PART 3 COAL LIQUEFACTION

Section 10

RECENT LIQUEFACTION DEVELOPMENT AT WILSONVILLE PLANT WITH CLOSE-COUPLED REACTORS

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ABSTRACT

Two integrated runs were completed during the past year at the Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama with direct coupling of the two reactors using Illinois No. 6 and Wyodak coals. In both these runs a catalytic second-stage reactor was used while the first reactor was operating either with a catalyst or without a catalyst. Both unimodal and bimodal catalysts were tested in these runs.

Results from these runs will illustrate the promising advancements being made in coal liquefaction technology by current research. Product yield and product quality data will be discussed. Catalyst performance will be discussed in terms of deactivation rates and replacement rate. Results from batch deactivation of a Ni-Mo catalyst in the first stage and their implications in the context of catalyst cascading will be discussed. Relative economics of various process options will be presented on a broad basis. Finally some of the results from the ITSL process modeling work will be presented.

INTRODUCTION

The Advanced Coal Liquefaction R & D Facility at Wilsonville, Alabama has been operating for over 13 years to develop alternate technologies for producing low cost fuels. A recently completed close-coupled integrated (CC-ITSL) scheme was an important development in the Wilsonville program for making clean 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 UE & C -Catalytic, formerly known as Catalytic, Inc., under the management of Southern Company Services, Inc. Amoco Oil Corporation became a sponsor in 1984 through an agreement with EPRI. UE & C -Catalytic became a sponsor beginning FY 1987. Kerr-McGee Corporation and Hydrocarbon Research, Inc. have participated by providing Critical Solvent Deashing (CSD) technology and H-OIL® ebullated-bed hydrotreater design, respectively.

The close-coupled process consists of two H-OIL® ebullated-bed reactors and a CSD unit. A supported hydrotreating catalyst is used in the second reactor while a catalyst is optional in the first reactor. The current CC-ITSL process option has evolved from the ITSL operation. The reconfigured ITSL (RITSL) was a step between the ITSL and CC-ITSL process developments. ITSL employed the CSD unit between the two reaction stages while RITSL and CC-ITSL employed the two reactors in series followed by the CSD. Accordingly, the hydrotreating catalyst was exposed to an ash-, unconverted coal (UC)-, and preasphaltene-rich environment in the RITSL and CC-ITSL configurations. As the name implies, in the CC-ITSL mode the two reactors were directly coupled without any pressure letdown. The interreactor cooling was done only to the extent required to control the second reactor temperature. Such close-coupled operation should offer several process benefits such as increased overall thermal efficiency, reduced potential for retrogressive reactions which may take place in the absence of hydrogen at longer residence times, and improved product quality.

This paper is focused on two stage coal liquefaction process performance with close-coupled reactors (Slide 2). Results are presented for two runs: Run 251 and Run 252. Run 251 was conducted in three parts. The first part (Run 251-I) was with a catalytic first-stage and Illinois No. 6 coal. The second part (Run 251-II) was with a thermal first-stage and Wyodak coal. The third part (Run 251-III) was with a catalytic first-stage and Wyodak coal. Run 252 was a catalytic-catalytic run with Illinois #6 coal to study the major aspects of the catalyst cascading concept. Product yield and product quality data are discussed. Appropriate comparisons of catalyst and configurations are made in terms of product yields. The effect of higher system space velocity is discussed. The performance of the catalysts is discussed in terms of process derived deactivation trends and catalyst replacement rates. The relative economics of the CC-ITSL process are discussed on a broad basis. Finally results from the ITSL process modeling work are presented (9).

PROCESS DESCRIPTION

A block flow diagram of the catalytic-catalytic CC-ITSL process is shown in Slide 3. The process consists of a slurry preparation step and two catalytic reaction stages followed by hydrotreated solvent recovery and critical solvent deashing systems. The system was integrated by the recycle of CSD resid, hydrotreated solvent, and low-pressure flash bottoms containing ash, unconverted coal, hydrotreated resid, and hydrotreated solvent. Solids recycle allowed an increased concentration of solids in the CSD feed and hence a lower CSD feed rate. The solvent recovery system consists of atmospheric flash and vacuum flash equipment. Note that an interstage vapor separator was installed between the two reactors. In Run 252 the recycle distillate was fractionated in a vacuum tower to reduce the light ends (650°F⁻ fraction) in the recycle solvent.

CATALYSTS

Unimodal and bimodal catalysts were used in the two runs (Slide 4). Amocat IA is a bimodal CoMo catalyst and was used as a first stage catalyst in Run 251 with bituminous coal. Amocat IC is a NiMo bimodal catalyst and was generally used in the second stage. However, in Run 252, an Amocat IC blend of different aging histories was used in the first stage to determine the stability of the catalyst relative to a CoMo catalyst. Shell 324 is a NiMo unimodal catalyst and was used in both the stages of Run 251 Part III with subbituminous coal.

SOLIDS RECYCLE

The concept of solids recycle was first tested in Run 249 with subbituminous coal in the RITSL mode and was further explored near the end of thermal-catalytic Run 250. A significant finding was 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 that had been demonstrated in an integrated operation in a sustained manner. Solids recycle reduced the CSD feed rate by about 50% which would have a significant impact on CSD plant capital requirements. Also there was a 1-2% improvement in coal conversion in the solids recycle mode. Some of the undesirable effects of solids recycle are concentration of "refractory" type resid in the recycle stream, increased maintenance costs for pumps, lines, and valves, and possibly reduced coal throughput.

With current knowledge it is premature to say that solids recycle is the preferred way of integration because the penalties associated with the solids recycle are not clearly understood at this time. However, because of its significant impact on potential TSL distillate yield (distillate plus resid), solids recycle has been continued from Run 251 onwards. A detailed study is warranted to better understand the effects of solids recycle on reaction performance and other aspects of the process.

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 (1,2). 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.

RUN 251 - PART I STUDIES

Part I of Run 251 employed a catalytic first stage with Illinois No. 6 coal (Slide 5). Amocat 1A, a bimodal CoMo catalyst, was used in the first reactor and Amocat 1C, a bimodal NiMo catalyst, was used in the second reactor. Based on the positive results from ash recycle observed in Run 250, solids recycle was continued in Run

251. The highest distillate yield obtained in Run 251 was 70% MAF at a coal throughput of 300 MF lb/hr. The product quality was similar to Run 250. Other results are shown in Slide 5.

RUN 250 (SOLIDS RECYCLE) vs RUN 251-I COMPARISON

The main difference between Run 250 (solids recycle) and Run 251-I is the first stage catalyst. A thermal first stage was used in Run 250 compared to a catalytic first stage in Run 251-I. A comparison of the operating conditions (Slide 6) shows that a 45°F lower first-stage temperature, about 68% higher coal feed rate, about 65% higher second stage space velocity, and a more highly aged second stage catalyst were employed in the catalytic-catalytic CC-ITSL run.

Comparing the yields, distillate yield was the same for both modes of operation, being about 61% (Slide 7). However, the gas yield was significantly lower with catalyst in the first stage, 5% MAF coal in Run 251-I vs 8% in Run 250H. The lower gas yield is reflected in lower hydrogen consumption in Run 251-I compared to Run 250H. The main effect of first-stage catalyst was to increase coal throughput through additional resid conversion in the first stage without a corresponding increase in C₁-C₃ gas yield. In the first stage, the C₄+ distillate yield was 43% MAF with catalyst (Run 251-IB) compared to 33% MAF without the catalyst (Run 250H). The selectivity of C₁-C₃ to C₄+ distillate yield in the first reactor was lower by a factor of 1.5 with the catalyst. All these yield improvements with the catalyst in the first stage were obtained without a penalty in the coal throughput. This can be seen by comparing the coal throughputs, which were 280 lb/hr in Run 250H versus 470 lb/hr in Run 251-IB.

SPACE VELOCITY STUDIES

Run 251 started with a high coal feed rate of about 480 MF lb/hr at which the two-stage resid yield was a little above 5% MAF. This extra resid could be converted either by increasing the reactor temperature(s) or by reducing the coal feed rate. The latter option was selected based on a consideration of improving the overall yields rather than just converting the excess resid. The coal feed rate was dropped from 480 MF lb/hr in Run 251-IC to 300 MF lb/hr in Run 251-IE. Other operating conditions as shown in Slide 8 are similar except that the catalyst age was higher in both the reactors at the lower coal feed rate.

The yield results in Slide 9 show impressive improvements at the lower coal feed rate conditions. The C₄+ distillate yield was 70% MAF in Run 251-IE which was the highest ever achieved at Wilsonville. This was accomplished without a significant negative resid yield. In Run 251-IE, the hydrogen consumption was higher but the hydrogen efficiency was similar. The increase in C₁-C₃ gas make at lower coal feed rate was not significant compared to that expected from a proportionate temperature increase in the first stage to convert the excess resid. Organic rejection was significantly lower in Run 251-IE through the use of a stronger CSD deashing solvent.

PRODUCT QUALITY

A product quality comparison for thermal-catalytic and catalytic-catalytic is shown in Slide 10. The data were obtained on blends by mixing product streams in the proportions of their production rates. The coal space velocities were roughly similar in Run 250H and Run 251-IE but the second stage catalyst age was higher in Run 251-IE by a factor of four. For comparable fractions the hydrogen contents were similar, but there was more naphtha and distillate in Run 250H blend. The higher first-stage temperature in Run 250H might have promoted the cracking reactions to form more light cuts. From the data presented in Slide 10, naphtha production rate appears to be a strong function of reactor temperature rather than of space velocity. The nitrogen and oxygen were lower in the products from the low space velocity catalytic-catalytic portion of Run 251-I. Also, sulfur contents were particularly low in the catalytic-catalytic configuration. The gas oil fraction was a higher percentage of the product blend in the catalytic-catalytic tests. Lower first-stage temperatures and/or higher coal feed rate during the catalyticcatalytic test periods are some possible reasons.

CATALYST ANALYSES

The second stage catalyst analyses are given in Slide 11. In general, there were significant losses in pore volume and surface area in all the runs. Most of these losses were recovered to a significant extent after the coke burn-off step. The small differences in the carbon contents might be related to the operating temperature differences. In spite of the higher age on the Run 251-I catalyst, the catalyst had more pore volume, surface area, and a lower amount of titanium. This may be related to the guard bed action provided by the first-stage catalyst and the lower resid concentration in the second-stage feed.

At the end of Run 251-I, both Amocat 1A (first-stage) and Amocat 1C (second-stage) had the same age (Slide 12). Since Amocat 1A was at the beginning of the reaction train and was exposed to the highest temperature in the process, it accumulated more carbon and metals than the second-stage catalyst. The fractional loss in naphthalene activity was also higher for the first-stage catalyst which is consistent with the resid conversion activity trends.

RUN 251 PART II

The second part of Run 251 was with Wyodak coal in a thermal-catalytic closecoupled configuration (Slide 13). Iron oxide catalyst was added to the coal slurry. Based on the favorable results obtained at the end of Run 249 solids recycle was employed throughout the run. The operability of the run was good. There are two key accomplishments in this run. First, the distillate yield was the highest ever seen with subbituminous coal in the Wilsonville operations, the yield being 61% MAF. Second, the organic rejection was the lowest ever seen in the Wilsonville operations with any coal. The organic rejection was 9% MAF coal. All these improvements were obtained at a moderately high space velocity.

A comparison of the close-coupled operation with the RITSL operation is shown in Slides 14 and 15. Note that solids recycle was employed in both the runs. The coal feed rate was about 40% higher in the close-coupled run and this required higher reactor temperatures. The iron oxide dosage in the close-coupled operation was about half that of the RITSL operation. Because of the solids recycle, the total iron oxide input to the reactor was about three times that of the net addition rate. Note that in Run 249H, the CSD was not operated during the solids recycle period and the ash was removed by purging vacuum bottoms.

In the yield table (Slide 15), two types of yield structures are shown for the RITSL run. The actual yields are obtained with the vacuum concentrate as the ash purge stream. Near the end of Run 249, the CSD was operated separately with the vacuum concentrate feed collected from the previous solids recycle operations. Based on this CSD performance, the solids recycle two-stage yields were adjusted to include CSD in the process loop and the adjusted yields were shown as projected

yields in Slide 15. By including CSD in the process loop, the organic rejection was reduced from 26% to 14% MAF and the two-stage resid yield increased from -7% to +4% MAF due to the recovery of the resid and distillate in the vacuum bottoms.

Comparing CC-ITSL with RITSL, the organic rejection was significantly lower in the CC-ITSL operation. The distillate yield in the CC-ITSL operation was the highest ever achieved, being 61% MAF. This was accomplished at a 40% higher coal throughput.

RUN 251 PART III

The third part of Run 25] was with Wyodak coal in a catalytic-catalytic closecoupled configuration (Slide 16). Shell 324 NiMo catalyst was used in both stages. Iron oxide catalyst was added to the coal slurry. The operability of the run was good. There are two accomplishments in this run. First, the product quality was better and second, the products were lighter, compared to the thermal-catalytic run. However, the hydrogen efficiency was lower mainly due to more water and C_1-C_3 gas formation. The catalyst deactivation rate was low in the first stage and was insignificant in the second stage in the range of catalyst age studied.

A comparison of the catalytic-catalytic operation (Run 251-IIB) with the thermal-catalytic operation (Run 251-IIIB) is shown in Slides 14 and 15. At a first look at the operating conditions in Slide 14 it may be surprising to notice a higher first-stage temperature with a catalyst in the first stage, particularly when the coal feed rate was the same in both the periods. The run started at a lower first-stage temperature but the coal conversion was low which prompted to increase the first-stage temperature. The resid conversion activity of the Shell 324 catalyst was excellent as indicated by a low first-stage resid yield of 21% MAF coal in Run 251-IIIB versus 34% MAF in Run 251-IIB.

In general the two-stage yields did not improve by using a catalyst in the firststage (Slide 15). Compared to the thermal-catalytic operation the distillate yield was the same; the C_1-C_3 gas make, hydrogen consumption, and water yields were significantly higher; and the hydrogen efficiency was lower. Fresh catalyst and a higher temperature in the second-stage may have contributed to the slightly higher organic rejection in Run 251-IIIB.

At the same coal feed rate, the (resid + UC) conversion across the two reactors was the same, being equal to 13% MAF, with and without a catalyst in the first stage. Further, this equal (resid + UC) conversion in catalytic-catalytic operation was obtained at a much higher thermal severity in both reactors. These results indicate an imbalance in the reactor temperatures. An experiment was conceived near the end of the run to lower the first-stage temperature in an attempt to lower the C1-C3 gas make and shift part of the resid conversion load from the first stage to the second stage. But the run ended without completing the test due to time limitations.

The "optimum" conditions for processing Illinois #6 and Wyodak coals are completely different because the kinetic rates of two key reaction steps, namely, coal conversion and resid conversion, differ drastically for the two coals. In order to achieve a high (resid + UC) conversion the limiting step with Illinois #6 coal is resid conversion whereas with Wyodak coal it is coal conversion. Solvent quality demands are much more for Wyodak coal than for Illinois #6 coal. A good balance between the first and second stage temperatures is crucial to the Wyodak coal conversion. A more exhaustive study is needed to identify the preferable region of operating conditions for Wyodak coal. There is a good potential to improve the yields and/or increase the coal throughput with Wyodak coal.

WYODAK PRODUCT QUALITY

A product quality comparison for RITSL thermal-catalytic, CC-ITSL thermalcatalytic, and CC-ITSL catalytic-catalytic is shown in Slide 17. For comparable fractions the hydrogen contents were similar, but there was more naphtha in the CC-ITSL catalytic-catalytic operation. The higher first stage temperature and first-stage catalyst may be the reasons for the lighter product slate in Run 251-IIIB. The nitrogen contents of the gas oil fractions were higher in CC-ITSL runs for reasons not obvious. It is surprising to notice higher nitrogen with a fresh NiMo catalyst in the first stage and a higher first stage temperature.

Illinois #6 and Wyodak coal liquids from the CC-ITSL catalytic-catalytic operations are compared in Slides 10 and 17. The product slate for Wyodak coal was much lighter and the gas oil fraction had about 1% more hydrogen. Again, the reason for higher nitrogen content in the Wyodak gas oil fraction is not known.

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 (3). Such a plot is shown in Slide 18 for both the stages in Run 251. General observations are: 1) second stage catalyst deactivation rate was insignificant with both the coals 2) first stage catalyst deactivation rate was low and essentially the same for both the coals. It should be noted in Slide 18 that the lines were drawn only up to the point the data was collected. Run 251 was the first Wilsonville run in which record high catalyst ages were reached. The highest age was about 2800 lb (resid + CI)/lb catalyst. The details of catalyst deactivation equations are available in the run report (5).

CATALYST CASCADING

Catalyst replacement rate estimations using the process derived deactivation and reaction kinetics showed considerably lower replacement rates in catalyticcatalytic compared to the thermal-catalytic operation. Catalyst cascading has the potential to further reduce the replacement rate. This concept is based on using the withdrawn catalyst from the second stage for replacement of the first stage catalyst. In a commercial operation, fresh catalyst will be added to the second stage and the catalyst withdrawn from the second stage will be added to the first stage (Slide 19). If the first stage requires more than the amount of catalyst withdrawn from the second stage.

RUN 252 - CASCADING SIMULATION

It is not possible to perform a true steady-state cascading run at Wilsonville since only one of the two close-coupled reactors has catalyst addition-withdrawal capability. Therefore, the cascading operation was simulated to the extent possible by loading a blend of aged Amocat IC catalysts from the second stage and fresh Amocat IC catalyst to the first-stage and collecting batch deactivation data. The batch deactivation trends can then be used to bracket the catalyst requirements for the first stage. The key information obtained from Run 252 was the stability of the NiMo Amocat 1C catalyst under the high temperature conditions in the first reactor. Prior to doing Run 252 there were some preconceived objections to the use of nickel-based catalysts in the high temperature first stage. The results from HRI and Wilsonville did not indicate any major problems, with respect to the reaction performance maintenance, with Amocat 1C in the high temperature reactor.

