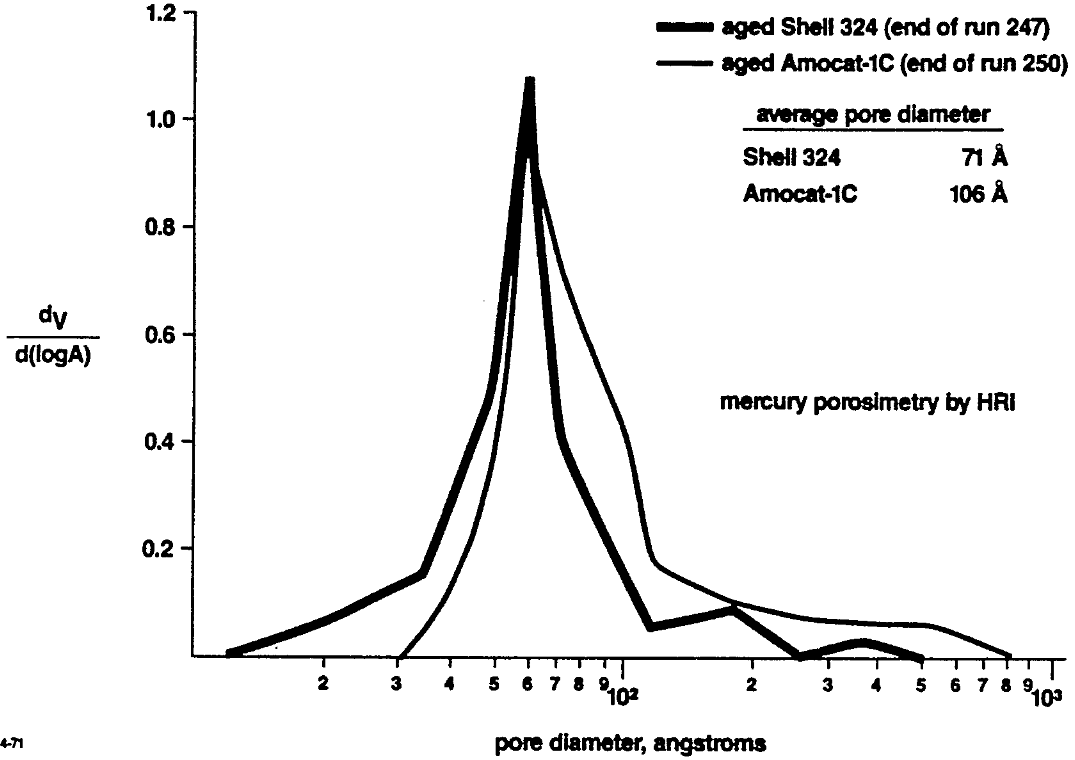
unimodal and bimodal pore size distributions



9223-71

CATALYTIC

aged catalyst pore size distributions



9224-71

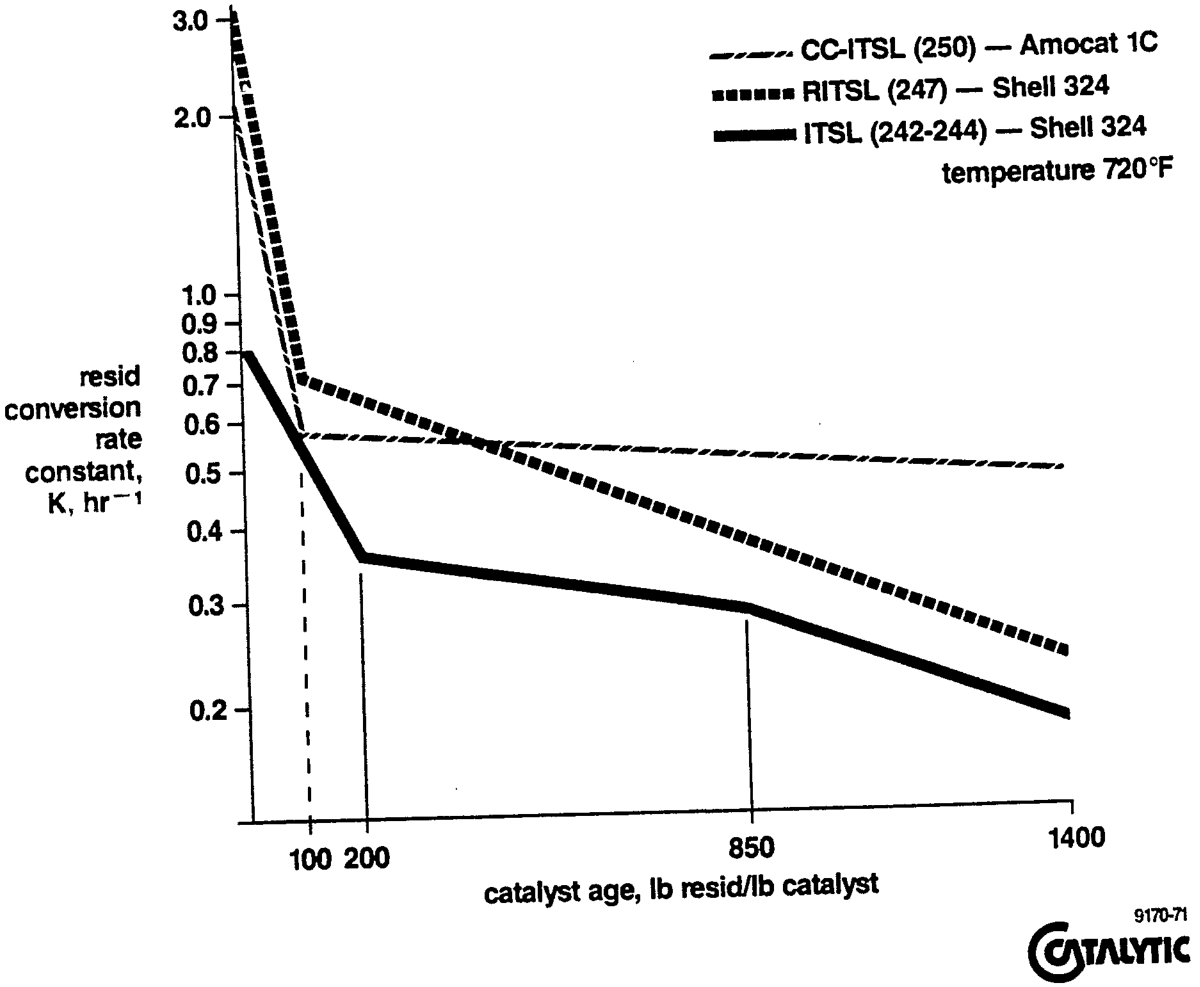
carbon and metal deposition lower for bimodal catalyst on pore volume basis