In general, the operability in Run 252 was good until the unit was shutdown due to a plug in the first-stage reactor which formed after the ebullating pump was shutoff. The yields and product quality were similar to Run 251. The first stage catalyst deactivation rate in the early stages was similar to the Amocat IA decay rate in Run 251. The second stage deactivation rate was insignificant (Slide 20).

A comparison of the performance with Run 251 (Amocat 1A) is shown in Slides 21 and 22. In Run 252-B1, the coal feed rate was higher by 50 lb/hr; the second-stage catalyst was younger but this advantage was partly offset by a lower second-stage temperature. There were no major differences in the yields. The distillate yield was 70% MAF in Run 251-IE and 69% MAF in Run 252-B1.

FIRST STAGE CATALYST DEACTIVATION

Run 252 first-stage resid + UC conversion rate constant was plotted as a function of catalyst age in Slide 23. On the same plot the rate constants calculated using Run 251 deactivation parameters are shown as a dashed line. Since the first stage catalyst was a blend, a weighted average rate constant was calculated by summing the activity contributions from each fraction of mixed population. There were no assumptions in this calculation other than the standard CSTR assumption. In fact this procedure was implicitly used in the catalyst requirement calculations which are routinely being done at Wilsonville and other places.

The agreement between the actual performance in Run 252 and the performance predicted from Run 251 data was good up to a mean catalyst age of 2800. There was a major disagreement near the end of the run. The limited number of data points at the end suggest either a flat or rising activity trend. Several factors could have collectively contributed to the observed deviation. First, in Run 251 the deactivation line was extrapolated after an age of 2800. Second, there was a coal pile change in the vicinity of the observed deviation. Third, catalyst fines were noticed in the reactor when the reactor was opened after the plug formation. Smaller catalyst particles would have higher effective activity (higher effectiveness factor) than larger particles.

The solid line in Slide 22 represents calculated data using Run 251 deactivation parameters up to an age of 3000 and assuming a lower deactivation rate (an arbitrary value of 0.00005) after 3000 age, instead of extrapolating Run 251 data. This change in rate parameters helped to improve the fit. The three deactivation parameters listed in Slide 22 give a good fit between calculated and actual Run 252 data in an overall sense. Of course, one could improve the fit by including more parameters but the reliability of the parameters may be questionable with limited data. The above set of parameters is by no means the optimal one and is simply one of the several possible sets. Another possible set based on asymptotic approach is available in the run report (10).

FIRST STAGE GUARD BED EFFECTS

In catalytic-catalytic operation the first-stage catalyst accumulates some of the components responsible for catalyst deactivation, thereby reducing their concentration in the second-stage feed which in effect slows down the second-stage catalyst deactivation rate. A comparison of the second stage catalyst deactivation trends (Slide 24) in thermal-catalytic (Run 250) and catalytic-catalytic (Runs 251 & 252) runs shows an order of magnitude difference in the deactivation rate constant which clearly supports the guard-bed concept.

A second observation from Slide 24 is that the second stage feed reactivity was significantly reduced by putting a catalyst in the first stage. In catalytic-catalytic operation most of the "easily-convertable" resid was converted in the first stage leaving the difficult parts to the second stage.

CATALYST REQUIREMENTS IN CASCADING

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 an "all-distillate" product slate. The usefulness of this approach has been demonstrated in the Wilsonville Run 245 (4).

The catalyst replacement rates as a function of the first-stage resid yield are shown in Slide 25 for two different coal feed rates. The estimates are based on fresh catalyst additions to both the reactors. In actual cascading operation the second stage catalyst would be added to the first stage. However, the estimates shown in Slide 25 are useful to place a lower limit on the rates and to understand the interrelationships among first-stage resid yield, replacement rates, and coal feed rates. The curves in Slide 25 were generated under the conditions of 300 lb catalyst in each reactor, 810°F first stage temperature, 760°F second stage temperature, 2:1 solvent-to-coal ratio, 12% CI and 38% resid in recycle solvent; 93% coal conversion, and 9% CSD resid rejection.

Coal feed rate had a tremendous impact on the catalyst requirements and the distribution of load between the two reactors. The minimum total catalyst requirement at 500 MF lb/hr coal rate is double that at 375 MF lb/hr. More interesting is the result that the "optimum" first stage resid yield is significantly lower at the higher coal feed rate. Another interesting result is that at the higher coal feed rate the second stage catalyst replacement rate is insignificant compared to the first stage rate. This simulation result suggests that the economic benefits from cascading may not be as great as one would envision from equal replacement rates to both the reactors. Cascading may become economically more attractive if reactor work loads are "optimized" through an experimental search of the severity space.

It should be noted that the actual replacement rates shown in Slide 25 may not be accurate but the trends and the relative values are important in understanding the subject of catalyst replacement rates.

PRODUCT QUALITY

Run 252 product quality data is given in Slide 26. The recycle distillate was fractionated in a vacuum column to reduce the light ends in the recycle solvent. The product blends were made before and after fractionation. A comparison of the results with and without fractionation shows small improvements in product quality with fractionation. The gas oil was 30% of the blend with fractionation versus 35% without fractionation. The product end-point was reduced from 910°F without

fractionation to 870°F with fractionation. Also, the API gravity of the gas fraction was higher with fractionation. It should be noted that no attempt was made, in terms of changing the reaction conditions, to reduce the gas oil fraction in the product.

Although small improvements were noticed with fractionation in Run 252, there were no major differences between Run 251-IE and Run 252-Bl (with fractionation). This result indicates that on the whole there was no major shift in the distribution of the distillation cuts by recycling a heavier distillation cut.

RELATIVE ECONOMICS

The ultimate utilization of coal liquefaction technology will depend heavily on economics. The impact of recent process developments on relative process economics was discussed in a previous paper (6).

A summary of those results is shown in Slide 27. The cost factors of the two-stage processes are shown relative to the H-Coal process. The total plant capital and operating costs both increased as the plants became more sophisticated in their modes of integration. However, these increased costs were accompanied by increased product rates and improved product qualities, so the value of the products was increased. The required product selling price combines these factors to give a relative cost of crude-oil-equivalent product.

It was concluded that the results through Run 250 would provide a reduction in required product selling price of approximately 20-25% relative to H-Coal (6). The results obtained in Run 251 indicated an additional 3-5% improvement in economics due to increased yields and higher space velocities. Thus, theses recent results demonstrated process advancements that show a 25-30% economic advantage over the H-Coal process. Amoco Corporation studies indicate much higher improvements, of the order of 60% (11).

These results illustrate the significant advancements being made in coal liquefaction technology by current R & D. A detailed cost study is needed to evaluate the many tradeoffs that must be considered within the selected processes.

ITSL PROCESS MODELING

ITSL process modeling was one of the major tasks at Wilsonville in FY 1986. The main objective of this task is to reduce the enormous amount of yield data collected over a period of two to three years into a compact and more usable form. The model was developed for Illinois No. 6 bituminous coal. Process data from the pilot plant Runs 243, 244, 245, and 248 in the ITSL configuration and from the batch autoclave kinetic runs were used in the model development. A unique feature of the Wilsonville pilot plant is that truly representative steady-state data are obtained since the process is operated in a continuous manner. This significantly enhances the data used in the modeling effort.

There has been an enormous amount of work done at universities and research institutions on liquefaction kinetics. Unfortunately, these models are not applicable to the Wilsonville process for a variety of reasons, the most important being the use of solubility-phenomena-based product lumps in the literature models. In the Wilsonville pilot plant, the process yields are measured in terms of gases and distillation cuts. Thus, a significant part of the modeling effort was to develop kinetic models for the thermal reaction section as well as the catalytic reaction section. We developed kinetics for all the products from the individual units using data from the plant as well as from a batch autoclave. The batch autoclave system used in the kinetic studies is one of the best in the country for obtaining accurate yield data (7).

Reactor models were developed by combining the kinetic equations and the material balance equations for the reactors. A CSTR model was used for the thermal reactor based on a radioactive tracer study completed in 1984. Finally, ASPEN was used to integrate the unit models and some key flash separators. The ASPEN runs were made on the Pittsburgh Energy Technology Center's (PETC) computer through a cooperative arrangement between PETC and Catalytic, Inc. for ASPEN (Public) application in the Wilsonville ITSL process modeling.

The ITSL process modeling work is described in detail in a separate topical report (8) and a paper (9). Slide 28 shows a comparison of the model fitted data to the elementally-balanced plant data for a selected material balance period. The stream flow rates as well as the yields are seen to compare closely.

1986 ACCOMPLISHMENTS

There are several noteworthy accomplishments in 1986. These are listed in Slide 29 and are self explanatory. Improvements were made in several areas including process yields, coal throughputs, catalyst replacement rates, process modeling, and process economics. The magnitude of these improvements were not expected prior to doing the research work. Further advancements in coal liquefaction technology are possible through additional research.

FUTURE WORK

Various aspects of the future work are listed in Slide 30. In catalyst cascading, more work can be extracted out of the catalyst by grinding the catalyst withdrawn from the first reactor and adding it to the coal slurry. The elimination of the interstage separator without a large sacrifice in yields or coal throughput would have a significant impact on coal liquefaction economics. Perhaps the best potential candidate in the list for reducing the dollars per barrel of the liquid product is system pressure. Lower system pressure could significantly reduce capital and operating costs. Up to now the Wilsonville plant has concentrated on two coals: Illinois No. 6 and Wyodak coals. The future plans include testing other coals with two objectives. First, to expand the close-coupled technology data-base and second, to improve the coal liquefaction economics.

Other future experimental studies are related to process solvent modifications and alternate catalyst evaluations. Process modeling work will be continued with the objective of developing a simulation model for the close coupled ITSL process.

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project organization

sponsors

- U.S. Department of Energy
- Electric Power Research Institute
- □ Amoco Corporation
- □ Southern Company Services, Inc.
- UE&C-Catalytic

participants

- UE&C-Catalytic
- □ Kerr-McGee Corporation
- Hydrocarbon Research, Inc.

introduction

- 🗆 two runs
- close-coupled configuration thermal-catalytic catalytic-catalytic solids recycle
- 🗆 coals
 - bituminous subbituminous
- □ catalysts
 - iron oxide
 - Shell 324 Amocat 1A
 - Amout IA
 - Amocat 1C

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



catalyst (size)	Shell 324	Amocat IC	Amocat 1A	Shell 317	
RUN(s)	250,251	250,251 250-252		253-	
shape	(- cylindrical)	tri-lobe	
size	1/32"	(1/	16")	1/20"	
Ni (wt%)	2.7	2.3		2.7	
Co			2.5		
Мо	13.2	10.4	9.8	11.6	
surface area, m ² /g	165	190	235	235	
pore volume, cc/g	0.48	0.85	0.80	0.75	
pore size distribution	unimodal	(- bimodal	·)	
compacted bulk density, lb/ft ³	54	42	41	36	

Wilsonville CC-ITSL catalyst properties

RUN 251 - part I close-coupled catalytic-catalytic ITSL

features	results
☐ Illinois no. 6 coal □ catalysts first stage - Amocat 1A	□ good operability □ highest distillate yield - 70% MAF
second stage - Amocat 1C	 product quality similar to Run 250 increased coal throughputs "all distillate" product slate product quality not affected
	 Iow organic rejection (resid+UC) conversion decay rate first stage - low second stage - very low

close-coupled ITSL thermal vs catalytic 1st stage bituminous coal solids recycle

TSL operating conditions

run no	250H	251-IB
first stage		······································
catalyst	none	Amocat 1A
average reactor temperature ('F)	835	790
inist hydrogen partial pressure (psi)	2400	2600
coal feed rate (Ib/hr MF)	280	470
snace velocity [ib feed/br-ib cat]	-	4.2
solvent-to-coal ratio	2.0	2.0
solvent resid content (wt%)	40	40
catalyst age[ib (resid + Ci)/ib cat]	-	850-1050
second stage		
catalyst	(Am	ocat 1C)
reactor temperature ("F)	760	760
space velocity [ib feed/hr-ib cat]	2.3	3.8
feed resid content (wt%)	46	40
catalyst age[Ib (resid + CI) /Ib cat]	500-650	1300-1450

close-coupled ITSL thermal vs catalytic 1st stage bituminous coal solids recycle

solids recycle	TSL yield structures		
run no first stage catalyst	250H none	251-IB Amocat 1A	
yield (Xmaf coal) C ₁ - C ₃ gas (total gas) water C ₄ + distillate resid hydrogen consumption hydrogen efficiency (16 C ₄ + dist/16 H ₂ consumed)	8(13) 9 62 7 -6.5 9.5	5(9) 11 61 5 -6.2 9.9	
distillate selectivity (ib $C_1 - C_3$ /ib C_4 + dist) energy content of feed coal rejected to ash conc. (%)	0.12 18	0.08 23	
organics rejected to ash conc. (%maf coal)	15	20	

close-coupled catalytic-catalytic ITSL space velocity studies bituminous coal solids recycle

TSL operating conditions

run no	251-IC	251-IE
first stage		
catalyst	(Amo	cat 1A)
average reactor temperature ("F)	805	810
injet hydrogen partial pressure (psi)	2550	2450
coal feed rate (Ib/hr MF)	480	300
space velocity[lb feed/hr~lb cat]	4.2	2.7
solvent-to-coal ratio	2.0	2.0
solvent resid content (wt%)	40	40
catalyst age[ib (resid + Ci) / ib cat]	1200-1700	2150-2250
second stage		
catalyst	(Amo	cat 1C)
reactor temperature ("F)	760	760
space velocity[ib feed/hr-ib cat]	3.8	2.3
feed resid content (wt%)	40	40
catalyst age[lb (resid + Cl) / lb cat]	1550-2000	2300-2350

close-coupled catalytic-catalytic ITSL space velocity studies bituminous coal solids recycle	TSL yield structures		
run no	251-IC	251-IE	
yleid (Xmaf coal)			
C ₁ - C ₃ gas (total gas)	6(11)	7(12)	
water	10	10	
C4 + distillate	61	70	
resid	6	-1	
hydrogen consumption	-6.0	-6.8	
hydrogen efficiency (ib C_4 + dist/ib H_2 consumed)	10.1	10.3	
distillate selectivity (ib $C_1 - C_3$ / ib C_4 + dist)	0.10	0.11	
energy content of feed coal rejected to ash conc. (%)	19	17	
organics rejected to ash conc. (%maf coal)	18	15	

properties of distillate products thermal-catalytic vs catalytic-catalytic comparison close-coupled ITSL mode bituminous coal

		elemental (wt%)					
distilation cut	crude	С	Н	Ν.	S	O(diff)	•API
RUN 250H (thermal-cat)							
naphta (IBP-350°F)	26.8	84.54	14.04	0.03	0.11	1.28	50,4
distillate (350-650°F)	51.7	87.54	11.59	0.17	0.07	0.63	24.4
gas oli (650°F+)	21.5	88.88	10.21	0.28	0.08	0.55	14.1
RUN 251C (cat-cat, high WHSV)							
naphta (IBP-350'F)	21.1	84.29	13.87	0,03	0.04	1.77	53.2
distillate (350-650°F)	49.2	86.75	11.24	0.20	0.02	1.79	23.7
gas oil (650°F+)	29.8	88.45	10.27	0.33	0.03	0.92	10.6
RUN 251-1E (cat-cat)							
naphta (iBP-350°F)	20.9	85.90	13.98	0.03	0.05	0.04	50.9
distillate (350-650°F)	42.9	87.77	11.81	0.13	0.02	0.27	24.2
gas oil (650°F+)	36.2	89.64	10.04	0.21	0.03	0.08	09.4

'nitrogen by Kjeldahi

second stage catalyst analyses bituminous coal

catalyst (size)		Shell 324 (1/32)			
run	fresh	250		251-1	247
solids recycle		по	yes	yes	no
age lib (resid + Ci)/lb cat]	0	1205	670	2780	1225
highest average bed temp (°F)	-	750	760	775	710
analyses *pore vol /cc/n cathaged	0.70	0.31	0.43	0.41	0.24(0.45)+
after coke burn-off		0.58	0.63	0.60	0.38
*surface area (m²/g cat)-aged	253	165	212	196	163(185) ⁺
after coke burn-off		226	243	229	
carbon (wt%)		10.3	9.9	11.1	8.3
titenium (wt%)		1.0	0.7	0.6	0.6
iron (wrthi)		0.2		0.2	0.3
calcium (wt%)		Ó	0	0.1	0.1
eodium (wt%)		0.2	0.1	0.6	1.5
naphthaiene activity (millimoles Ha consumed)	185	100	99	70	78(255) +

*by mercury porosimetry +values in parentheses are for fresh Sheil 324

catalyst analyses first stage vs second stage comparison bituminous coal

catalyst (size)	Amoc: (1/1	Amocat 1C (1/16)	
reactor		first	second
<u>run</u>	fresh	251-1	251-1
age [Ib (resid + Cl)/Ib cat] highest average bed temp (°F) analyses	0	2780 835	2780 775
*pore vol (cc/g cat) -aged after coke burn-off	0.67	0.31	0.41(0.70)+
*surface area (m²/g cat)-aged after coke burn-off carbon (wt%) titanium (wt%) iron (wt%) calcium (wt%) sodium (wt%)	306	157 215 13.5 0.7 1.1 0.1 0.6	196(253) ⁺ 229 11.1 0.6 0.2 0.1 0.6
H ₂ consumed)	135	18	70(185) +

*by mercury porosimetry +numbers in parentheses are for fresh Amocat 1C

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RUN 251 - part II close-coupled thermal-catalytic ITSL

fe	eatures re	results			
	Wyodak coal	good operability			
	catalysts first stage - iron oxide] highest coal conversion - 96% maf			
	second stage - Amocat 1C] highest distillate yield - 61% maf			
	solids recycle	l lowest organic rejection - 9% maf			
r		improved yields at higher coal space rate compared to ITSL and RITSL			

RITSL vs CC-ITSL comparison subbituminous coal solids recycle

solids recycle		TSL operating	conditions
run no	249H	251-IIB	251-IIIB
configuration	RITSL	CC-ITSL	CC-ITSL
first stage catalyst average reactor temperature (*F)	none 805	none 820	Shell 324 825
inlet hydrogen partial pressure (psi) coal feed rate (lb/hr mf)	2170 250	2510 350	2600 350
space velocity[b feed/hr-ib cat] solvent-to-coal ratio solvent resid content (wt%)	- 2.0 21	- 2.0 25	3.5 2.0 25
catalyst age[ib (resid+Cl)/ib cat] iron oxide (wt%)	- 1.5	- 0.8	750-1050 0.85
catalytic stage catalyst reactor temperature (*F) space velocity [lib feed/hr-lib cat] feed resid content (wt%) catalyst age [lib (resid + Cl)/lib cat]	Shell 324 700 1.6 25 1700-1850	Amocat 1C 745 2.8 30 900- 1000	Shell 324 720 2.3 30 350-500
critical solvent deashing unit	off-line	on-line	on-line

RITSL vs CC-ITSL comparison subbituminous coal

solids recycle			TSL yi	ela structures
run no configuration first stage catalyst	249H RITSL non o	- -	251-IIB CC-ITSL none	251-IIIB CC-ITSL Shell 324
yield (Xmaf coal) C ₁ - C ₃ gas (total gas) water C ₄ + distillate resid hydrogen consumption bydrogen afficiency (ib C ₄ + dist/ib H ₂)	7 (16 14 56 -7 -6.3 8.9) [57] [4]	8(18) 14 61 4 -6.3 9.7	11(17) 18 60 2 -7.7 7.8
consumed) distillate selectivity (lib C1- C3/lib C4 + dist)	0.12		0.13	0.18
energy content of feed coal rejected to ash conc. (%)	-	E 180	13	15
organics rejected to ash conc. (%maf coal)	(26)	+ [14]	9	11

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'numbers in [] are projected yields with CSD + vacuum concentrate organic rejection

RUN 251 - Part III close -coupled catalytic-catalytic ITSL

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features	results
🗌 Wyodak coal	good operability
catalysts tst stage - Shell 324	🗆 distillate yield - 60% maf
& iron oxide 2nd stage - Shell 324	(resid+UC) conversion decay rate 1st stage - low 2nd stage - very low
☐ solids recycle ☐ exploratory study	 compared to thermal catalytic more water less CO_X more 1st stage resid conv. lower hydrogen efficiency better quality products more naphtha & distillate

properties of distillate products close-coupled ITSL mode subbituminous coal

	wt% of_		elem	ental (wt%)		
distillation cut	crude	С	Н	N*	S	O(diff)	'API
RUN 249H (RITSL thermal-cat)							
naphta (IBP-350°F)	27.9	84.85	13.88	0.09	0.08	1.10	47.2
distillate (350-650°F)	55.8	85.74	11.80	0.19	0.02	2.25	23.0
gas oil (650°F+) RUN 251-IIB (therm-cat)	16.3	88,45	11.21	0.15	0.01	0.18	16.2
naphta (IBP-350°F)	28.4	84.16	14.10	0.10	0.11	1.53	45,6
distillate (350-650°F)	47.3	86.69	11.91	0.26	0.04	1.10	25.7
gas oli (650°F+) RUN 251-IIB (cat-cat)	24.3	88.31	10.79	0.47	0.02	0.41	11.7
naphta (IBP-350°F)	35.9	85.31	14.05	0.09	0.09	0.46	49.0
distillate (350-650°F)	51.3	87.21	11.88	0.30	0.03	0.56	24.3
gas oil (650'F+)	12.8	88.59	10.78	0.47	0.02	0.14	13.9

'nitrogen by Kjeldahl



catalyst cascading



RUN 252 close-coupled catalytic-catalytic ITSL catalyst cascading simulation

features	results
🗆 Illinois no. 6 coal	good operability
catalysts first stage - Amocat 1C	□ yields similar to run 251
(mixed ages) second stage - Amocat 1C	☐ product quality similar to Run 251
🗆 solids recycle	(resid+UC) conversion decay rate first stage - low to moderate second stage - insignificant
□ batch trends	

close-coupled catalytic-catalytic ITSL Amocat 1A vs Amocat 1C in first stage bituminous coal

solids recycle **TSL** operating conditions run no 251-IE 252-B1 first stage catalyst Amocat 1A Amocat 1C average reactor temperature (*F) 810 810 Inlet hydrogen partial pressure (psi) coal feed rate (Ib/hr MF) space velocity[Ib feed/hr-Ib cat] 2500 2500 300 350 2.7 3.2 solvent-to-coal ratio 2.0 2.0 solvent resid content (wt%) 40 40 catalyst age[lb (resid + Cl) /lb cat] 2150-2250 2650-2850 second stage catalyst (- - -- Amocat 1C - - - -) reactor temperature ("F) 760 750 space velocity[ib feed/hr-ib cat] 2.3 3.0 feed resid content (wt%) 40 40 catalyst age[lb (resid + Cl) /lb cat] 2300-2350 900-1050

close-coupled catalytic-catalytic ITSL Amocat 1A vs Amocat 1C in first stage bituminous coal solids recycle

solids recycle	TSL yield structures			
run no	251-IE	252-B1		
	(Amocat 1A)	(Amocat 1C)		
yleki (Xmaf coal)				
C ₁ - C ₃ gas (total gas)	7(12)	7(12)		
water	10	10		
C4+ distillate	70	69		
resid	-1	-1		
hydrogen consumption	-6.8	-7.1		
hydrogen efficiency (ib C_4 + dist/ib H_2 consumed)	10.3	9.9		
distillate selectivity (ib $C_1 - C_3$ /ib C_4 + dist)	0.11	0.11		
energy content of feed coal rejected to ash conc. (%)	17	20		
organics rejected to ash conc. (%maf coal)	15	17		



second stage catalyst (Amocat 1C) activity trends -(resid+UC) conversion rate constant





catalyst replacement rates close-coupled catalytic-catalytic configuration resid extinction mode

properties of distillate products effect of recycle distillate fractionation close-coupled ITSL mode bituminous coal

		ciemental (wt%)					
distillation cut	crude*	С	Н	N°	S	O(diff)	*API
RUN 252-B1 (without fractionat	ion; 69% dis	tillates)					
naphta (IBP-350°F)	24.1	85.10	14.26	0.02	0.03	0.59	45.8
distillate (350-650°F)	40.6	86.97	11.68	0.09	0.00	1.26	18.2
gas ol (650°F+)	35.3	89.45	10.26	0.27	0.00	0.02	02.9
RUN 252-B1 (with fractionation	; 69% distilla	tes)					
naphta (IBP-350°F)	22.1	85.53	14.22	0.02	0.05	0.18	44.7
distillate (350-650°F)	47,6	87.68	11.77	0.09	0.01	0.45	22.8
gas oll (650°F+)	30.4	89.30	10.38	0.17	0.01	0.14	09.7
RUN 251-E (no fractionation; 7	0% distillates)					
naphta (IBP-350°F)	26.0	85.90	13.98	0.03	0.05	0.04	50.9
distillate (350-650°F)	43.9	87.77	11.81	0.13	0.02	0.27	24.2
gas oil (650'F+)	30.1	89.64	10.04	0.21	0.03	0.08	09.4

"nitrogen by Kjeldahl + by simulated distillation on GC

	H-Coal	NTSL	ITSL	CC-ITSL
total plant cost	1.0	1.0	1.16	1.10
total capital required	1.0	1.0	1.16	1.11
operating cost	1.0	1.14	1.45	1.35
annual production cost	1.0	1.07	1.31	1.22
annual production rate	1.0	1.03	1.31	1.59
required product selling price ¹	1.0	1.04	1.00	0.77

relative cost factors

¹ first year price





1986 accomplishments

demonstrated close-coupled ITSL thermal-catalytic catalytic-catalytic	demonstrated solids recycle lower organic rejection lower CSD feed rate
Illinois and Wyodak coals good operability	tested Amocat 1C in first stage performance comparable to
🗆 high distillate yields	Amocat 1A
Winois no. 6 - 70% maf	indication of cascading viability
Wyodak - 61%	🗖 low catalyst replacement rates
□ lighter and better quality products Wyodak coal in catalytic-	☐ improved economics
catalytic	ITSL process simulation model
□ high coal throughputs	

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future work

catalyst cascading
alternate catalysts
eliminate interstage separator
process solvent studies solvent-to-coal ratio %resid in solvent heavy solvent recycle
alternate coals
system pressure
CC-ITSL process modeling

Section 11

COAL LIQUEFACTION CATALYST DEACTIVATION

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Amoco Oil Company

ABSTRACT

Three spent catalysts from a coal liquefaction pilot plant at Amoco have been extensively characterized in order to understand the causes of catalyst deactivation. XPS and NO chemisorption data indicate a good correlation between exposed metals (Co and Mo) and distillate yield. Controlled oxidation of the catalysts at increasing temperatures coupled with measurements of the surface composition by XPS suggest the loss of exposed metal is due to carbon coverage. Sintering, observed by TEM and electron microprobe, may also play a role. An analysis of the deposited carbon by CEELS, TPO, and C^{13} NMR suggests sp² carbon increases from the topmost surface layers of carbon into the bulk and that the surface aromatic carbon is related to distillate yield. BET surface areas and pore volumes of spent catalysts from three different pilot plants, including HRI and Wilsonville, were also found to correlate well with the bulk carbon content irrespective of the processing conditions.

INTRODUCTION

Over the past decade, improvements in coal liquefaction technology have been steady and impressive. Compared to the single-stage H-coal work, with distillate yields near 50 wt%, the Department of Energy sponsored Wilsonville pilot plant has recently demonstrated distillate yields of 70 wt% with Illinois coal in the close-coupled catalytic/catalytic fully integrated mode.⁽¹⁾ Hydrogen utilization, selectivity, and throughput have also improved, reducing sharply the projected costs for direct coal liquefaction.⁽²⁾ Amoco has maintained an active interest in all aspects of coal utilization through contracts with the Electric Power Research Institute,⁽³⁾ DOE,^(4,5) and by participating in the Cattletsburg and Wilsonville programs. Currently an EPRI sponsored program is focussed towards developing improved catalysts for direct liquefaction.⁽⁶⁾ One objective is to gain a better understanding of factors responsible for catalyst deactivation.

DISCUSSION

A schematic of the two-stage close-coupled pilot plant is shown in Figure 1. Experiments were conducted in a continuous feed, once-through mode, using Illinois No. 6 coal and a Wilsonville derived recycle solvent in a ratio of 1:2. Firststage catalysts were aged for one (51-177) or four weeks (51-175, -176) at 765°F, 2400 psig hydrogen and 0.5 LHSV on MAF coal. Pertinent characteristics of the THF-extracted aged Amocat^N-1A (Co/Mo) catalysts are given in Table 1. For comparison, data for Amocat^N-1A or -1C (Ni/Mo) catalysts obtained from Hydrocarbon Research Inc. and Wilsonville are included. The HRI catalysts include a secondstage -1A catalyst operated at ~825°F and first- and second-stage -1C catalysts operated at 775°F and 815°F respectively, all with Illinois No. 6 coal and for periods of four weeks. The Wilsonville catalysts include a -1C sample from the end of the Thermal/Catalytic Run 250H and a first-stage -1A from the Catalytic/ Catalytic Run 251G. The Wilsonville tests used Illinois No. 6 coal and lasted about two months.

Catalysts tested in the Amoco facility were subjected to extensive characterization including chemical analyses, digisorb and porosimetry, X-ray Photoelectron (XPS) and Core-Energy Electron Loss Spectroscopy (CEELS), Electron Microscopy, Temperature Programmed Oxidation (TPO), Chemisorption, and C¹³ Nuclear Magnetic Resonance. The HRI and Wilsonville catalysts were less extensively analyzed.

Figure 2 shows a plot of catalyst B.E.T. surface areas and pore volumes, obtained from nitrogen desorption, versus weight percent carbon. The correlation is good for all catalysts irrespective of the processing unit used and indicates that for the bimodal Amocat^N catalysts, carbon deposition occurs in the same manner for either first- or second-stage catalysts, although the relative amounts differ. In general, the catalyst in the lowest severity reactor has the lowest carbon buildup and also deactivates more slowly.

Pore size distributions for both the meso- and macropore (>1200°A) ranges are shown in Figure 3 for samples 51-175, -176, and -177. Porosity is lost with carbon deposition throughout the pore size range with the average pore diameter moving to smaller values. Most of the pore volume loss occurs in the meso-pore region with the macropores being less affected, reflecting one advantage of bimodal catalysts. The shapes of the hysteresis loops for these same catalysts, determined by nitrogen adsorption/desorption (shown in Figure 4) indicate slit-shaped meso-pores.⁽⁷⁾ The increasing area of the hysteresis loops with increased carbon deposition suggests some poremouth plugging of the meso-pores. Separate analysis of the macropore

region, however, suggests that carbon buildup occurs in a radial pattern and that they maintain their integrity to a larger extent than the meso-pores with increasing carbon deposition.

Controlled oxidations of the catalysts to remove carbon results essentially in a complete regeneration of catalyst surface areas and pore volumes. An example is shown in Figure 5 and indicates a good degree of catalyst support stability in that no permanent support changes occur during use in the harsh liquefaction environment.

To gain a better understanding of the role of carbon in any deactivation mechanism, several analytical techniques were utilized. The nature of the surface carbon on ground extrudates was determined by CEELS,⁽⁸⁾ Figure 6. This technique is sensitive only to the first few monolayers of carbon and determines the state of hybridization of carbon. Samples 51-175 and -176 have similar contents of sp^2 -type carbon despite the different total carbon contents of ~25 and 16 wt%, respectively. Sample -175, however, contains significantly more sp^3 -type carbon within the first few monolayers. As discussed subsequently, samples -175 and -176 show similar activities for distillate yields suggesting surface carbon of the sp^2 -type is more controlling than aliphatic-type carbon.

The nature of the total carbon, as opposed to the surface carbon determined by CEELS, was determined for samples -175, -176 and -177 by C^{13} NMR and TPO. Results are given in Table 2. C^{13} NMR data indicates increasing aromaticity with total carbon content. This is consistent with the increase in the peak temperatures obtained from TPO. Due to surface charging, sample -177 could not be analyzed by CEELS but the C^{13} NMR data suggests that sample -177, which had the highest activity for distillate yield, would also have a lower surface aromatic-type carbon content. Together the results of the carbon analysis suggest a depth profile of increasing aromaticity of carbon with aliphatic carbon disposed more towards the surface. The asymmetry of the oxidation peaks during TPO tend to confirm this observation.

Surface compositions of molybdenum and carbon on sample -176, determined by XPS, are shown in Figure 7. They were determined on the as-received sample, and then after regeneration in air for four hours at a series of increasing temperatures. Results indicate an increase in the molybdenum exposure with carbon removal suggestive of carbon coverage of molybdenum. At high temperatures, molybdenum surface concentration decreases, possibly due to sintering and crystallite growth. Although not shown, exposed cobalt and sulfide follow expected trends.

Figure 8 shows a relationship between exposed surface molybdenum for samples -175, -176, and -177 as determined by XPS and total end-of-run distillate yields. The zero percent point represents thermal distillate yields while the 12% point represents fresh catalyst activity for all three catalysts. The lines drawn simply indicate a trend and do not imply a first-order relationship. Figure 8 also indicates that in catalytic/catalytic processing the first-stage high-temperature catalyst determines to a great extent the overall process performance. This has been observed previously in our work and has been recently confirmed by results from Wilsonville.⁽¹⁾

As a supplement to the XPS work on carbon coverage and molybdenum exposure, NO adsorption experiments were also conducted. XPS, due to limited detectability of emitted electrons, provides only a surface analysis,⁽⁹⁾ and at best, measures surface concentrations only in the macropores whereas NO has the ability to provide a measure of molybdenum within the mesopores as well.

NO uptakes were measured at room temperature on samples -175, -176 and -177 after THF extraction, drying at 110°F and reduction with hydrogen at 500°C. NO uptakes, shown in Table 3, are consistent with XPS measurements of surface molybdenum in that there is a decrease from the fresh catalyst to the catalyst with 8% carbon and a further decrease to similar values for the 16% and 25% carbon samples. These latter samples also had similar activities for distillate production and comparable molybdenum exposures, as measured by XPS, as discussed previously.

Sintering of active metals is another possible cause of deactivation. Although the data is limited and no firm conclusions can be drawn, examination of the Amoco, HRI, and Wilsonville samples by Electron Microscopy and Microprobe does reveal sintering of nickel, or cobalt, and molybdenum. For example, sample -176, which was aged at 765°F, showed 5-10µ particles of sintered cobalt sulfide. Similar results were observed for the HRI-227-20-2 sample operated at 825°F. Both catalysts had been onstream for about 30 days. In contrast, the Ni/Mo sample, 227-32-2 from HRI, after 30 days at high temperatures, showed sintering of both nickel (1-3µ) and molybdenum the latter appearing as amorphous "clouds" ranging in size from 5 to 30 microns.