	Shell 324 (run 247 end)	Amocat-IC (run 250 end)
age, lbs (resid+Cl)/lb cat.	1225	1205
carbon,* mg/cc pore volume	213	176
(V+Fe+Ca+Na+Ti), mg/cc pore volume	65	25

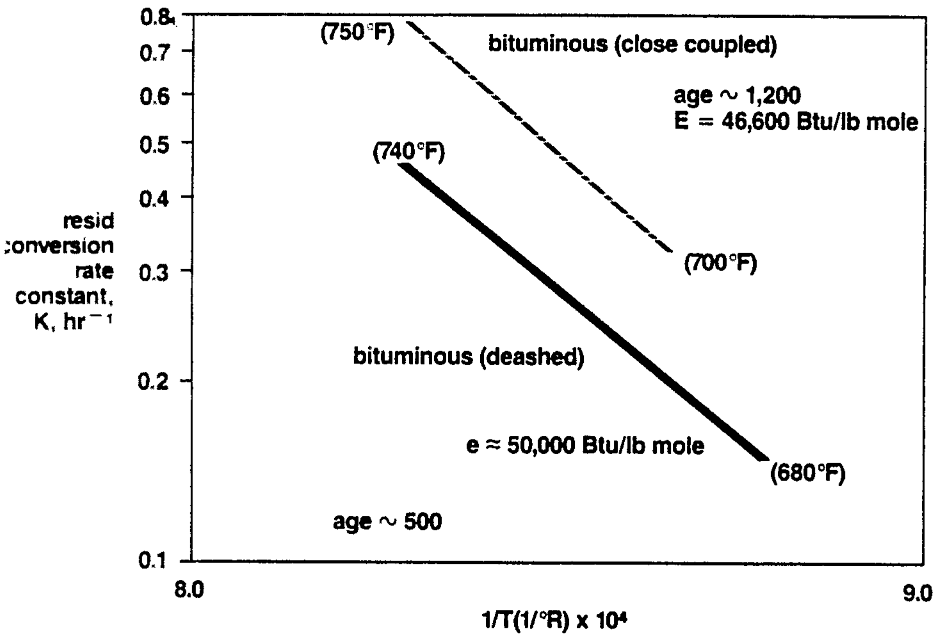
*THF extracted

CATALYTIC