No sintering was observed for the HRI Ni/Mo sample after operation of 775°F nor for other Amoco Ni/Mo samples operated below 765°F. Co/Mo Wilsonville samples from Run 251, examined after operations at 807°F and 834°F for extended periods of time both showed cobalt and molybdenum sintering, the latter appearing as very large, up to

100 micron, "clouds." The data tend to suggest a time-temperature effect on the extent of molybdenum sintering and that cobalt may sinter at a lower temperature than nickel. Additional analyses are required to confirm these trends and to determine the effect of the degree of sintering on catalyst deactivation.

Summary

Analyses of Amocat $^{\mathbb{M}}$ catalysts from Amoco, HRI, and Wilsonville pilot plants indicates:

- A good correlation between carbon content and reductions in catalyst surface areas and pore volumes. Preferential carbon deposition appears to occur for the mesopores with evidence of pore mouth plugging. The macropores are less effected by carbon deposition.
- Analysis of deposited carbon by CEELS and C¹³ NMR suggests an increase in aromaticity of the carbon with depth, with the surface being richer in aliphatic carbon. The aromatic carbon content appears more important with respect to catalyst activity. Additionally, TPO experiments suggest increasing aromaticity with total carbon content.
- XPS and NO chemisorption data indicate coverage of active molybdenum sites by carbon in that exposed molybdenum increases with removal of carbon by controlled oxidations.
- Catalyst activity, as determined by distillate yields, appears to be related to exposed molybdenum sites.
- Initial experiments on active metals sintering suggests a timetemperature relationship for the extent of molybdenum sintering. Additional work is needed to determine effects of metal sintering on catalyst activity and concommittant reduction in exposed active molybdenum sites.
ACKNOWLEDGMENTS

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Figure 1. Schematic of Two-Stage Continuous Liquefaction Pilot Plant

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Figure 2. Effect of Total Carbon on Catalyst Surface Areas and Pore Volumes. (o) Amoco, (\blacksquare) HRI, (\blacktriangle) Wilsonville



Figure 3. Pore Size Distribution vs. Carbon Content for Fresh and Ages Catalysts



Figure 4. Nitrogen Adsorption/Desorption Porosity Hysteresis Loops for Fresh and Aged Catalysts











Figure 7. Effect of Regeneration Temperature on Carbon and Molybdenum Surface Composition, Sample-176





TABLE 1

AGED Amocat[™] - CHARACTERISTICS

	HRI		Атосо		Wilsonville			
Designation	227-32-1	227-32-2	227-20-2	51-177	51-176	51-175	250H	251G
Metals	Ni	/Мо	•	Co,	/мо		Ni/Mo	Co/Mo
Temperature °F	775	815	825	765	765	765	760	834
Carbon, wt%	10.3	19.6	22.7	8.2	16.1	25.3	8.4	13.5
B.E.T. Surface area m ² /g	120	96	67	136	87	36	151	122
N ₂ Pore Volume cc/g	0.30	0.25	0.18	0.40	0.26	0.11	0.46	0.38

\mathtt{C}^{13} NMR AND TPO DATA FOR $\mathtt{Amocat}^{\mathtt{N}}\mathtt{-}\mathtt{lA}$ CATALYSTS

Sample	Carbon, Wt%	sp ² Carbon	Peak Temperature, °C
51-177	8.2	70	429
-176	16.1	85	442
-175	25.3	90	452

Table 3

COMPARISON OF NO CHEMISORPTION AND XPS RESULTS

Sample	Wt% Co	Wt% Mo	NO Uptake cm³ g ⁻¹
Fresh Sulfided	1.7	10.6	2.3
-177 (8% C)	1.5	9.2	0.63
-176 (16% C)	0.3	1.6	0.24
-175 (25% C)	0.4	1.8	0.23

Section 12

WILSONVILLE-KINETIC MODELS AND ITSL SIMULATION

A. Prasad, R. V. Nalitham and T. E. Pinkston UE & C - Catalytic, Inc.

ABSTRACT

Material balance only simulations have been performed for the Integrated Two-Stage Liquefaction (ITSL) process using the ASPEN process simulator. Illinois No. 6 Bituminous coal liquefaction was considered. All the recycle streams were converged and user-defined reactor models were interfaced with ASPEN. Reactor models have been developed for the thermal and catalytic reactors. A Critical Solvent Deashing Unit (CSD) correlation have been developed to predict the organic rejection in the ash concentrate, and ITSL simulations. Sensitivity analysis has been performed for the ITSL process.

INTRODUCTION

Direct coal liquefaction has undergone rapid change in recent years. Improved processes have shown increased distillate yields and more efficient hydrogen utilization. There is a need to understand the basic principles within these processes without being enmeshed in the complicated and numerous molecular reactions of coal liquefaction. Such an understanding can lead to higher product yields as optimum operating conditions can be defined. It will also allow simulation of existing processes so that process comparison and cost evaluation studies can be performed.

To understand the process and determine the optimum operating conditions, a donor solvent coal liquefaction kinetic model was developed. This model along with a resid upgrading model and a Critical Solvent Deashing (CSD) process model was integrated into an ASPEN flowsheet of the Integrated Two-Stage Liquefaction (ITSL) process. A summary of the research effort in kinetic modeling and coal liquefaction process flowsheet simulation for Illinois No. 6 bituminous coal is presented in this paper.

ITSL PROCESS DESCRIPTION

The ITSL process consists of three distinct stages: a thermal liquefaction stage (TLU), a critical solvent deashing stage (CSD), and a resid hydrotreating (HTR) stage (1). The three units are integrated by recycling the hydrotreated resid to the thermal stage. The net yield is a resid-free product.

ITSL REACTION COMPONENTS

The ITSL product slate is reported in terms of lumped components which are:

- cresol insolubles (mainly coal)
- resid (cresol soluble but non-distillable at 600°F under 0.1 mm
 Hg pressure.)
- distillate (cresol soluble and distillable at 600°F under 0.1 mm Hg pressure.)
- C₄-C₆ gases
- C₁-C₃ gases

- heterogases (NH₃, H₂O, H₂S, CO, CO₂)
- hydrogen consumption

Since a substantial portion of the C_4-C_6 compounds is found in the distillate, C_4-C_6 gases are usually lumped with the distillates to form a C_4+ distillate lumped component.

TLU KINETICS

The ITSL lumped components which are categorized on a physical separation basis contain numerous compounds. As a result, the reactivity of lumped components may change with concentration and certain reactions may become dominant beyond certain concentration levels. It was desired to develop an overall reaction scheme applicable to a wide range of conditions which would simulate this behavior. Fortunately one set of parameters gave reasonable predictions for the complete ITSL database.

Thermal Reaction Scheme

As coal liquefaction reaction kinetics should be process independent, the reaction network was developed in the VaSTeC autoclave where a systematic one variable study was performed. Isothermal kinetics were established by varying the residence time at various temperature levels. The concentration of the lumped components in the feed was kept constant to maintain a comparable reactivity. The concentration selected was similar to that used in the ITSL feed during the ITSL operation

Table 1 contains the operating conditions for the VaSTeC autoclave experiments. The constant conditions are representative of the pilot plant operations. Figure 1 shows the reaction scheme arrived at with the VaSTeC data. The reaction scheme was developed for two primary variables: reactor temperature and batch residence time above 700°F. Heterogases were not considered in the reaction scheme because the amount produced was comparable to the experimental error and the data showed no definite trends. Numerous irreversible and reversible schemes were considered before the final model was selected (2). Selection was based on fit and stability of the model at all temperatures. Rate constants were assumed to follow the Arrhenius temperature dependency law and the selected model showed compliance to this law. Figure 2 shows the model fits at 750°F and 795°F.

Batch kinetic equations for the reaction scheme are presented below:

$$\frac{dC_{out}}{dt} = -k_1 C_{in} + k_2 R_{in}$$

$$\frac{dR_{out}}{dt} = -(k_2 + k_3)R_{in} + k_1C_{in}+k_4D_{in}$$

$$\frac{dD_{out}}{dt} = -k_4 D_{in} + k_3 R_{in}$$

$$C_1C_3 = k_5t$$

C_{in}, R_{in}, and D_{in} are the weight fractions of cresol insolubles, resid, and C₄₊ distillate in the slurry charge ($C_{in}+R_{in}+D_{in}=1$). C_{out}, R_{out}, and D_{out} are the normalized weight fractions of cresol insolubles, resid, and C₄₊ distillate in the slurry product ($C_{out}+R_{out}+D_{out}=1$). C₁C₃ is the weight fraction of C₁-C₃ produced.

The rate constant expressions for the batch reaction scheme were found to be:

 $K_1 (min^{-1}) = 97.19 \exp(-15527/RT)$ $K_2 (min^{-1}) = 2.054 \exp(-13233/RT)$ $K_3 (min^{-1}) = 1.96E6 \exp(-46661/RT)$ $K_4 (min^{-1}) = 2.46E12 \exp(-81594/RT)$ $K_5 (min^{-1}) = 1.09E7 \exp(-59454/RT)$

Using the rate constants at a particular temperature, the batch kinetic equations can be solved to give the weight fraction of the various components for various residence times.

According to the model, at 795°F, K₃ was comparable to K₄. These rate constant values suggested that if the feed solvent was reacted without the feed coal at 795°F and 40 minutes, no significant C₄+ distillate would be produced. The results of the experiment are shown in Table 2. The amount of C₄+ distillate produced was negli-gible.

Application of Batch Model to TLU Reactor

Once the thermal reaction kinetics was established, it was coupled with the TLU reactor hydrodynamics to predict the TLU reactor yield slate. The TLU dissolver hydrodynamics was characterized with a radioactive tracer (3) and was accurately modeled by 1.2 CSTRs (or two unequally sized CSTRs in series). For all practical purposes the hydrodynamics can be adequately modeled by a single CSTR. The actual slurry residence time and the average reactor temperature were used with the CSTR equations to predict the TLU reactor yield slate.

The TLU reactor comprises of a tubular reactor with a bubble cap distributor called the dissolver, a non-isothermal preheater, and the transfer line from the preheater to the dissolver. The hydrodynamics of the preheater and the transfer line has not been characterized. Due to a lack of any better approximation, the hydrodynamics was assumed to be similar to that of the dissolver. This approximation required an assmption that the CSTR equations could be used to simulate the TLU reactor if a corrected total residence value was used. The total residence time value was corrected by multiplying it by a factor. Theoretically, the factor would be equal to 1.0 if the preheater and transfer line volume was negligible. Therefore, the simulation results would be poor for low residence time pilot plant runs because the relative volume of preheater and the transfer line would be large compared to dissolver volume.

The isothermal model developed in the VaSTeC autoclave considers the non-isothermal liquefaction to occur at a constant temperature. The average reactor temperature was considered to be the reaction temperature for the model. This simplification requires that the activation energy for each rate constant be modified. Furthermore, as the activation energies for the batch model were based on only two temepratures, modificatoin of the activation energy values for pilot plant reactor can be further justified. Only two temperatures were considered because the concentration of the resid in the feed solvent changed for the higher temperature runs. This change had significant effect on the yield slate and the rate constant values obtained could not be used (2). The data at the higher temperatures, however, were used to check the reaction scheme.

The above discussion shows the need to modify the activation energies of the batch model and the actual slurry residence time values of the TLU reactor. The actual slurry residence time was calculated using the radioactive tracer study correlations

after performing an ASPEN FLASH of the slurry at reactor conditions. The actual slurry residence values can be modified by lumping the correction factor with the Arrhenius factors to obtain modified Arrhenius factors.

Therefore, both the activation energy and the Arrhenius factor of the rate constants need to be modified or regressed to get an adequate expression. If so many parameters are regressed, a good fit is bound to be obtained. Therefore, a more rigorous test for the reaction network would be if only the Arrhenius factors for the different rate constants are modified and the batch activation energies are assumed to be valid for the thermal reactor.

The final correlations for all the components are listed in Table 3. The final reaction model is shown in Figure 3. The parity plots for the major components are presented in Figures 4 and 5. Since correlations were not developed in the VaSTeC autoclave for the heterogases, irreversible semi-kinetic correlations were developed for these components. Yields for these components were regressed with heteroatom content in the feed stock, actual and nominal residence time values. The set of variables which gave the best regression results was accepted. An interesting observation was made that within the pilot plant operating zone there was a good correlation between nominal residence time and the actual residence time. The relationship is shown in Figure 6. The relationship provides a simple method for calculating the actual residence time.

HYDROTREATER KINETICS

The limited time of the contract prevented the development of a bench scale catalytic model for heavy coal liquid hydrotreating. Non-interactive irreversible kinetics models were developed with pilot plant data. Catalyst deactivation was based on an earlier model developed during ITSL operation (4). Several primary and secondary variables were considered while developing correlations to predict the yield slate in the hydrotreater. The variables considered were:

- temperature
- WHSV
- resid concentration
- H/C ratio
- catalyst age

- preasphaltene concentration
- oxygen, nitrogen, and sulfur concentration
- hydrogen in the feed and product

The final correlations are presented in Table 4. The parity plots for the major components are presented in Figure 7.

CRITICAL SOLVENT DEASHING UNIT CORRELATIONS

Time, insufficient funding for the project, and the complexity of the CSD unit prevented the development of an in-depth model of each vessel in the system. The model presented here is an empirical correlation for the CSD deashing. The model defines the CSD product streams based on the feed stream to the CSD. The variables considered were:

- cresol insolubles (UC in the feed)
- resid to CI ratio
- resid to ash ratio
- preasphaltene to CI ratio
- preasphaltene to ash ratio
- percent preasphaltene
- percent preasphaltene in the feed resid
- DAS strength

The final correlation is presented in Table 5. This correlation calculates the organic rejection in the ash concentrate. The parity plot is presented in Figure 8. Note that the correlation is purely empirical and does not contain CSD input variables such as deashing solvent strength, temperature, and pressure. Nevertheless, the correlation can be used to estimate the organic rejection as a function of the coal conversion and feed coal ash, assuming that a suitable DAS is available.

ITSL FLOWSHEET SIMULATION

The ITSL flowsheet contains numerous mixing and separation vessels which can be adequately simulated by the ASPEN process simulator. Coal liquids are characterized in ASPEN by dividing it into pseudo-components defined by boiling point ranges.

Numerous correlations have been developed to predict the different thermo-physical properties of the pseudo-components and better correlations are still being developed. Based on recommendations of Gallier et al. (5), pseudo-component correlations were introduced into ASPEN. Only material balance simulations were performed and only those correlations required for such simulations were used. Redlich-Kwong-Soave equation of state was used in all ASPEN simulations. This selection was based on work done by Khan et al. (6) and Mckeegan et al. (7). All the vessels in pilot plant flowsheet, except for the reactors, were simulated with built-in ASPEN operation blocks. ASPEN (Public) distillation blocks were not used as there are some problems with their coding. All distillation columns were simulated with an ASPEN FLASH2 block by selecting the proper conditions. The kinetic equations developed were incorporated into ASPEN through ASPEN USER blocks to simulate the reactors.

Aspen Prediction of Coal Liquefaction Unit Operation Data

ASPEN, with the selected pseudo-component correlations and the selected equation of state, was tested for its ability to predict high pressure separation data. The results are presented in Table 6. The selected pseudo-component correlations and the equation of state were found to be adequate for coal liquefaction material balance simulations.

Thermal Liquefaction Unit (TLU) Simulation

The ASPEN flowsheet used to simulate the TLU flowsheet is presented in Figure 9. An ASPEN simulation of the thermal liquefaction unit was performed in which the recycle gas was converged. A comparison of the ASPEN simulated stream from the TLU to the CSD (T102 bottom stream) with the actual stream is presented in Table 7. The table shows that the TLU section has been adequately simulated.

Critical Solvent Deashing (CSD) Unit Simulation

As mentioned earlier, the CSD flowsheet was simulated with a single ASPEN USER block where the organic rejection correlation was used. The correlation gives an estimate of the resid rejected in the ash concentrate. All the UC and ash were assumed to be rejected in the ash concentrate. The amount of distillate present in the ash concentrate was assumed to be negligible. The hydrotreater feed stream was then calculated by difference.

Hydrotreater (HTR) Unit Simulation

The hydrotreater flowsheet was simulated with the ASPEN flowsheet presented in Figure 10. Recycle gas was converged during simulation. The actual streams leaving the hydrotreater were compared with the ASPEN stream flowrates and the results are presented in Table 8. The comparison shows that the hydrotreater unit flowsheet has been adequately simulated.

Integrated Two Stage Simulation

The complete ITSL flowsheet was simulated by integrating the three units simulated above. The three units were integrated by recycling the hydrotreated resid containing stream (V1067) from the HTR unit to the TLU. The T102 bottom stream in the TLU was sent to the CSD were the ash concentrate stream was removed and the ash-free stream was sent to the hydrotreater. The solvent required in the hydrotreater was obtained from the T102 overhead stream. All streams in the integrated flowsheet were converged. Yields were calculated after convergence and they were compared to the two stage yields seen in the pilot plant. The comparison is shown in Figure 11. Excellent agreement is seen signifying that the ITSL flowsheet has been adequately modeled.

SENSITIVITY ANALYSIS

Process simulation is a cost effective method of studying the effect of different process variables on the product slate. The effect of numerous process variables such as coal feed rate, first stage reactor temperature, second stage reactor temperature, reactor size for each stage, can be studied. Such studies allow the selection of parameters for optimum product yields. Steps have been outlined to study the sensitivity of the yields to different process variables. The effect of one such variable, the coal feed rate is presented here. All other parameters such as the solvent to coal ratio in TLU feed, solvent to resid ratio in the HTR feed, reactor temperatures and pressures were kept constant. The results are presented in Figure 12. The figure shows that the coal fed rate operating zone was between 180 MF lb/hr to 290 MF lb/hr with a first stage temperature of 825°F, second stage temperature of 720°F, solvent to MF coal ratio of 1.8, and a catalyst age of 1134 lb resid coal/lb cat. The figure also shows that distillate yield and the coal conversion are the highest at low coal feed rates. Unfortunately gas yield is high when coal feed rate is low.

SUMMARY

A major achievement of modeling has been that it has created an extensive data base for the ITSL process where relevant data have been collected from different sources and arranged in a systematic manner.

A kinetic model has been developed for the thermal liquefaction of coal. With some modification this model can be used to simulate other coal liquefaction processes. A semi-kinetic model has been developed for the catalytic hydrotreating of the coal liquid products. These models give insight to coal liquefaction mechanism. An ASPEN flowsheet which can adequately model the ITSL process has been created. With this flowsheet, sensitivity analyses with the different process can be studied and the ITSL process can be optimized for optimum parameters operating conditions. Moreover the interface between the reactor models and the ASPEN plant flowsheet has been established. This simulation can be used as a guideline for any new coal liquefaction simulation with ASPEN.

The simulation can be coupled with cost blocks and used for economic evaluation of the ITSL process. When cost blocks are included in the above model, sensitivity analyses can be performed for optimum parameters with respect to overall cost. The results can then be used to compare the ITSL performance with respect to other processes based on the cost of the product.

RECOMMENDATIONS FOR FUTURE WORK

Develop CC-ITSL Model

As the current Close-Coupled ITSL configuration shows promising yields, this process should be simulated and the optimum yields for the process should be found. The optimum yields can then be verified by a pilot plant run. Most of the ITSL modeling work should be applicable for a CC-ITSL model. The thermal kinetic model can be used to define the thermal reactions in the reactors. A more fundamental catalytic model needs to be developed to define the interaction of different components. Such a model will allow the separation of the catalytic reactions from the thermal reactions. This understanding can lead to higher yields and more stable products.

Incorporate secondary variables

Besides product yields, other process variables such as system pressure, product quality, gas and coal liquid separation and recycling scheme, extent of solid recycle, to mention a few, need to be considered in the kinetic models.

Incorporate cost model

A cost model should be coupled with the process model so that the process can be evaluated on a cost basis. The cost model can easily be incorporated into the ASPEN process model with the help of ASPEN cost blocks. Such an approach would be a cost effective method for making synthetic crude as a viable source of energy.

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NOMENCLATURE

CC-ITSL	Close-Coupled Integrated Two-Stage Liquefaction.
Cresol Insolubles	Organic Material that is insoluble in hot cresol.
CSD	Critical Deashing Unit
CSTR	Continuous Stirred Tank Reactor.
Distillate	A coal derived product which is distillable at 600°F at 0.1 mm Hg
	in a laboratory batch distillation apparatus.
Dissolver	Thermal stage reactor.
HTR	Hydrotreater Unit
Hydrotreater	Resid upgrading stage catalytic reactor.
ITSL	Integrated Two Stage Liquefaction
MAF	Moisture and ash-free
MF	Moisture-free
Preheater	A vessel before the dissolver where the slurry feed is heated to
	desired temperature.
R	BLU/1b mole °R
Resid	A cresol soluble product of the coal liquefaction process which
	is non-distillable at 600°F and 0.1 mm Hg in the laboratory.
TLU	Thermal Liquefaction Unit

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VASTEC AUTOCLAVE OPERATING CONDITIONS

Coal	Burning Star Illinois No. 6
Solvent	ITSL Recycle Solvent
Solv:MF Coal	1.80
Coal Ash	10.75-11.10% MF Coal
H ₂ Charge Press.	1500 psig
Max. Press.	1180-2380 psig
Temperature	750-845°F
Residence Time	0-180 Min

	VaSTeC Yield (W/O Coal) <u>% Solv</u>	Model Yield (W/O Coal) <u>% Solv</u>	VaSTeC Yield (With Coal) % MAF
Distillate	-0.4	-1.0	22.6
Resid	-1.2	-2.0	57.3
Coa 1	0.1	2.4	8.8

COMPARISON OF THERMAL REACTIONS WITH & WITHOUT COAL AT 795°F AND 40 MIN

TLU FINAL CORRELATIONS

- 2. t_{act}: Actual residence time above 700°F, min.
- 3. t_{nom}: Nominal residence time, hr
- 4. WC: weight fraction of MAF coal in ash-free slurry
- 5. MAF : MAF coal rate, lb/hr
- 6. R = 1b mole/BTU °R

$$\frac{C_1-C_3}{WC} = \frac{K_{C_1C_3} t_{act}}{WC}; K_{C_1C_3} = 7.5711*10^{16} * e^{-95784.8/RT}$$

 $\frac{C_4-C_6}{WC}: y_{C_4C_6} = \frac{K_{C_4C_6} t_{act}}{WC}; K_{C_4C_6} = 2.4896*10^{15} * e^{-89946.7/RT}$

$$H_2S$$
: $y_{H_2S} = \frac{C_S X_S (34/32)}{MAF} * 100$

where $C_S = Sulfur$ in feed coal (1b/hr)

X_S = Fraction sulfur removed

$$= \frac{1}{1 + \frac{1}{K_{H_2S} t_{nom}}}$$

K_{H_2S} = 6.0543*10²³ * e^{-136188.9/RT}

<u>H₂0</u>: $y_{H_20} = \frac{C_0 X_0 (18/16)}{MAF} * 100$

where $C_0 = 0xygen$ in the feed coal (lb/hr)

X₀ = Fraction oxygen removed

$$= \frac{1}{1 + \frac{1}{K_{H_20} t_{nom}}}$$

K_{H_20} = 3.1243*10²⁰ * e^{-117514.7/RT}

Table 3 (continued) TLU FINAL CURRELATIONS

<u>NH3</u>: $y_{NH3} = 0.25$ <u>CO-CO2</u>: $y_{COCO2} = K_{COCO2} t_{nom}$; $K_{COCO2} = 5.5265*10^{31} * e^{-182895/RT}$ <u>H2 consumption</u>: $y_{H2} = (0.2164792)Y_{C1C3} + (0.169045) y_{C4C6} + (2/34) Y_{H2S} + (2/18) y_{H2O} + (3/17) y_{NH3} - y_{HL}$ where $y_{HL} = {}^{K_{HL}} t_{nom}$; $K_{HL} = 1.4269*10^{38} * e^{-224449.3/RT}$ <u>Coal conversion, Resid, and C4+ distillate yield models</u>:

<u>Coal conversion</u>: $X_{C} = \frac{C_{in} CRDIN - C_{out} CRDOT}{C_{in} CRDIN} * 100$

<u>Resid yield</u>: $y_{R} = \frac{R_{out} CRDOT - R_{in} CRDIN}{C_{in} CRDIN} * 100$

<u>Cq+ distillate yield</u>: $y_D = \frac{D_{out} CRDOT - D_{in} CRDIN}{C_{in} CRDIN} * 100$

$$R_{out} = \frac{R_{in} + \frac{K_{1}t C_{in}}{1+K_{1}t} + \frac{K_{4}t D_{in}}{1+K_{4}t}}{1 + (K_{2}+K_{3})t - \frac{K_{1}K_{2}t^{2}}{1+K_{1}t} - \frac{K_{3}K_{4}t^{2}}{1+K_{4}t}}$$

Table 3 (continued) TLU FINAL CORRELATIONS

$$C_{out} = \frac{C_{in} + K_2 t R_{out}}{1 + K_1 t}$$

$$D_{out} = \frac{D_{in} + K_3 t R_{out}}{1 + K_4 t}$$

$$K_1 = 247.708e^{-15527/RT}, min^{-1}$$

$$K_2 = 2.397e^{-13233/RT}, min^{-1}$$

$$K_3 = 826214.9e^{-46661/RT}, min^{-1}$$

$$K_4 = 25.97e^{-81594/RT}, min^{-1}$$

HTR FINAL CORRELATIONS

Note: 1. All yields as % solvent-free resid 2. R = 1b mole/Btu °R 3. WHSV = Weight hourly space velocity 4. age = Catalyst age, lb resid/lb cat. 5. $f_R = \%$ resid in feed $C_1-C_3: y_{C_1C_3} = \frac{K(100)^2}{(WHSV)(f_R)}$ where K = 0.1806 * (% tR * (H/C) feed) $\frac{10}{3} * e^{-40360}/RT$ C_4-C_6 : $y_{C_4-C_6} = \frac{K(100)^2}{(WHSV)(\% f_R)}$ where K = $1.9145 \times 10^{11} \times e^{-74495/RT} \times e^{-0.000773}$ (age) (0+N+S) removed: $y_{ONS} = \frac{C_{Het} * X * (100)^2}{(\% f_R)}$ where CHet = heteroatom (O+N+S) wt. frac. in feed X = fract. heteroatom removal $= F - \sqrt{F^2 - 1}$ $F = 1 + \frac{WHSV}{2 C_{Het} K}$ K = 1.915 * 10¹⁴ e^{-67186/RT}

Resid: $y_{\text{resid}} = \frac{-100}{1 + \frac{\text{WHS}}{\text{K}^{1}}} + 100$

Table 4 (continued)

HTR FINAL CORRELATIONS

where $K^{1} = 0.062466 * K/(fraction resid in feed)^{3.86}$

 $K = K_0 e^{-(50000/R)} * (1/T - 1/1180)$

$$K_0 = \begin{cases} 0.78 \text{ e}^{-0.004} \text{ (age)} & \text{age} < 200 \text{ lb resid/lb cat} \\ 0.38 \text{ e}^{-0.00035} \text{ (age)} & 200 < \text{age} < 850 \\ 0.53 \text{ e}^{-0.00075} \text{ (age)} & \text{age} > 850 \end{cases}$$

H₂ consumption: $y_{H_2} = 0.1928 (y_{C_1-C_3} + y_{C_4-C_6}) + 0.1272 y_{ONS} + y_{HUP}$

where $y_{HUP} = \frac{872.1 * (WHSV) - 0.3 * e^{-15334/RT} * e^{-0.000136} (age)}{\text{frac. resid in feed}}$

 $H_2S+H_2O+NH_3: y_{HX} = 1.1272 y_{ONS}$

Distillate: $y_{dist} = 100 + y_{H_2} - y_{C_1-C_3} - y_{C_4-C_6} - y_{resid} - y_{HX}$

CSD FINAL CORRELATION

Note: 1. All yields as % MAF
2. W_{ASH} = weight fraction ash in MF coal
3. F_{UC} = UC in CSD feed, lb/hr
4. F_{ASH} = Ash in CSD feed, lb/hr

5. All UC in the CSD feed is rejected

Resid rejection = $0.7735 \times \frac{W_{ASH}}{1 - W_{ASH}} \times 100$

UC rejection = $F_{\text{UC}} * \frac{W_{\text{ASH}}}{F_{\text{ASH}}} * 100$ F_{ASH} 1 - W_{ASH}

Organic rejection: resid rejection + UC rejection

<u>Component</u>	Actual Flowrate _(lb/hr)	ASPEN Flowrate <u>(lb/hr)</u>
IBP-200°F	0.00	0.37
200-250°F	0.00	0.71
250-300°F	0.00	0.51
300-350°F	0.55	0.72
350 - 450°F	4.54	6.20
450-500°F	5.99	6.85
500 - 550°F	7.37	8.11
550 - 650°F	27.95	30.96
650 - 850°F	142.99	149.28
850°F-EP	84.68	86.89
<u>Resid</u>	414.44	414.44
Total	688.50	705.04

ASPEN PREDICTION OF HIGH PRESSURE*

*V1258 Bottom Comparison.

	Actual	ASPEN
	Flowrate	Flowrate
Component	<u>(]b/hr)</u>	(1b/hr)
IBP-200°F	0.00	0.00
200-250°F	0.00	0.00
250-300°F	0.00	0.00
300-350°F	0.00	0.00
350 - 450°F	0.00	0.01
450-500°F	0.00	0.02
500-550°F	0.03	0.02
550 - 650°F	0.16	0.16
650 - 850°F	5.11	2.96
850°F-EP	12.57	14.85
Resid	229.34	231.49
Total	247.21	249.51

	Actual	ASPEN	Actua]	ASPEN
	V1078	V1078	V1067	V1067
	Flowrate	Flowrate	Flowrate	Flowrate
<u>Component</u>	<u>(1b/hr)</u>	<u>(1b/hr)</u>	<u>(1b/hr</u>	<u>(1b/hr)</u>
C ₁ ,C ₂ ,C ₃	0.03	0.03	0.02	0.02
C4,C5,C6	0.13	0.13	0.02	0.02
CO	0.0	0.0	0.0	0.0
C0 ₂	0.0	. 0.0	0.0	0.0
H20	0.53	0.45	0.0	0.0
H ₂	0.0	0.0	0.05	0.05
H ₂ S	0.01	0.01	0.0	0.0
NH3	0.01	0.01	0.0	0.0
IBP-200°F	2.33	2.42	0.02	0.02
200-250°F	2.61	2.71	0.07	0.07
250-300°F	1.63	1.69	0.08	0.09
300-350°F	1.21	1.25	0.12	0.13
350-450°F	3.10	3.19	0.81	0.87
450-500°F	2.49	2.56	1.35	7.44
500 - 550°F	2.73	2.80	2.48	2.62
550-650°F	7.35	7.48	14.43	15.14
650-850°F	11.15	11.28	102.00	106.28
850°F-EP	0.70	0.70	42.74	44.42
Resid	0.0	0.0	155.88	149.30
Total	36.01	36.71	320.07	320.47

HTR UNIT STREAM COMPARISON


- K_1-K_4 : First Order Rate Constants
- C: Cresol Insol.
- R: Resid
- D: C₄+ Distillate
- $C_1C_3:C_1-C_3$ Gases



















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Figure 7. HTR Parity Plots



Figure 8. CSD Parity Plot





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Figure 11. Integrated Two-Stage Process Simulation

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Section 13

ASSESSMENT OF RAPID METHODS FOR PREDICTING STABILITY AND COMPATIBILITY OF RESIDUAL FUEL OILS

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ABSTRACT

In recent years there has been a significant decrease in the quality of residual fuel oils available to the electric utility industry. Conventional fuel oil analyses and specifications are inadequate to predict or prevent handling problems due to instability or incompatibility. The objective of this project is to develop and evaluate rapid practical tests which utilities can use as an aid in preventing problems resulting from fuel instability and incompatibility.

In an earlier Phase I of this project, utility-supplied "problem" and "nonproblem" fuel oils were analyzed in an effort to understand the reasons for reported problems. Baseline tests for determining instability and incompatibility charateristics were developed. These baseline tests were used for the evaluation of candidate rapid predictive tests which utilities could use for the prediction of stability and compatibility characteristics.

The just-completed Phase IIA of the project has dealt with the development and evaluation of these potential predictive methods using supplemental residual fuels supplied by utilities and refineries. The results of this second phase of the program have provided the basis for recommendations for implementation of predictive testing at selected utilities. Sediment by hot filtration, the Shell accelerated dry sludge test, sediment by extraction (coke), and a modified spot test have been shown to correlate with stability characteristics of residual fuels. The Exxon compatibility prediction based on solubility parameters for the solvent and asphaltene fractions of the fuel is also promising for field application. A very sin le compatibility test based on only two parameters, gravity and modified spot test, shows promise but needs further evaluation.

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INTRODUCTION

The concern of utility operators and managers with problems stemming from the prevalence of lower quality residual fuels in this decade was evidenced by papers and comments presented at the 1985 and the 1986 EPRI Fuel Oil Utilization Workshops $(\underline{1}-\underline{2})$.

Deterioration of residual fuel oil quality has resulted from a combination of factors reviewed by Mueller (1). Foremost has been the depletion of light, sweet, high quality, crude oils and the attendant increase in the use of heavy crudes. It is estimated that as much as 30% of the petroleum refined today in the U.S. contains a heavy crude component (3). Heavy crude oils are typically high in heteroatom content (oxygen, nitrogen, sulfur, etc.), metals content, and asphaltenes. These components are particularly deleterious to product quality.

Decreased demand for residual fuel oil has led to more severe processing, including thermal and catalytic cracking, to convert the very heavy components of crude oil into distillate products. Stability problems are generally minimal in straight-run products, increase in catalytically cracked products, and are the most troublesome in thermally cracked material.

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This report describes the most recent investigations and results (Phase IIA) which have centered on the evaluation and implementation of baseline tests for instability and incompatibility and the evaluation of simple, rapid tests which can be used for the prediction of instability and incompatibility problems.

EXPERIMENTAL AND RESULTS

EARLIER FINDINGS FROM PHASE I

In an earlier report $(\underline{4})$, accomplishments and results obtained from initial studies (Phase I) were presented. The results and conclusions presented at that time included:

- A literature survey was conducted to obtain background information for this project.
- A data base of residual fuel properties was established to provide an indication of the ranges of properties observed in currently available commercial fuels.
- The commonly used tests for characterization of residual fuel oils were investigated and found inadequate to allow prediction of handling problems.
- Problems with fuel oils experienced by utilities could be reproduced in the laboratory, in some cases, and satisfactorily explained.
- A baseline test for determination of stability of residual fuels involving long-term aging at elevated temperatures was developed.
- Concentration of carbon free radicals as determined by electron spin resonance spectroscopy (ESR) correlated with viscosity instability.
- Residual fuel oils containing significant levels of coke exhibited viscosity instability.
- A potential correlation between sediment formation on long-term aging and the Shell accelerated dry sludge test was established.
- Solvent quality (Bureau of Mines Correlation Index, BMCI) and the solvent demand (toluene equivalence, TE) appeared to correlate with incompatibility of residual fuel oils.
- Determination of both solvent quality (BMCI) and toluene equivalence (TE) require moderately complex laboratory and mathematical procedures.
- There was a potential correlation between strong acids and problem fuel behavior, but suitable techniques for field application were not apparent.