catalyst deactivation trends



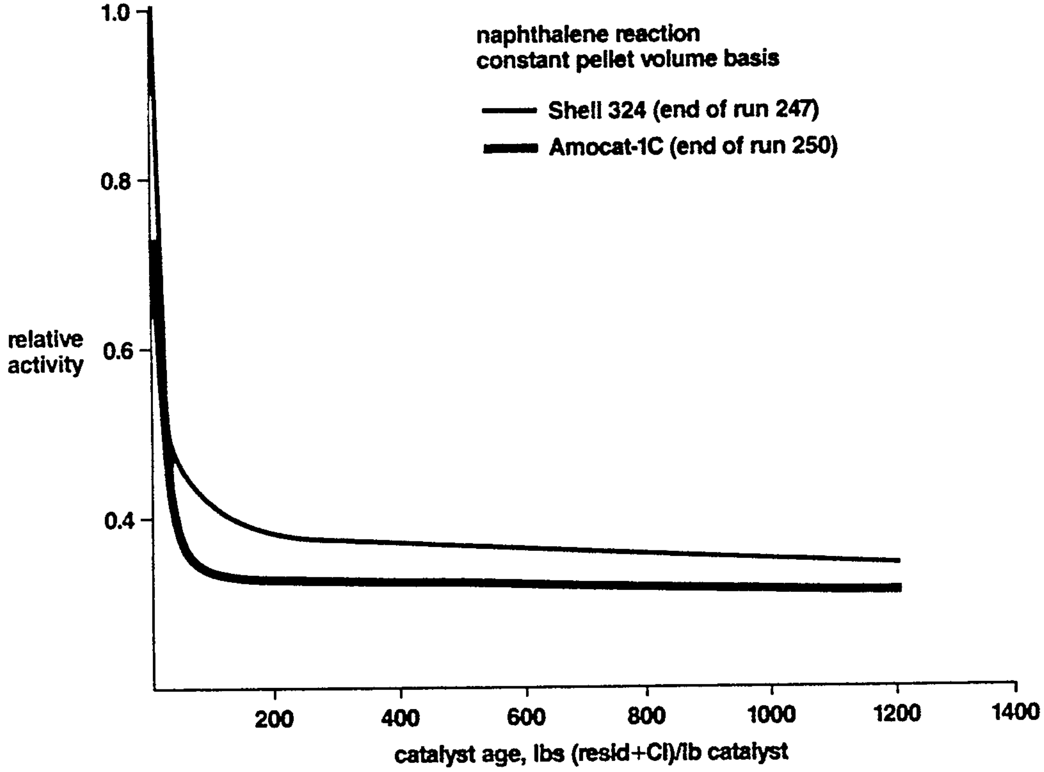
comparison of resid conversion rate constants



9171-71

CATALYTIC

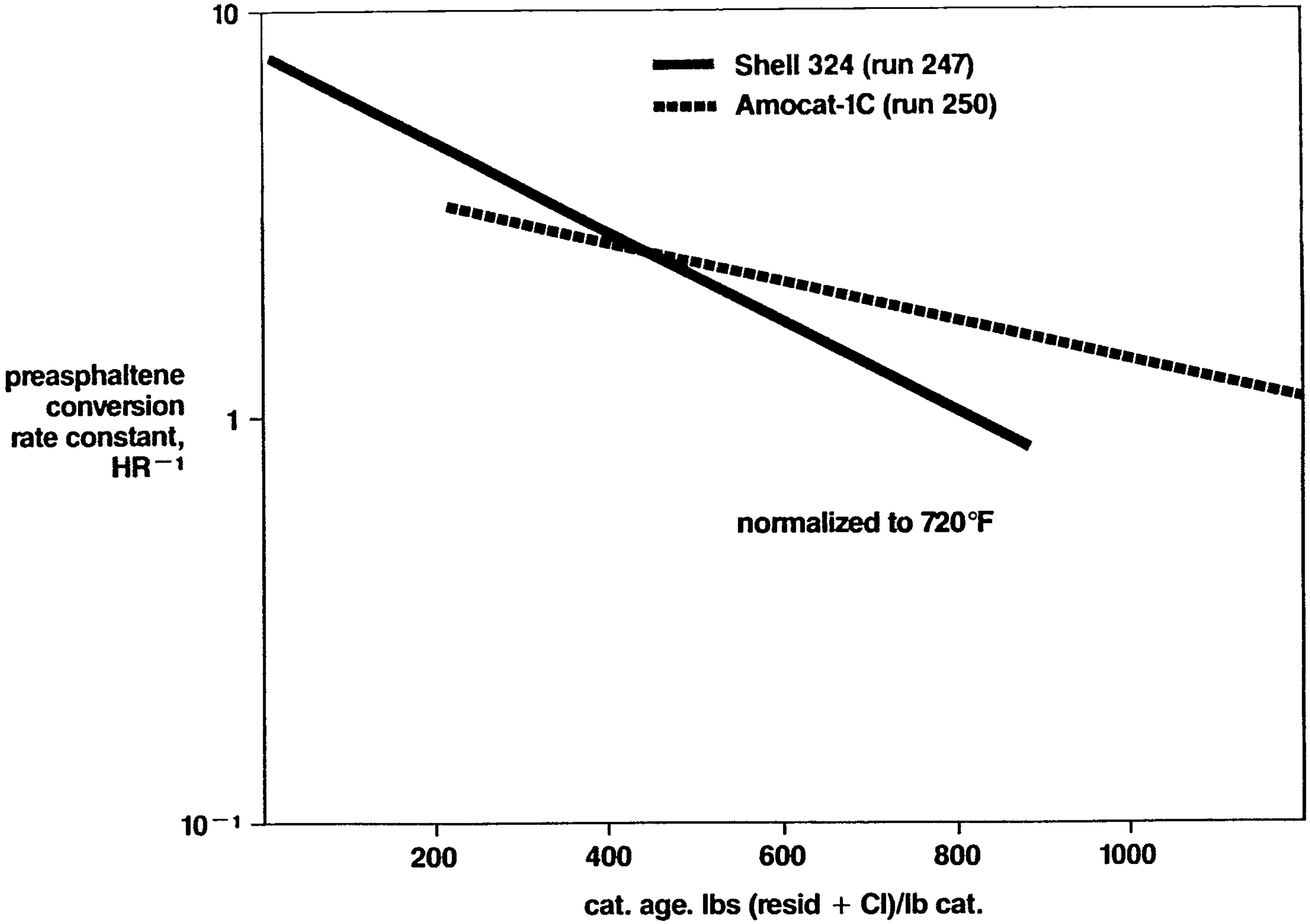
unimodal and bimodal catalyst activity trends



9226-71

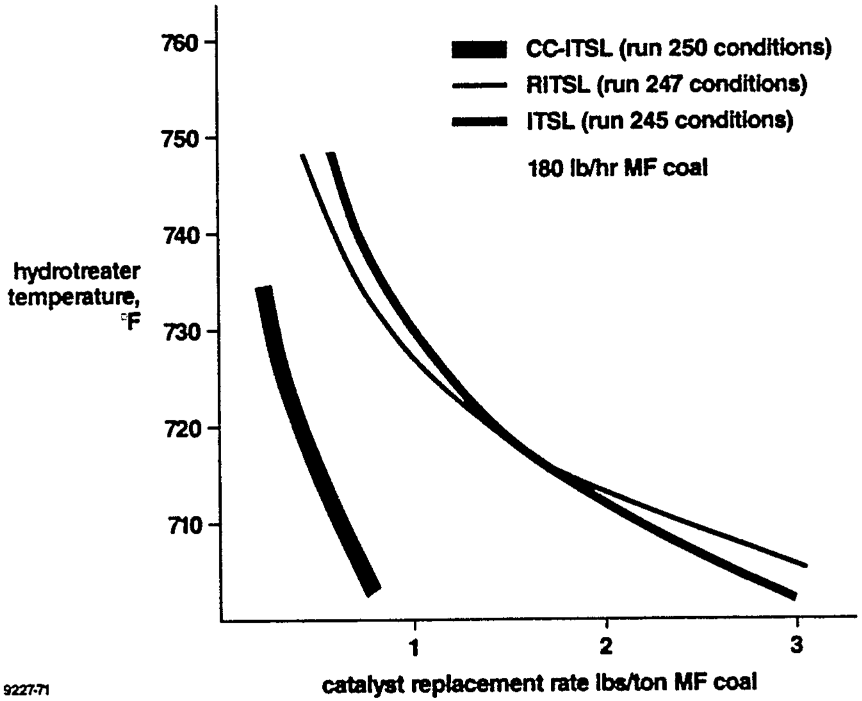
CATALYTIC

catalyst deactivation trends



9235-71

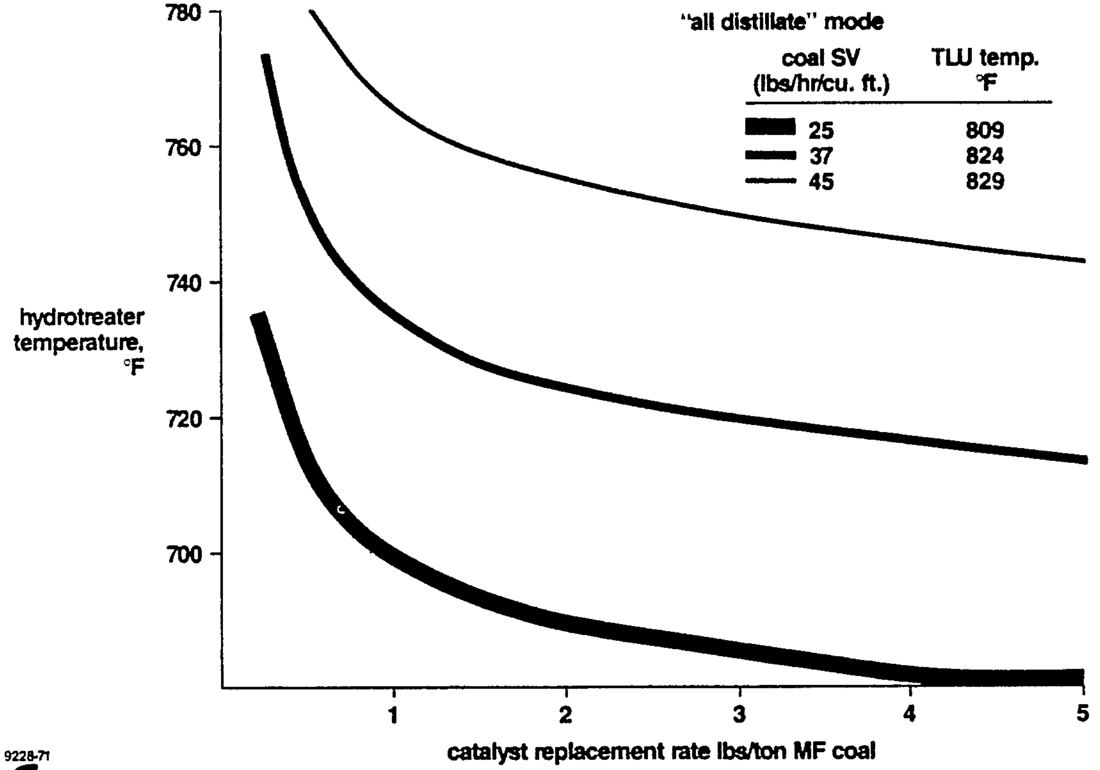
comparison of catalyst replacement rates in various configurations