PHASE IIA STUDIES

The development of stability and compatibility tests in Phase I was hampered by a limited number of fuels available for comprehensive stability and compatibility testing. Ultimately, 66 additional samples were obtained through the cooperation of utilities and refineries. Processing history provides with some fuels was a definite advantage.

Supplemental samples were subjected to three levels of testing. Intermediate level testing included all of the following tests:

- modified ASTM spot test
- sediment by hot filtration
- Shell accelerated stability
- coke content
- simulated distillation
- API gravity
- viscosity
- Bureau of Mines Correlation Index (BMCI)
- toluene equivalence (TE)
- asphaltene content

All of the listed tests except viscosity were applied to more than 40 fuels. The following additional testing was performed on a subset of 33 of the above 40 fuels:

- determination of stability by baseline test (viscosity change and sediment formation during 80° C (175° F) aging)
- additional characterization including elemental analysis (C, H, and N by Perkin Elmer Elemental Analyzer, S by LECO), ash, and pour point

Fifty-nine blends of residual fuels were evaluated by the following tests:

- prediction of incompatibility by BMCI and TE
- determination of incompatibility by baseline method.

Table 1 is a tabulation of the initial physical and chemical property determinations for the supplemental fuels.

To provide a quick overview of the properties of these supplemental samples, Figures 1 through 7 are histograms that show the number of samples in a specific property range.

Stability/Compatibility Baseline Tests

A major motive in the adoption of a baseline stability test was to reproducibly differentiate, in the laboratory, between problem and nonproblem fuel oils. Problems experienced by utilities are sometimes of local origin and can not be correlated reproducibly with any particular property.

In Phase I, most baseline stability data for residual fuels were obtained by subjecting them to long-term aging at 80° C (175° F) in a beaker covered with aluminum foil. Subsequently, a set of experiments was run with controlled atmospheres to determine the optimum conditions for use in the extended investigations.

Six residual fuels were aged at 80° C (175° F) in three environments. One set of samples was stored in sealed bottles with an argon atmosphere, a second set of samples was stored in sealed bottles with an air atmosphere, and a third set of samples was stored in a bottle with a slow air bleed purging the atmosphere above the fuel at a rate of 20 mL/minute.

At the end of eight weeks of aging, the viscosity, sediment by hot filtration and alphaltene contents were determined. Viscosity and hot sediment data are summarized tables 2 and 3. Results of prior stability testing are included for comparison.

Viscosity increases during thermal stress with air purge showed the largest change of all properties measured. Samples were aged in duplicate, and viscosities were generally in good agreement between duplicates.

An evaluation of these data and prior results suggested that significant and meaningful results might be obtained over a shorter span of storage time if storage temperature were increased. Data from Phase I tabulated in table 4 indicated that aging for 4 weeks at 100° C (212° F) was essentially equivalent to aging for 8 weeks at 80° C (175° F).

Based on these results and observations, the baseline stability testing protocol was altered to include air purge with sampling for viscosity and hot sediment determinations at 4 and 8 weeks at 100° C (212° F) (5). Asphaltene content was determined on each fuel at the end of the aging experiment.

Sediment by Hot Filtration

The basic test used as a measure of residual fuel oil sediment content is based on the new method of the Institute of Petroleum, Test for Total Sediment in Residual Fuel Oils, IP-375. The method is for determination of total

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sediment up to 0.50 percent w/w in residual fuel oil having a maximum viscosity of 130 cSt at 80° C (175° F). In summary, 10 grams of sample is filtered through the prescribed apparatus at 100° C (212° F), and after solvent washing and drying, the total sediment on the filter is weighed.

Sediment in excess of 0.1 weight percent is considered an indication of potential fuel handling/operational problem behavior, and the fuel is categorized as contaminated or unstable.

Determination of Coke-like Material

Coke-like material is determined by ASTM D 473, Sediment in Crude Oils and Fuel Oils by the Extraction Method. Materials insoluble in toluene are measured. Since the sediment that is measured by hot filtration (HFS) includes coke-like material, it is often unnecessary to measure sediment by extraction if the hot filtration sediment is low. In addition to coke-like material, inorganic material such as rust, dirt, catalyst fines, etc. are included in the sediment by extraction value. The presence of inorganic matter may be detected by ash determination. In this work, inorganic matter did not interfere significantly with the determination of coke-like material.

Table 5 contains a tabulation of properties as related to stability testing of 33 residual fuels. Sediment by extraction (coke) is included. The coke data are plotted in figure 8 which shows that all fuels with a coke content of 0.1 percent or higher displayed a greater than 200 percent viscosity increase after 4 weeks of accelerated aging. Since a number of fuels with lower coke content also showed dramatic increases in viscosity, it was concluded that excessive coke indicates potential viscosity instability, but a low coke content does not necessarily imply viscosity stability.

Shell Accelerated Stability Test

The Shell test for the determination of potential dry sludge content (SMS 2696-83, Accelerated Dry Sludge Content of Residual Fuel Oils) involves the addition of a small amount of poor solvent (10 parts residual fuel, 1 part cetane) and aging at 100° C (212° F) for one hour followed by the determination of sediment by hot filtration. The technique for determination of sediment after the cetane addition is similar to the IP method for sediment by hot filtration but differs in a number of minor respects.

In an extended study, the Shell accelerated stability test was compared with sediment measured after 8 weeks of storage at 100° C (212° F) and continuous air purging. Data from these measurements are reported in table 5. These data showed that Shell accelerated dry sludge correctly predicted stability characteristics of 88 percent of all samples. The same rating criteria for Shell accelerated dry sludge were used as described previously for sediment by hot filtration. That is, a value of 0.1 weight percent or greater pinpoints a fuel with potential stability problems.

Figure 9 shows the correlation obtained between these values. The figure shows three fuels that were predicted to be stable by Shell accelerated dry sludge while sediment by hot filtration after 8 weeks accelerated baseline testing exceeded our arbitrary limit of 0.1 weight percent, and there was only one sample that was predicted unstable by accelerated dry sludge that was sediment free after 8 weeks of storage.

Modified Spot Test

During the evaluation of baseline test methods amenable to field application, one method which was exceedingly simple was ASTM D 2781-82, Standard Test Method for Compatibility of Fuel Oil Blends by Spot Test, but this method was found to be unsatisfactory for predicting compatibility or stability. A modified version of the test described by Yokshida et al., $(\underline{6})$ is under consideration for adoption by ASTM and was used to obtain data in this study.

The modified method employs a 9 cm No. 2 Whatman filter which is suspended in a level horizontal position. The oil is heated to 100° C and stirred or otherwise carefully mixed. One drop is placed on the filter paper which is maintained at 100° C for 1 hour. The paper is removed, and the spot is compared to six reference standards. Based on the comparison, a number from one to six is assigned with number one indicating a minimum of suspended solids and a stable fuel while number six is the worst case and indicates potential, if not probable, stability problems.

Table 1 contains modified spot test results for all supplemental samples acquired for Phase IIA of this program. Generally the spot test results compare fairly well with sediments as determined by hot filtration. There also appears to be good agreement between the spot test and accelerated dry sludge values. It may be assumed that a spot test rating of 1 or 2 indicates a stable fuel (or blend) while any higher rating indicates instability. It is also assumed that a Shell accelerated dry sludge content of ≥ 0.1 weight

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percent indicates a potential problem fuel. With these criteria, there is 90% agreement between the spot test and Shell accelerated dry sludge test.

COMPATIBILITY TESTS

Incompatibility generally results from blending a high asphaltene fuel with another fuel or diluent of low solvent power. Testing in Phase I of this project indicated the potential usefulness of techniques first published by Griffith and Siegmund $(\underline{7})$ of Exxon for predicting incompatibility on blending of residual fuel oils.

Exxon used the Bureau of Mines Correlation Index (BMCI) as a measure of aromaticity and the toluene equivalence (TE) as a measure of the degree of aromaticity required to keep the asphaltene fraction of the fuel in solution. This and alternative methods for incompatibility predictions are discussed in following sections.

Bureau of Mines Correlation Index

During Phase I of this study, BMCI was derived from specific gravity and average boiling point determined by simulated distillation. To differentiate among the various options available for calculating BMCI, subscripts have been used to identify the derivation. Thus BMCI derived from average boiling point obtained by simulated distillation (sd) is BMCI_{sd}. Calculated values of BMCI_{sd} for individual fuels are tabulated in Table 1. The formula for this calculation is:

BMCI_{sd} = 87552/(ABP + 460) + 473.7 SG - 456.8 Equation 1 where:

ABP = Average boiling point, °F SG = Specific Gravity, 60/60 °F

As an alternate, BMCI may be determined from viscosity and specific gravity. Abbott, et al. ($\underline{8}$) investigated correlations between kinematic viscosity, gravity, and Watson K factor. Abbott's equations for viscosity can be solved for Watson K factor which can be used to subsequently solve for average boiling point and, sequentially, calculate BMCI. These correlations are based on kinematic viscosity at 210° F.

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Toluene Equivalence

Toluene equivalence is a measure of a fuel or resid's "solvent requirement", or the amount of aromatic character required of a diluent to completely dissolve the asphaltenes in the fuel or mixture. The test is not complex nor difficult, but it is labor intensive, and there is speculation that modifications to the existing procedure or the use of an alternate procedure such as Heithaus Flocculation might reduce the time requirements for obtaining this value. Experimentally derived toluene equivalence is subsequently indicated as TE_{p} .

To eliminate particulates that would interfere with toluene equivalence estimations, a procedural change was adopted which consists of pressure filtration of a neat fuel through a double Whatman GF/A glass fiber filter at 125-150° C using a nitrogen pressure of 50 psig. This preliminary step requires about 30 minutes to filter a 125 mL sample ($\underline{5}$).

Even with the modified filtration procedure, the toluene equivalences remained at 100 for 6 samples. Four of these samples are believed to have high wax content. In these cases, the TE is measuring something other than the solubility of asphaltenes. A solution for the "false" TE values of 100 is being pursued.

Prediction of Incompatibility From BMCI and TE

The basic relationship for predicting incompatibility for BMCI and TE is that incompatibility will result when (BMCI - TE) < approximately 10. To apply the compatibility test to the prediction of the result of mixing two or more fuels, a number of blends was prepared, and the amount of sediment formed was determined. Composition of blends and calculated $BMCI_{sd}$ and TE_e of the blends are summarized in Table 6.

BMCI for a blend is calculated from the BMCI's of the components and the volume percentage of each component. Thus:

BMCI of blend =
$$(V_a)(BMCI_a) + (V_b)(BMCI_b)$$

(of A and B) $(V_a) + (V_b)$

Equation 2

where:

 V_a = volume of A V_b = volume of B $BMCI_a = BMCI \text{ of } A$ $BMCI_b = BMCI \text{ of } B$

According to Griffith and Siegmund $(\underline{7})$, the TE of a blend is dependent on the asphaltene contribution of each component to the asphaltene content of the blend. Thus the TE of blend of A and B is:

TE of Blend = $(W_a)(A_a)(TE_a) + (W_b)(A_b)(TE_b)$ Equation 3 (of A and B) $(W_a)(A_a) + (W_b)(A_b)$

where:

 W_a = weight of A W_b = weight of B A_a = % asphaltene in A A_b = % asphaltene in B TE_a = TE of A TE_b = TE of B

BMCI's and TE's reported in Table 6 were calculated according to these equations.

There were eleven (24.4 percent) wrong predictions in Table 6. Of these, seven predictions indicated incompatibility when, in fact, the blends were compatible. If it is acceptable to a utility that a limited number of blends be predicted incompatible when the blend is in fact compatible, then this prediction technique showed only three unacceptable predictions (6.7 percent). Six of the seven blends for which wrong predictions of incompatibility were obtained had one or more components with a TE of 100 and a low asphaltene content. In such cases, a value of TE of 100 indicates that something is being measured other than solubility of asphaltenes and therefore is considered a false or suspect TE value.

Two of the three wrong predictions of satisfactory compatibility contained a very aliphatic fuel component, D-13. It thus appears that this material has the ability to precipitate asphaltenes beyond that predicted by its low BMCI. The satisfactory predictions for this method ranged from 76 (right/wrong) to 93 (fail/safe) percent.

Two series of blends were made representing a range of compositions from 100% A to 100% B to demonstrate the ability of the (BMCI - TE) comparison to predict compatibility over a range of compositions. The compositions, sediment by hot filtration, and $(BMCI_{sd} - TE_{e})$ are shown in figure 10.

For the blends of D-4 and D-9, there is no sediment for blends containing up to 60% D-4. (BMCI - TE) for these blend compositions remains greater than 10. When the amount of D-9 is increased to 70%, the amount of sediment increases sharply. Note that (BMCI - TE) has dropped to approximately 10 at this composition. As the amount of D-4 is increased beyond 80%, the amount of sediment begins to decrease, and (BMCI - TE) begins to increase above 90% D-4. At 100% D-4, there is still a significant level of sediment, and (BMCI -TE) remains less than 10.

For the blends of D-9 and D-13, there is no sediment for blends containing up to 40% D-13. When the amount of D-13 is increased to 50%, the amount of sediment increases sharply. Note that at this point, (BMCI - TE) has decreased to 11. As before, the level of sediment increases through a maximum and then begins to decrease. In this case, the level of sediment decreases to zero at 100% D-13 although this is not correctly predicted by (BMCI - TE).

A SIMPLIFIED COMPATIBILITY ESTIMATION

In the interests of simplification, and hopefully, without significant deterioration of prediction accuracy, we have developed a correlation that requires only two simple and rapid tests to predict compatibility. The first part of this correlation uses a simplified version of BMCI based solely upon API gravity. These values were derived from a simplified version for calculation of BMCI:

BMCI = 527.9 (SG) - 0.166 (viscosity) - 442.5 Equation 4

Omitting the viscosity term and substituting API gravity for specific gravity, the equation becomes:

BMCI_g = 527.9 x [141.5/(API gravity + 131.5)]-442.5 Equation 5

in which ${\rm BMCI}_{\rm q}$ is based on gravity alone.

Solving equation 5 for a series of hypothetical gravities and applying linear regression analysis to resulting data, provided the following equation:

 $BMCI_q = [API Gravity \times (-3.601)] + 122.96$ Equation 6

Similarly, when experimental values of TE were averaged in groups corresponding to spot test ratings and plotted, an equation was obtained for an estimated toluene equivalence (TE_s) using linear regression analysis:

$$TE_s = (4.965)(spot test rating) + 28.326$$
 Equation 7

Prediction of Incompatibility from BMCIg and TEs

The simplified compatibility prediction is based on the same assumptions as applied to BMCI/TE. That is, the difference between solvent quality and solvent demand is a function of compatibility. Therefore the simplified compatibility estimation is:

The ${\rm BMCI}_{\rm g}$ for blends is calculated from the ${\rm BMCI}_{\rm g}$ of the components and the volume percentage of each component in the same format as shown in Equation 2.

The composite of TEs for blends of fuels was calculated by two equations. The first incorporated the asphaltene content as suggested by the work of Griffith $(\underline{7})$ and the second used only a weighted average of TE_s calculated as described previously for BMCI_g. By eliminating asphaltene content from the equation, it was possible to calculate blend composite values using volume rather than weight.

The average difference in TE_s calculated by the two methods for 25 residual fuel blends with an average TE_s in the range of 33 was only 2.61. Based upon this difference and the primary goal of simplification of prediction methods, it is recommended that composite TE_s of blends be calculated as follows:

$$TE_{s} = (V_{a})(TE_{s} \text{ of } A) + (V_{b})(TE_{s} \text{ of } B)$$
$$(V_{a} + V_{b})$$

Equation 8

where:

 V_a = Volume percent of component A V_b = Volume percent of component B TE_s = Toluene equivalence derived from spot test ratings Spot test data were available for only a portion of the fuels used in the 45 blends that were prepared and studied. The data in Table 7 include only those blends for which spot test ratings were available. Based on these 25 blends, $(BMCI_{sd} - TE_e)$ predictions were 60 percent correct while $(BMCI_g - TE_s)$ predictions were 96 percent right. However, eight of the ten wrong $BMCI_{sd}$ - TE_e predictions indicated incompatibility when the blend was actually compatible, and five of these eight had one or more components with false or suspect TE's of 100. Predicting occasional erroneous incompatibility should be an acceptable error to utilities, and if so, the fail/safe prediction accuracy of $BMCI_{sd}$ - TE_e becomes 92 percent.

The conclusion from this study is that it may be possible to predict compatibility for blends of residual fuels by simply measuring gravity and making a very quick and simple spot test on individual fuels. Calculations can be based upon component volumes so that no conversion from volume to weight is required. Asphaltene content is not required nor is distillation, viscosity, or toluene equivalence. No measured properties of the blend are required. This simplified compatibility estimation, requiring only gravities and spot tests of the fuels to be blended, may produce a prediction that is 96 percent effective in preventing problems arising from comingling of fuels.

RELATIONSHIPS BETWEEN CRUDE SOURCE, REFINERY PROCESSING, AND FUEL PROPERTIES

Most samples provided in this study were purchased on the spot market, and information related to crude source was not available. However, processing data were provided for thirteen of the residual fuels tested in this program.

The primary observations made in regard to crude source were that highly aliphatic, low sulfur, waxy crudes offer the potential for incompatibility on blending. Straight run materials are generally of good stability, while severe thermal processing can induce severe viscosity instability.

Catalytically cracked materials or hydrocracked materials can be of variable stability depending on the severity of processing.