9227-71

CATALYTIC

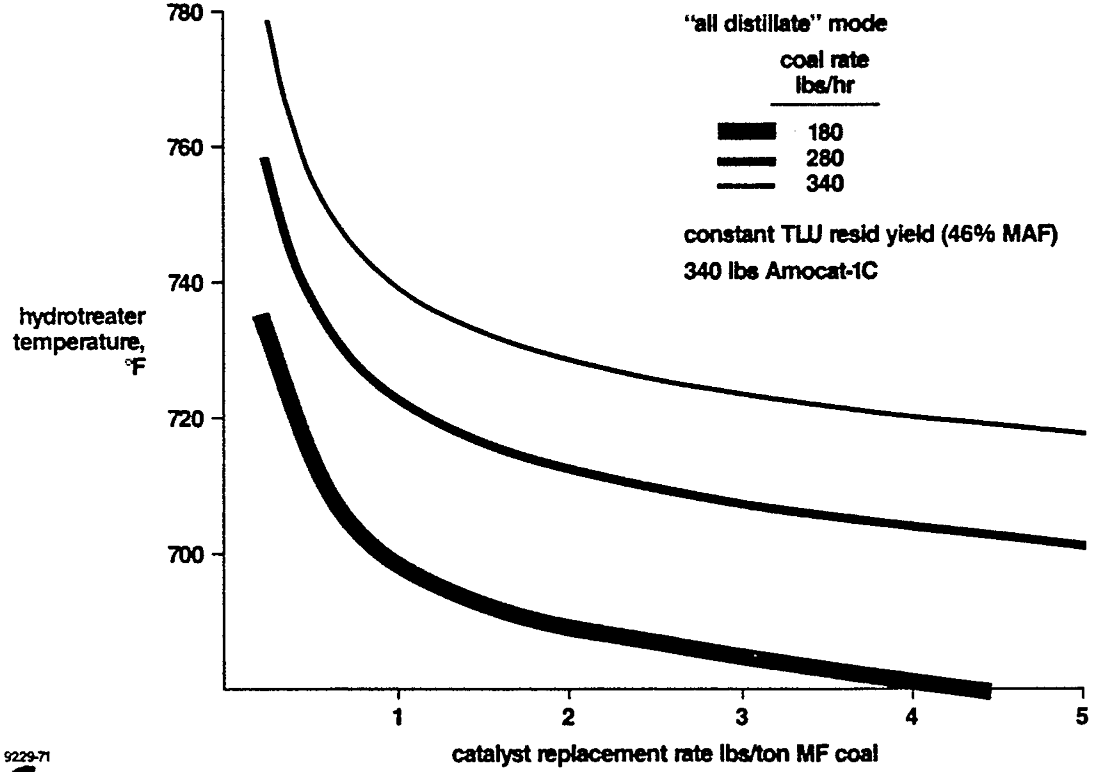
effect of coal space rate on catalyst replacement (run 250)



9228-71

CATALYTIC

effect of coal feed rate on catalyst replacement—constant TLU resid yield



9229-71

CATALYTIC

ACKNOWLEDGMENTS

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WILSONVILLE PROCESS STUDIES AND ENGINEERING EVALUATION OF IMPROVED OPTIONS

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Catalytic, Inc.

ABSTRACT

Results will be presented for three runs that were completed during the past year in the Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama. Several configurations of integrated two-stage liquefaction were investigated using both bituminous and subbituminous coal feeds. The effect of the addition of iron oxide to the coal slurry as a disposable catalyst was tested with both coal feeds. Recent results using bituminous coal and a close-coupled reactor configuration will be presented.

The process results from the runs will be characterized by the presentation of representative product yields and product quality data. Also, a discussion will be given concerning the effect of process options on relative economics.

INTRODUCTION

This paper will present results from the Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama. Sponsors are the U.S. Department of Energy, the Electric Power Research Institute and Amoco Corporation. The facility is operated by Catalytic, Inc., under the management of Southern Company Services, Inc. Kerr-McGee has participated by supplying deashing technology at Wilsonville. The technology for the design of the hydrotreater was provided by Hydrocarbon Research, Inc.

The Wilsonville facility began operation of a 6 T/D single-stage plant for the production of solvent-refined coal in early 1974 and has continued over the intervening twelve years. Over this period the plant has evolved to the current advanced coal liquefaction facility by developments made possible by three major additions to the facility. In 1978, a Kerr-McGee Critical Solvent Deashing (CSD) unit replaced the filtration equipment that had been used for solids removal from the SRC product. In 1981, an H-Oil® ebullated-bed hydrotreater was installed for upgrading of the recycle solvent and product. The hydrotreater increased the flexibility of the facility and allowed the investigation of two-stage liquefaction configurations. In 1985, a second reactor was added in the hydrotreater area to allow operation with close-coupled reactors.

Material balance data since 1984 have been taken based upon the chemical elements of the feed, intermediate, and product streams.

Three runs have been completed since the last EPRI conference and highlights of the results will be reported in this paper. Run 248 employed a smaller dissolver to investigate the effect of reduced residence time on performance with bituminous coal feed. Run 249 was a test using subbituminous coal that involved hydrotreating of nondeashed feed from the liquefaction stage. Bituminous coal was used in Run 250, which was the first test of close-coupled reactors at Wilsonville.

RUN 248

The configuration that has been used most at Wilsonville is the Integrated Two-Stage Liquefaction (ITSL) mode, as illustrated in Slide 1. In the ITSL configuration, the deashed resid is fed to the hydrotreater, along with the heavier fraction of the thermal distillate. The recycle process solvent is composed of hydrotreated distillate and resid.

At the beginning of Run 248, a variation called the Double Integrated Two-Stage Liquefaction (DITSL) configuration was used. It is shown in Slide 2. This differs from the ITSL mode in that only the Light Thermal Resid (LTR) is processed through the hydrotreater. The heavier Thermal Resid (TR) is recycled directly to the thermal stage. This configuration was used earlier at Wilsonville with subbituminous coal (1). Potential advantages of the DITSL configuration are that a smaller hydrotreater might be possible and catalyst deactivation rate could be reduced because only the LTR stream is hydrotreated.

The feed coal for Run 248 was Illinois No. 6 bituminous coal (see Slide 3). Before beginning the run, the 12-inch diameter dissolver was replaced by a 5.2-inch diameter Low Contact Time (LCT) dissolver. This was done to allow operation at higher thermal unit space velocity than could be achieved with the 12-inch dissolver. The intent was to investigate reaction times somewhat longer than had been used in the Short Contact Time (SCT) tests in Run 242 (2). The results from that run were interesting in that low gas make and high hydrogen efficiency had been indicated. The off-sets of the SCT results were that distillate yields were low and energy rejections were high, relative to ITSL performance at longer contact times.

Work at Kerr-McGee had shown that the use of iron oxide as a disposable catalyst with Illinois No. 6 coal was effective in increasing the resid conversion to distillates in the liquefaction stage (3).

In the DITSL configuration, the heavy thermal resid is recycled to the liquefaction stage without going through the hydrotreater. Thus, the TR must be converted in the thermal stage for the DITSL mode to be viable. The iron oxide was used primarily to promote resid conversion. Dimethyl Disulfide (DMDS) was added to the coal slurry to assure a source of hydrogen sulfide to convert the iron oxide to pyrrhotite as the slurry flowed through the preheater. This was the same method that was used successfully in Run 246 (1).

Run 248 Results

Operation in the DITSL configuration was difficult. The major operability problem was high viscosities of the coal slurry. The recycle of the heavy TR directly from the CSD unit resulted in a buildup of preasphaltenes, which caused the high viscosities.

Selected operating conditions and process yields are shown in Slides 4 and 5. the results obtained in the DITSL mode are listed as period 248A. The period was characterized by high resid production and low distillate yield. Yields were not optimized, but distillate yield was only 45% and the resid make was 18%. The resid viscosity limitations prevented proper optimization of CSD operations, resulting in high energy rejection during the DITSL mode.

Process variable adjustments were made in an attempt to achieve viable operations in the DITSL mode. The dissolver outlet temperature was raised to 840°F to increase the severity for resid conversion. Repeated attempts were made to reduce the rate of heavy TR to the dissolver and increase the rate of light thermal resid (LTR) to the hydrotreater, but this resulted in increased TR viscosities.

Satisfactory operability was obtained by changing to the ITSL configuration (248D). The distillate yield was 64% and the resid make was 3%. The two-stage product (distillate + resid) for 248D was 67%, which compares favorably to the 64-65% previously obtained at Wilsonville (1). Because of process variable differences, it cannot be concluded whether iron oxide caused an improvement in distillate yield.

The addition of iron oxide and DMDS was stopped to begin a series of tests at different reactor volumes. After a three-day test at 100% LCT volume without iron oxide, the dissolver volume was reduced successively to 50% and then to 25% LCT dissolver volume.

Coal conversion with volumes of 100%, 50% and 25% were 92%, 90%, and 88% MAF, respectively. As expected for the reduced contact times, resid makes increased and distillate makes and hydrogen consumptions decreased.

Conditions and two-stage liquefaction (TSL) yields for the 50% LCT period are compared to Run 242 SCT results in Slides 6 and 7. Coal space velocities using reaction volume above 700°F were comparable for these two conditions. The yields were very similar, though SCT showed an advantage in lower gas make and hydrogen consumption. Careful examination of the process data indicates that the actual effective temperature of Run 242 was lower than 248 because of cooling in the transfer line. This would explain the higher gas make for Run 248.

RUN 249

Run 249 had a number of objectives that are reflected in Slide 8. A major objective was to obtain process yield data using subbituminous coal with a forced back-mixed dissolver. In the previous run with subbituminous coal the temperature gradient of 30-50°F in the dissolver indicated that mixing was not perfect at the 50% and 75% dissolver volumes that were used (1). For this run, it was desired to operate at 100% of the 12-inch dissolver volume to obtain maximum coal conversion at moderate temperatures. The model developed from the mixing study in Run 247 indicated that the 100% volume would be equivalent to 2.2 CSTRs (4). For these reasons, it was decided to install a pumparound loop, much like that on the hydrotreater, to provide back mixing of the 12-inch dissolver. This pumparound mixing reduced the temperature gradient to 5°F at full pumping rate.