Finally, sever processing of heavy crudes in a PDU has been documented as producing products of poor stability/compatibility.

SUMMARY AND CONCLUSIONS

Preliminary studies included a literature survey and the creation of a residual fuel oil data base to provide further insight into the problems to be addressed to develop and evaluate potential predictive tests. To eliminate

uncertainties regarding fuel quality, a baseline stability test was developed. The test ultimately adopted was conducted at 100° C (212° F) with a continuous air purge of each sample container. Sediment formed in 4 weeks at 100° C correlated with sediment formed in 8 weeks at 80° C (175° F).

Phase IIA was initiated in mid-1986 to continue the development/evaluation of potential predictive tests and their comparison with the baseline stability and compatibility tests. Subsequently, 66 additional samples were acquired from participating utilities and refineries.

Tests that were performed on all or a portion of these additional samples as well as some of the initial fuels included:

- sediment by hot filtration
- Shell accelerated dry sludge
- coke content (toluene insolubles + carbon/hydrogen analysis (when appropriate)
- simulated distillation
- API gravity
- viscosity
- Bureau of Mines Correlation Index (BMCI)
- toluene equivalence (TE)
- asphaltene content
- elemental analysis
- ash
- pour point
- prediction of incompatibility by BMCI and TE
- determination of instability by baseline method
- determination of incompatibility by baseline method

Baseline tests (Table 5) showed that only 9 of 33 fuels formed unacceptable sediments during 4 weeks of accelerated aging at 100° C (212° F), and one of these was borderline. At 8 weeks, 11 of the same 33 fuels showed instability. Four weeks at 100° C (212° F) should be the equivalent of several years storage at normal storage temperatures for residual fuels which is in the range of 120 to 150° F.

The efficacy of several rapid predictive tests was demonstrated by testing with a wide range of residual fuels. These tests are included accelerated dry sludge, coke content, (BMCI - TE), and a modified spot test.

The Shell accelerated dry sludge test correctly predicted stability characteristics of residual fuels for 88 percent of 33 fuels tested. From these data it would appear that the accelerated dry sludge is an acceptable stability prediction method for those utilities with modest laboratory facilities. The presence of sediment by extraction (coke) in excess of 0.08-0.10 weight percent is effective in the prediction of viscosity instability. However, the converse is not valid.

BARANA CO. - WANT - AND

The Bureau of Mines Correlation Index (BMCI) and toluene equivalence (TE) were shown to be effective in predicting compatibility of fuel blends. Although there are several techniques for calculating BMCI, the use of gravity and viscosity would probably find the widest applicability from the standpoint of laboratory requirements.

Of 45 blends of residual fuels, the (BMCI - TE) prediction of compatibility was correct for 75.6 percent of the blends as measured by sediment by hot filtration. This prediction was based upon a value of +10 or greater for (BMCI - TE) indicating compatibility while values below +10 indicated incompatibility. If it is acceptable to a utility that a limited number of blends will be predicted incompatible when the blends are actually compatible, then (BMCI - TE) was 93 percent accurate as a fail/safe predictive measure. The test results produced false predictions of compatibility for only 3 of 45 blends.

A modified spot test was found to be in 90 percent agreement with the Shell accelerated dry sludge test. The simplicity of this test and the availability of a commercial field test kit make the method worthy of consideration for smaller utilities that lack adequate laboratory facilities.

An alternate method for compatibility prediction was developed which utilizes only API gravity and a modified spot test. Both test procedures are simple and rapid. The conclusions from this study were that it may be possible to predict compatibility effectively using this greatly simplified procedure but further testing is required before it can be recommended for field application.

RECOMMENDATIONS

The objective of a continuing program of research (Phase IIB) would be implementation of predictive testing at selected utilitites. The purpose of this effort would be to establish the effectiveness of the recommended test methods in field application. The candidate test methods have been previously discussed and are tabulated below:

- Modified spot test
- Sediment by extraction (coke)
- Sediment by hot filtration
- Accelerated dry sludge

- Bureau of Mines Correlation Index (BMCI)
 from specific gravity and average boiling point
 from specific gravity and viscosity
 from API gravity only
- Toluene equivalence
 experimental
 from spot test rating
- Compatibility prediction from BMCI and TE

To achieve the technology transfer objectives listed above, the following contractor research and support is recommended:

- Establish testing methodology at participating facilities
- Provide expertise to train utility personnel in testing protocol
- Provide equipment for specialized testing
- Serve as a referee lab to monitor test results and act as a trouble shooter
- Provide baseline testing by long-term accelerated storage
- Provide counseling to utility technicians
- Investigate modified prediction tests and new approaches to further simplify predictive testing

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Table 1

			Viscos	14.0	Pour		Acabal			S inu	lated						
	Gravil	łu	cSt.	Point	Ach	tones ²	Soot	E (14	Day Studes ⁵	110	L Des Idus	Accele	rated	Distill	<u> </u>		
	Spec if ic	*API	180° F	. ۵۱۵۰۰	Wit 12	Wr t	Jost 3	ut v ⁴	ury studge ,	607	Residue,	BUC, 5	10 luene 7		t leme	ntal	~~~
		<u></u>	<u> </u>	<u>`</u>	91_2		iesc		ML A	20%		mu	<u>Equiv.</u>	<u> </u>	<u></u>	<u></u>	<u></u>
۸1	0.9927	11.0	14.81	0	0.082	3, 65	1	0,14	0, 12	746	24	86.0	52	87,93	10.04	0.08	0.98
A 2	0.9924	11.1					1	0.14	0, 10	770	25	84.5	52				
A- 3		(12.8)			(0.06)	(4,6)	2										(0.96)
A · 4	0.9974	10.4	42,65	40	0.096	6.85	5	0,19	0, 25	909	45	79.6	60	86, 75	10,06	0.45	1.02
ΑS	0.9964	10.5	53, 89	30	0.073	2,86	4	0,19	0, 18	949	46	77.3	43	86, 92	10.52	0.30	0.95
A 6	0.9969	10.4	54.80	35	0.112	4, 26	5	NF	ЯF	938	45	78.1	55	86.82	10.58	0.39	0.98
A-8	0,9975	10.4	57, 32	45	0.126	4.78	6	NF	NF	976	48	76.7	64	86, 28	10.60	0.39	0.96
A 9	0.9981	10.3	50.04	25	0.045	1.67	2	0,01	0.03	924	43	79.3	33	87.99	10.44	0, 48	0.93
A 10	0.9921	11.1	63.52	60	0.034	2.20	2	0.03	0,00	961	47	74.8	33	87.92	10.70	0.40	0.97
A-11	0.9816	12.7	45, 75	45	0.042	4.98	2	0.02	0,03	953	47	70.1	56	87.64	10.87	0.36	1.03
A 12							2			976	48				10107	0,00	1105
A 13							1										
A 14							1										
A-15							1										
A 16							1										
A- 17		(11.2)			(0,06)	(3,9)	1										(0 22)
A-18		(11.3)			0.05	(2.8)	1										(0.95)
R·1	0,9588	15.1	69.42	70	0.020	1.15	1	0.00	0,01		58	60.3*	100	86.98	11.72	0, 45	0.27
82	0.9351	19.8	21.08	35	0.022	1,69	1	0.00	0,00	827	20	54,5	22	86, 79	12.19	0, 53	0.25
B- 3	0.9284	20.9	32.78	105	0.021	0.07	2	0.00	0.01	954	46	44.9	100	85.87	12.66	0, 35	0.24
C 1	0.9760	13.5					1	0.03	0.04	917	43	69.1	16				
C 2	0,9633	15.4			(0.05)		1	0.00	10.0	935	44	62.3	37				(0.85)
с з	0.9647	15.3			(0.06)		1	0.01	0.01	948	46	62.4	58				(0.03)
C-4	0.9651	15.1	79, 19	60	0.032	8, 20	1	0.01	0.01	923	10	63.7	36	86.09	11 40	0.26	0.06
C-5	0.9647	15.2			(0.08)		1	0.03	0.02	899	17	64.6	51	00.05	11.45	0.00	(0.00)
C 6	0.9620	15.7			(0.07)		,	0.01	0.01	012	39	67.7	.10				(0.97)
c 1	0.9653	15.1			(0.05)		•	0.01	0.01	889	35	65 4	43				(0.00)
с. в	0.9629	15.5			(0.08)		1	0.01	0.01	0.17	33	6) 6	30				(0.00)
C-9	0.9641	15.3	41.85	80	0.039	4.10	2	0.01	0.02	94/	46	62 7	41	96.20	11 45	0.20	(0.83)
€-10	0.9670	14.8	46. 31	85	0.039	5.64	، ۱	0.10	0.05	88t 273	43	66 3	50	06.08	11,45	01.0	1.08
C 10	0.9366	19.6	23.88	80	0.020	2 89	4	0.05	0,14	000	37	60.3	00	00.5/	13.10	0, 32	1.03
6.42	0 9623	15 5	23.00		0.017	6,00	1	0,00	0.10	010	JI 41	53,5	41	00,23	12,13	0.22	1.05
S 16	0.7023	13.3					1		0,10	A10	41	01.0	37				

RESIDUAL FUEL OIL ANALYSES¹

Values within parentheses were reported by the utility. Others were determined at HIPER.

Asphaltene content determined at HIPER was by ASIM 0 3279.

Run by modified (proposed) ASTH "Method for Stability and Compatibility for Residual Fuels by Spot Test," 100° C/1 hour.

A Sediment by hot filtration values determined at NIPER was by IP-375 "lest for lotal Sediment in Residual fuel Oils," dual filter method.

Film by Shell Method, SHS 2696 83. 6 Sureau of Mines Correlation Index, calculated from simulated distillation data except those with an asterisk are calculated from viscosity data. 7 Exxon Analytical Method Specification 79 004 (Revised).

										Simul	ated						
			<u>Viscos ity</u>	Pour		Asphal -		llot	Accelerated	Disti	11., °F						
	Gravit	<u>y</u>	cSt.	Point,	Ash,	tenes',	Spot	Filt.,	Dry Sludge ⁵ ,	BP,	Res idue .		loluene		E leme	ntai	
	Spec if ic	<u>PAPI</u>	180* F	<u>•F</u>	<u>WL X</u>	WL X	<u>Test</u> ³	WL X4	WL X	50%	<u> </u>	<u>19401</u> 6	Equiv.7	<u>_xc</u>	<u>xH</u>	XH	xs_
C 13	0.9587	16.1					1			895	39	62.0	36				
C 14	0.9391	19.2	24.22	80	0.019	2.20	ı	0.01	0.00	830	30	55.9	24	86, 38	12.11	G. 44	1.03
C 15							1										
C-16	0.9517	17.2	47, 27	50	0.024	5.65	1		0.0?	932	43	56.9	57	86.44	11.72	0.53	0.99
C-17	0,9370	19.5					ı		0.00				16				
C 18	0.9942	10.8	59.40	65	0.047	4.78	1	0.03	0.05	1001	49	74.1	31	87.36	10,50	0, 32	1.00
C-19	0.9554	16.6					1		0.02								
C 70	0.9486	17.7					1		0.01								
Ç-21	0,9550	16.7					1		0, 02								
C-22	0,9752	13.6	45.83	65	0.052	4.85	2	0.00	0, 47	886	38	70.2	53	B6. 96	11,28	0.37	1.03
C 23	0,9575	16,3					1										
C-24	0,9879	11.7					1										
C- 25	0.9733	13.9					1										
C-26							1										
C 27	0.9728	14.0	72.80	30	0.056	6.87	1	0.01	0.10	951	45	66.1	29	85.85	11.36	0.34	1.97
n-1	1.0279	6.16					1	0.03	0.04	776	,	100.0	a				
0.2	0.9845	12.2	11.24	100	0.040	0.45	,	0.03	0.05	917	12	79.24	۰. ۱	97 67	10 64	0.12	1 07
0-3	0.9758	13.5	231.80	90	0.013	4.05	1	0.00	0.00	••••	55	65.6	13	85.04	11 69	0.17	2 10
04	0.9035	25.1	9,862	65	0.007	1. 72	5	0.42	0.41	705	13	45 3	29	96 57	12 76	0.25	0.24
n 5	0.9604	15.8	50, 81	20	0.058	9, 59	1	0.00	0.02	801	76	67 6	20	87 52	11 46	0.62	5 DE
0.6	0,9863	12.0	60.27	80	0.014	1.02	i	0.00	0.00	903	30	74.6	40	95 17	10.97	0.02	2 16
07	0.9145	23.2	15.65	85	0.008	1, 12	2	0.08	0,10	857	31	42 9	42	96.25	12 69	0.00	0.09
0.8	0.9628	15.5	111.4	95	0.022	2.05	1	0.04	0, 07		67	61.0	48	86 93	11 66	0.12	0.00
n 9	1.0180	7.5	89.82	40	0, 103	14.1	1	0.01	0.04	880	42	90 R	52	87 23	9 84	0,33	1 72
B 10	0.9840	12.3					1			000		5010	51.	07,25	3.01	0.70	1.72
0-11	0.9825	12.5					1										
0.12	0.9636	15.3	73.78	90	0.022	1.34	1	0.07	0.02		60	52.5*	160	86 66	11 63	0.44	0.20
0 13	0.8936	26.8	5, 456	80	0.019	0.08	4	0.01	0.03	753	6	39.7	18	85 37	13 24	D 49	0.20
8-14	0.9556	16.4	99.57	95	0.014	1, 15	i	0.01	0.00		67	58.24	100	86 68	11 87	0 17	0.22
0 15							1						100	00.00		0, 3/	0.22
D 16							1										
0 17	1,0681	0,98	11.24	20	0.004	0.61	2	0.01	0.01	7.35	,	122.4	100	90, 49	8.14	0, 69	0.50
D 18	1.0661	1.23	18.10	40	0.049	1, 55	2	0.04	0.04	771	12	119.2	100	89.01	8.41	0, 59	1.69

		Tab	le 1	
RESIDUAL	FUEL	OIL	ANALYSES ¹	(continued)

Values within parentheses were reported by the utility. Others were determined at NIPER.

Asphaltene content determined at NIPER was by ASIM D 3279.

³Run by modified (proposed) ASTM "Method for Stability and Compatibility fo Residual Fuels by Spot Test," 100° C/1 hour.

Kin NY Modified (proposed) Asim "Method for statisty and comparising to restand rules by spot rest, for cylindr. ⁴Sediment by hot filtration values determined at NIPER was by IP 375 "lest for lotal Sediment in Residual Fuel Dils," dual filter method. ⁵Run hy Shell Method, SMS 2696 B3. ⁶Bureau of Hines Correlation Index, calculated from simulated distillation data except those with an asterisk are calculated from viscosity data, ⁷Exxon Analytical Method Specification 79 004 (Revised).

Table 2

VISCOSITY (AT 180° F) OF RESIDUAL FUELS AGED AT 80° C (175° F)

		Sample Number						
		<u>1956</u> 1	<u>1964</u> 2	<u>1954</u> 1	<u>1980</u> 2	2035	2103	
Viscosity	of Fresh Fuel, cSt:	23.60	30.31	65.60	47.45	97.84	69ء 60	
Viscosity 8 Weeks	After Aging, at 80° C (175° F)							
Flor	wing Air Bottle 1 Bottle 2	29.40	39.55	173.73	80.19 80.81	367.79 373.28	280.00	
	Avg. of Duplicates				80.50	370.54		
	% Increase (Over Fresh Fuel)	24.6%	30.5%	165.%	69.7%	279.%	302.%	
Clos	sed Bottle, Air Bottle 1 Bottle 2	24.06 24.01	31.03 30.65	72.17	53.98 52.15	105.49 128.19	78.88	
	Avg. of Duplicates	24.04	30.84		53.06	116.84		
	% Increase	1.86%	1.75%	10.0%	11.8%	19.4%	13.3%	
C109	sed Bottle, Argon Bottle 1 Bottle 2	23.61 24.03	31.53 30.28	71.88	53.72 49.82	100.82 104.62	80.16	
	Avg. of Duplicates	23.82	30.90		51.77	102.72		
	% Increase	0.93%	1.95%	9.6%	9.10%	4.99%	15.2%	
Previous E Aged 8 w (175°	Experiment Weeks at 80° C	25.80	38.44	155.87	69.07	(245.91 ³))(113.01 ³)	
(1/5	% Increase	9.3	27.	138.	46.	151.	62.	

1 2 Nonproblem 3 These were aged only 4 weeks at 175° F.

			Sample Number				
	1956	<u>1964</u>	<u>1954</u>	<u>1980</u>	2035	2103	
Sediment in Fresh Fuel, %	0.02	0.01	0.00	0.05	0.02	0.27	
Sediment After Aging ¹ , 8 Weeks at 80° C (175° F)							
Flowing Air	0.04	0.01	0.02	0.61	Unfilter-	2.53	
	0.04	0.01	0.03	0.64	able Unfilter-	2.39	
Avg. of Duplicates ²	0.04	0.01	0.025	0.625	able	2.46	
Closed Bottle, Air	0.02	0.00	0.00	0.09 0.08	0.02 0.04	0.40 0.40	
Avg. of Duplicates ²	0.02	0.00	0.00	0.085	0.03	0.40	
Closed Bottle, Argon	0.02 0.03	0.00	0.00	0.03 0.04	0.03 0.04	0.44 0.44	
Avg. of Duplicates ²	0.025	0.00	0.00	0.035	0.035	0.44	
Previous Experiment Aged 8 weeks at 80° C (175° F) (Aged in covered beaker)	0.20 ³	0.06 ³	0.03	1.35 ³ l	Infilter- able	3.92	

Table 3

HOT FILTRATION SEDIMENT OF RESIDUAL FUELS AGED AT 80° C (175° F)

 $^{1}\mathrm{Hot}$ filtration sediment was determined by the dual filter method except as noted. 2Duplicate determinations on fuel from the same bottle. 3Single filter method.