The Reconfigured Integrated Two-Stage Liquefaction (RITSL) configuration was used to provide a database for predicting process performance with subbituminous coal in a close-coupled configuration. The RITSL configuration is illustrated in Slide 9. The slurry preparation, thermal liquefaction, and fractionation steps are the same as in the ITSL mode. However, the vacuum bottoms containing the thermal resid, unconverted coal, and ash are fed directly to the hydrotreater. The feed to the CSD unit is the vacuum flashed bottoms from the hydrotreater. The recycle solvent is composed of the deashed resid from the CSD unit and hydrotreated distillate.

The third major factor to be addressed was enhancement of conversion of the subbituminous coal. The effectiveness of iron oxide with DMDS had been demonstrated earlier (1). However, it would be desirable if iron oxide addition could be eliminated because the solids contributed to wear-related operational problems and caused some additional organics loss when the solids were removed in the CSD unit. Work at the University of Wyoming had shown some very interesting results related to coal drying and the use of water in liquefaction of subbituminous coal (5). Coal conversions were improved when coal was not completely dried or even when water was added back to a coal slurry of dried coal before liquefaction. The water effect was found to be additive to the iron oxide effect on coal conversion. The effect of water addition was tested in Run 249 by adding water at the rate of 15% MF coal to the coal feed slurry after the subbituminous coal was dried in the slurry drier to a moisture content of 1.5%.

Run 249 Results

The run was started with the dissolver at 790°F and the hydrotreater at 670°F and with no iron oxide or water addition. The solvent-to-coal ratio was reduced to 1.5 for Run 249, compared to 1.8 in Run 246, and no pumping problems were caused. The coal conversion was 82%. To test for additional conversion of unconverted coal (UC) in the hydrotreater, coal conversion was calculated by forced-ash balance in the hydrotreater output stream. These results indicated that there was no UC conversion in the hydrotreater at 670°F.

Coal conversion was increased to 90% by adding iron oxide plus DMDS and by increasing the dissolver temperature from 790 to 810°F. Water addition increased coal conversion by 3%. Iron oxide and DMDS addition were discontinued to test whether water addition without iron oxide could maintain coal conversion. Coal conversion decreased significantly, from 92 to 84%. Thus, water addback did not enhance coal conversion enough to enable operation without the iron oxide.

For the 1.5% iron oxide addition rate, the coal sulfur content was calculated to be sufficient to convert the iron oxide to pyrrhotite. This was tested by stopping the DMDS addition and no reduction in coal conversion was observed. Therefore, iron oxide was used without the addition of DMDS for the last two months of the run.

Energy rejection was high throughout this run because the CSD feed was very soluble and the solubility changed with operating variable adjustments. CSD deashing conditions were varied to compensate for process-produced feed solubility changes. CSD feed solubility decreased when no iron oxide was added to the dissolver. Increasing hydrotreater temperature increased feed solubility and, as a result, solvent adjustments were required. Stopping water addition reduced preasphaltene content and this increased feed solubility. Energy rejection was reduced by changing solvent type and adjusting operating conditions.

The CSD experience gained in this run was also valuable in processing the highly soluble feeds that were encountered in the close-coupled operations.

Selected process conditions and yields are shown in Slides 10 and 11. The only difference in periods 249D and 249E is that water addback was used in 249D. Water addition caused a 3% higher coal conversion and energy rejection was reduced by 5%. However, the resid reactivity appeared to be negatively impacted by the water addition. The negative resid yield for 249E indicates that more resid was being converted than was being made, so that resid was being consumed from inventory. The C_4+ distillate yield for 249E would be about 53% if the resid yield had been zero. Thus, there was practically no effect of water addback on distillate yield for this comparison.

The high CSD feed solubility during Run 249 is reflected in the high energy rejections shown for 249E. The energy rejection was 30% and the organic rejection was 24%. Usually these two measures are in close agreement. The reason for the increased difference is that the elemental analysis of the ash concentrate, from which the energy rejection is calculated, had more hydrogenation for the RITSL mode, where the rejected organics have been hydrotreated.

The last major period of the run, designated 249H, was an ash recycle test. The purpose of this test was to remove ash from the system by using a purge of hydrotreater vacuum bottoms instead of using the CSD unit. The ash content of the purge stream was increased by recycling a portion of the hydrotreater atmospheric flashed bottoms to the dissolver. This recycled solvent contained ash, iron oxide, unconverted coal and hydrotreated resid and distillate. By using this method, the solids content of the vacuum bottoms purge stream was increased to about 50% unconverted coal and ash. The ash content was 32%.

The solvent-to-coal ratio was increased to 2.0 to allow for the 25% solids content in the recycle solvent. Thus, the solids-free solvent-to-coal ratio for 249H was 1.5. The increased solids in the process streams raised the hydrotreater space velocity and increased the rate of catalyst aging, as measured by the pounds of resid, UC and ash per pound of catalyst.

The recycle test resulted in significantly increased coal conversion. The 94% coal conversion obtained in period 249H is the highest obtained with subbituminous coal at Wilsonville. It is notable that this high conversion was obtained with a moderate dissolver temperature of 802°F. The increased coal conversion was probably due to additional conversion of the unconverted coal in the recycle stream. There is a possibility that the recycled ash and iron oxide may have contributed to enhanced reactivity.

The yield results are similar to 249E, but the hydrogen consumption was higher. The higher hydrogen consumption resulted from overconverting resid during the test. However, these results were encouraging and suggest that a vacuum tower could be used as an alternate method of removing ash from the system. The energy rejection of 35% reflects a solvent content of 8.3% on an ash-free basis, or 2.2% MAF coal. The energy rejection on a solvent-free basis would be 31%.

A comparison of results with the RITSL and ITSL configuration is shown in Slides 12 and 13. A number of differences are apparent in the operating conditions. In particular, Run 249E had a lower dissolver temperature and a considerably higher hydrotreater temperature. Also, 249E had a forced back-mixed dissolver while 246G did not. However, the yields are fairly similar. As a result of the transfer of resid conversion to the hydrotreater, 249E had a lower gas make. The 249E distillate yield was greater, but, as mentioned above, the resid make was -4. The sum of distillate and resid is comparable for the two periods. Resid conversion in the hydrotreater was 17% and 28% for 246G and 249E, respectively. Several factors may have contributed to the higher hydrogen consumption of 249E, but the RITSL configuration and overconverting resid are probably the main reasons.

The comparison of Runs 249 and 246 may also be considered for the effect of the back-mixed reactor in 249. However, as just mentioned, the differences of temperatures, configuration, etc., make any clear-cut conclusion difficult about the effect of back-mixing on yields.

At the end of Run 249, the back-mixing pump was stopped to determine the effects of not mixing. There was no significant effect on thermal unit yields.

The hydrotreater catalyst performed adequately throughout the run and a catalyst age of 1870 lb (resid + UC + ash)/lb was reached. The catalyst used for Run 249 was the Shell 324 catalyst used in Run 246, with an initial age of 617 lb resid/lb. Moderate catalyst deactivation was observed during the run, but the resid conversion activity appeared to be relatively constant over the last half of the run.

A comparison of the product liquid from Run 249 to the product of Run 246 is shown in Slide 14. The RITSL configuration resulted in a higher hydrogen content for each fraction than for those obtained in the ITSL configuration of Run 246. This same effect was seen in earlier comparisons of products from the RITSL and ITSL configurations using bituminous coal (6). The improved hydrogen content appears to be a natural consequence of having an increased content of hydrotreated product in the total product blend with the RITSL configuration. The percent of the total product that was from the hydrotreater was 44 and 53% for the ITSL and RITSL samples, respectively. The overall product with the RITSL configuration is lighter because of an increase in the fraction of naphtha product from 19 to 31% of the total. The heteroatom content also shows the quality improvement in the RITSL configuration.

RUN 250

Run 250 is briefly summarized in Slide 15. A more detailed discussion of Run 250 is presented in a separate paper (7). This was the first Wilsonville run in the Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL) configuration, which is shown in Slide 16. CC-ITSL is similar to RITSL (See Slide 9) except the output of the liquefaction stage is not depressured before being fed to the hydrotreater. This process simplification has economic impacts which will be discussed later.

For this run, no catalyst was used in the first stage. Two NiMo catalysts were tested in the hydrotreater. The run was begun with aged Shell 324, which has a unimodal pore structure. The second catalyst used was Amocat 1C, which has a bimodal pore structure. both catalysts performed adequately, but the bimodal catalyst appeared to have a lower deactivation rate (7).

Selected yield data are shown in Slide 17. For these periods, coal space velocity was varied from 25 to 45 lb MF coal/hr-ft^3 by changing coal feed rate from 180 to 340 lb MF coal/hr. As space velocity was increased the temperatures of both the thermal and catalytic stages were increased to maintain a level of resid conversion that would produce an "all-distillate" yield slate, which is defined as 0-5% resid yield. As can be seen, sufficient resid conversion was obtained at the two lowest space velocities. However, at the highest space velocity the resid yield was 7%.

The total liquid yield (distillate + resid) was in the 62-65% range, which is the same as previously obtained in the ITSL configuration (7). Thus, the CC-ITSL configuration did not show a significant yield advantage for bituminous coal. However, the run did demonstrate good operability and improved product quality for the CC-ITSL configuration.

ACCOMPLISHMENTS

The successful completion of RITSL runs with both bituminous and subbituminous coal demonstrated that catalyst deactivation would not be excessive in a close-coupled configuration. This was subsequently confirmed by the close-coupled run with bituminous coal. Comparative operating results were obtained using two hydrotreating catalysts.

The potential for improved coal liquefaction economics was demonstrated for the CC-ITSL configuration. Also, an alternate method of removing ash from the system was demonstrated by the ash recycle tests.

CSD operating experience was broadened by successful deashing of the different feeds that resulted from the hydrotreating before deashing in the RITSL and CC-ITSL configurations.

FUTURE WORK

Work continues in the experimentation with close-coupled reactors. The next run will use catalysts in both the liquefaction and hydrotreating reactors with ash recycle and will use bituminous coal. Tests will then be made using subbituminous coal in both thermal-catalytic and catalytic-catalytic versions of the close-coupled configuration. Evaluation tests are being made with alternate catalysts to determine the optimum combination of catalysts and conditions.