Tab	le	4
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Sample	Fresh	2 Weeks	4 Weeks	4 weeks	8 Weeks
<u>No.</u>		100° C	80°C	100° C	80° C
1953 2033 2035 2103 2115 2120	0.00 0.00 0.02 0.27 1.57 0.16	0.03 0.02 0.07 1.98 2.98 1.38	0.03 0.01 0.11 3.70 5.21 1.24	0.02 NF 3.56 8.86 1.41	0.03 NF 3.92 8.26 1.37

COMPARISON OF	- 80°	AND	100°	С	AGING
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NF = not filterable

Table 5

BASELINE STABILITY TEST

			Viscosity, Kinematic centiStokes at 180°F					Asphaltene Content D 3279				
	Accelerated Dry Sludge Wt %	celerated y Sludge <u>Storage Period Wks.</u> *		Sediment by		Storag	je Per	iod Wks.*	el Chara	Stor. Prd. Wks.*		
					LALIACTION			<u>» cnng</u>	<u> </u>	% Chng		8
A-1	0.12	0.15	0.15	0.20	0.14	14.81	47.89	223	69.89	372	3 65	8 54
A-4	0.25	0.19	0.38	0.34	0.10	42.65	199.6	368	246.5	478	6.85	13 56
A-5	0.18	0.19	0.11	0.00	0.12	53.89	222.1	312	313.1	481	2.86	7.84
А-б	NF	NF	1.92	4.40	0.14	54.80	200.9	267	319.5	483	4,26	10.54
A-8	NF	NF	2.81	5.84	0.08	57.32	142.8	149	292.4	410	4.78	10.46
A-9	0.03	0.01	0.00	0.00	<0.01	50.04	134.4	169	248.9	397	1.67	5.95
A-10	0.00	0.03	0.00	0.00	<0.03	63.52	135.0	113	163.9	158	2.20	8.78
A-11	0.03	0.02	0.06	0.57	<0.02	45.75	157.5	244	233.3	410	4.98	12,12
8-1	0.01	0.00	0.00	0.00	0.00	69.42	156.12	124	197.4	184	1,15	3.47
B-2	0.00	0.00	0.00	0.00	0.00	21.08	29.40	39	33.44	59	1.69	3.46
B-3	0.01	0.00	0.00	0.00	0.00	32.78	54.55	66	63.50	94	0.07	0.08
C-4	0.01	0.01	0.00	0.01	<0.01	79.19	168.50	112	224.3	183	8,20	12.08
C-9	0.08	0.10	0.09	0.06	0.09	41.85	70.65	69	94.22	125	4,10	8.25
C-10	0.14	0.05	0.90	1.82	<0.05	46.31	77.85	68	99.08	114	6.54	10.13
C-11	0.18	0.06	0.59	1.50	<0.06	23.88	33.24	39	39.40	65	2.88	5.82
C-14	0.00	0.01	0.00	0.00	<0.01	24.22	34.64	43	42.11	74	2.20	5.53
C-16	0.02	-	-	0.01	0.02	47.27	99.51	110	132.57	180	5.65	9,29
C-18	0.01	0.03	0.01	0.03	<0.03	59.40	112.78	90	146.3	146	4.78	9,18
C-22	0.02	0.00	0.02	0.65	0.00	45.83	99.11	116	141.6	209	4.85	0.21
C-27	0.00	0.01	0.00	0.00	<0.01	72.80	218.3	200	385.5	430	6.87	12.41
D-2	0.05	0.04	0.01	NF	<0.04	11.24	12.69	13	13.30	18	0.45	1.60
D-3	0.00	0.00	0.00	0.00	0.00	231.80	304.1	31	426.9	84	4.05	8.01
D-4	0.41	0.42	1.05	1.23	0.08	9.862	16.95	72	**	•••	1.72	4,96
D-5	0.02	0.00	0.00	0.03	0.00	50.81	154.26	204	309.7	510	9.59	14.96
D-6	0.00	0.00	0.00	0.00	0.00	60.27	101.34	68	120.5	100	1.02	2.49
D-7	0.10	0.08	NF	NF	0.06	15.66	23.82	52	30,98	98	1,12	4.22
D-8	0.07	0.04	0.00	0.00	<0.04	111.4	245.9	121	354.9	219	2.05	5.72
D-9	0.04	0.01	0.00	0.01	<0.01	89.82	1257.0	1299	374.6	3263	14.06	23.30
D-12	0.02	0.07	0.00	0.00		73.28	123.77	69	165.2	125	1.34	4.44
D-13	0.03	0.01	0.07	0.01	<0.01	5.456	7.483	37	6.323	16	0.08	2.47
D-14	0.00	0.01	0.02	0.00	<0.01	99.57	170.69	71	257.53	159	1.15	3.72
D-17	0.01	0.01	0.02	0.00	<0.01	11.24	21.23	89	27.17	142	1.55	7.44
D-18	0.04	0.04	0.03	0.00	<0.04	18.10	37.12	105	41.88	131	_	8.04
2103	NF	0.02	0.53									0.01

*100° C, air purge NF - not filterable
** Viscosity not measurable due to precipitate clogging viscometer.

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CALCULATION OF ${\rm BMCI}_{\rm sd}$ and ${\rm TE}_{\rm e}$ for blends

	Component A							Component B				Blend				
						Asphal-					Aspha	1-				
						tenes*					tenes	×				
No.	<u>ID</u>	<u>wt %</u>	<u>S. G.</u>	<u>BMC1</u> sd	<u>TE</u> e	<u>wt %</u>	ID	<u>w† %</u>	<u>\$.G.</u>	BMC1 sd	<u>TE</u> e	wt 发	BMCIsd	<u> </u>	BMCI_sd_TE_e	Sediment, wt. %
1)	2033	70	0.9911	72.7	24	12.0	D-13	30	0.8936	38.7	48	0.08	61.7	24.1	37.6	0.07
2)	2035	70	0,9961	76.1	61	12.1	D-13	30	0.8936	38.7	48	0.08	64.0	61.0	3.0	NF
3)	1980	50	0,9680	64.4	46	4.7	D-13	50	0.8936	38.7	48	0.08	51.0	46.0	5.0	0,46
4)	2103	65	1.0002	75.0	66	9.6	D-4	35	0.9035	46.3	38	1.72	64.3	63.5	0.8	1.12
5)	C-10	80	0.9670	66.3	60	6.54	C-11	20	0.9366	53.5	41	2.88	63.7	58.1	5,6	0.08
6)	C-18	80	0.9942	74.1	31	4.78	D-4	20	0.9035	46.3	38	1.72	68.1	31.6	36,5	0.04
7)	1953	60	0,9850	69.3	44	10.4	B-3	40	0,9284	44.9	100	0.07	59,2	44.3	14.9	0,05
8)	D-9	75	1.0180	90.8	52	14.1	D-13	25	0.8936	38.7	48	0.08	76,5	52.0	24.5	NF
9)	D-9	80	1.0180	90.8	52	14.1	D-4	20	0,9035	46.3	38	1.72	81.0	51.6	29.4	0.00
10)	1954	90	0.9630	61.3	40	9.8	D-13	10	0.8936	38.7	48	0.08	58.9	40.0	18.9	0.03
11)	C-4	90	0.9651	63.7	36	8.2	D-13	10	0.8936	38.7	48	0.08	61.0	36.0	25.0	0.00
12)	1953	60	0.9850	69.3	44	10.4	C-14	40	0,9391	55.9	24	2.20	63.8	41.5	22.3	0.01
י3)	2033	80	0,9911	72.7	24	12.0	C-11	20	0.9366	53.5	41	2.88	68.7	25.0	43.7	0.04
14)	2103	70	1.0002	75.0	66	9.6	8-3	30	0,9284	44.9	100	0.07	65.5	66.1	-0,6	NF
15)	D-9	70	1.0180	90.8	52	14.1	C-11	30	0.9366	53.5	41	2.88	79.1	51.1	28.0	0.00
16)	2033	40	0,9911	72.7	24	12.0	D-13	60	0.8936	38.7	48	0.08	51.5	24.2	27.3	NF
17)	2035	40	0,9961	76.1	61	12 .1	D-13	60	0.8936	38.7	48	0.08	52.7	60,9	-8.2	NF
18)	1980	20	0,9680	64.4	46	4.7	D-13	80	0.8936	38.7	48	0.08	43.5	46.1	-2,6	0,23
19)	2103	25	1.0002	75.0	66	9.6	D-4	75	0,9035	46.3	38	1.72	52.9	56.2	-3.3	0,91
20)	C-10	20	0.9670	66.3	60	6.54	C-11	80	0.9366	53.5	41	2.88	56.0	48.0	8.0	0.04
21)	C-18	20	0.9942	74.1	31	4.78	D-4	80	0,9035	46.3	38	1.72	51.4	35.1	16.3	0,19
22)	1953	40	0.9850	69.3	44	10.4	B-3	60	0.9284	44.9	100	0.07	48.8	44.6	4.2	NF

NF = not filterable

*D3279 (n-heptane insolubles)

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Table 6 (continued)

CALCULATION OF ${\tt BMCI}_{sd}$ and ${\tt Te}_{e}$ for ${\tt BLENDS}$

	Component A							Component B				Blend				
No		w + 2	S. G.	BMCL	TF	Asphal- tenes* wt %	ID	wt %	S. G.	BMCI	TE_	Asphal- tenes* wt %	BMCI	TE	BMCITE	Sediment, wt. 3
10.		<u> </u>		sd	<u>—</u> e						е		50		sue	
23)	D-9	25	1.0180	90.8	52	14.1	D-13	75	0.8936	38.7	48	0.08	50,5	51.9	-1.4	NF
24)	D-9	20	1.0180	90.8	52	14.1	D-4	80	0.9035	46.3	38	1.72	54.4	47.4	7.0	0.54
25)	1954	20	0,9630	61.3	40	9.8	D-13	80	0.8936	38.7	48	0.08	43.0	40.3	2.7	0.50
26)	C-4	20	0,9651	63.7	36	8.2	D-13	80	0.8936	38.7	48	0.08	43.4	36.5	6.9	0.34
27)	1953	40	0,9850	69.3	44	10.4	C-14	60	0,9391	55.9	24	2.20	61.1	39.2	21.9	0.00
28)	2033	20	0.9911	72.7	24	12.0	C-11	80	0.9366	53,5	41	2.88	57,2	32.3	24.9	0.07
29)	2103	30	1.0002	75.0	66	12.1	B-3	70	0.9284	44.9	100	0.07	53.5	66.5	-13.0	NF
30)	D-9	30	1.0180	90.8	52	14.1	C-11	70	0.9366	53,5	41	2,88	64.0	48.4	15.6	0.05
31)	8-1	70	0.9588	51.4	100	1.15	C-1	30	0,9760	69.1	16	0.63	56.6	84.0	-27.4	0,00
32)	D-8	70	0,9628	61.0	48	2,05	C-18	30	0.9942	74.1	31	4.78	64.8	39.5	25.3	0.02
33)	D-12	70	0,9636	62.5	100	1.34	C-22	30	0,9752	70.2	53	4.85	64.8	71.4	-6.6	0,00
34)	D-17	70	1.0681	122.4	100	0,61	D-1	30	1.0279	100.9	0	1.14	115.8	55.5	60,3	0.01
35)	D-18	70	1.0661	119.2	100	1.55	D-5	30	0.9604	67.6	29	9,59	102.6	48.4	54.2	0.03
36)	D-17	70	1.0681	122.4	100	0,61	D-6	30	0,9863	-76.6	40	1.02	107.9	75.0	32.9	0,00
37)	D-18	70	1,0661	119.2	100	1.55	D-6	30	0,9863	76.6	40	1.02	105.7	86,8	18.9	0.02
38)	D-8	70	0,9628	61.0	48	2,05	D-6	30	0,9863	76.6	40	1.02	65.6	46.6	19.0	0.00
39)	B-1	70	0.9588	51.4	100	1,15	C-22	30	0.9752	70.2	53	4.85	57.0	69.7	-12.7	0.01
40)	D-12	70	0.9636	62.5	100	1.34	D-1	30 ~	1,0279	100.9	0	1.14	73.5	73.3	0.2	0.06
41)	B-1	50	0.9588	51.4	100	1,15	D-17	50	1.0681	122.4	100	0.61	85.0	100.0	-15.0	0.00
42)	C-1	50	0.9760	69.1	16	-	D-1	50	1.0279	100.9	0	1.14	84.6	5.7	78.9	0.02
43)	D-17	50	1.0681	122.4	100	0.61	D-12	50	0.9636	62.5	100	1.34	90.9	100.0	-9.1	0.01
44)	D-6	50	0.9863	74.6	40	1.02	C-1	50	0.9760	69.1	16	0.63	71.8	30.8	41.0	0.01
45)	D-13	30	0.8936	38.7	48	0.08	2035	30	0,9961	76.1	61	12.1	58.4	49.1	9.3	NF
-12)	5 15	20			•		C-4	40	0,9651	63.7	36	8.2				

NF = not filterable

*D 3279 (n-heptane insoluble)

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ESTIMATION OF INCOMPATIBILITY OF RESIDUAL FUEL BLENDS

Blend	(1) Blend BMCI _{sd} *	(2) Blend, TE _e *	(3) Blend BMCIg [*]	(4) Blend TE _s *	Blend BMC1-TE (1)-(2)	Blend BMC1-TE (3)-(4)	Sediment, hot filtration, wt pct	Baseline, compatibility results	BMCI _{sd} compatibility prediction*	BMCI _g compatibility prediction*	Right/wrong predictions, ^{BMCI} sd	BMC I
5	63.7	58,1	66,12	36,35	5.6	29.77	0.08	с	1	с	W	ок
6	68.1	31.6	72,96	37.58	36.5	35,38	0.04	С	С	С	OK	OK
8	76.5	52.0	76.83	37.39	24.5	39.44	NF	1	С	C	W	W
9	81.0	51.6	82.02	37.66	29.4	44.36	0.00	С	С	c	OK	ок
11	61.0	36.0	64.07	34.89	25.0	29.18	0.00	С	С	С	ОК	ОК
15	79.1	51.1	82.1	38.02	28.0	44.08	0,00	С	С	С	ОК	OK
20	56.0	48.0	55.75	45.28	8.0	10.47	0.04	С	1	С	W	ОК
21	51.4	35.1	42.11	49,47	16.3	-7.36	0.19	I	C	I ,	W	OK
23	50.5	51.9	42.19	44.81	-1.4	-2.62	NF	1	I	ł	OK	OK
24	54.4	47.4	44.08	49.54	7.0	-5.46	0.54	1	I	t	OK	ОК
26	43.4	36.5	34.37	45.39	6.9	-11.02	0.34	1	I	1	ОК	OK
30	64.0	48.4	64.7	43.97	15,6	20.73	0,05	С	С	С	OK	OK
31	56.6	84.0	67.76	33.29	-27.4	34.47	0.00	С	1	С	W	ОК
32	64.8	39.5	72,11	33,29	25.3	38,82	0,02	С	С	C	OK	OK
33	64.8	71.4	69.69	34.77	-6.6	34.92	0.00	С	1	С	W	ок
34	115.8	55.5	113.68	36.73	60.3	76,95	0,01	С	С	С	ОК	OK
35	102.6	48.4	101.62	36.66	54.2	64,96	0.03	С	С	C	OK	OK
36	107.9	75.0	106.85	36,68	32.9	70.17	0.00	с	С	С	ОК	ок
37	105.7	86.8	106.25	36,68	18.9	69.57	0.02	С	С	С	ОК	OK
38	65.6	46.6	70.86	33,29	19.0	37.57	0.00	С	С	С	OK	OK
39	57.0	69.7	67.65	34.76	-12.7	32.89	0.01	С	1	С	W	OK
40	73.5	73.3	77.3	33.29	0.2	44.01	0,06	С	1	С	W	OK
41	85.0	100.0	90.74	35.64	-15.0	55,10	0.00	С	I	С	W	ок
43	90.9	100.0	92.33	35.65	-9.1	56.68	0,01	С	I	С	W	ОК
44	71.8	30.8	77.03	33,29	41.0	43.74	0.01	С	С	С	ОК	ок

* BMCl = Bureau of Mines Correlation Index calculated from ABP obtained from simulated distillation, Eq. 1, Section 5.2.5.1 TE = Toluene equivalence obtained experimentally, Section 5.2.5.2. BMCl = BMCl calculated from utilizing only API gravity, Eq. 5, Section 5.2.5.4. TE = TE calculated from utilizing modified spot test ratings, Eq. 6, Section 5.2.5.5. C = Compatible Summary

1 = Incompatible

 $BMCI_{sd}$ -TE_e = 10 wrong; 15 right $BMCI_{g}$ -TE_s = 1 wrong; 24 right

W = Wrong prediction OK = Right prediction .







Figure 2. Sulfur Content of Supplemental Residual Fuels











Figure 5. Range of Sediment By Hot Filtration For Supplemental Residual Fuels



Figure 6. Range of Accelerated Dry Sludge In Supplemental Samples







Figure 8. Correlation Between Coke Content and Viscosity Instability



Figure 9. Correlation Between Shell Accelerated Sludge and Residual Fuel Instability As Measured By Accelerated Aging





Section 14

ASSESSING THE ECONOMIC IMPACT OF TWO-STAGE LIQUEFACTION PROCESS IMPROVEMENTS

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Mitre Corporation

ABSTRACT

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

Improvements in two stage processing since the early demonstration of the Lummus Integrated Two Stage (ITSL) process in 1980 are shown to reduce the required initial selling price (RISP) of gasoline from coal liquids by about 16%. Further process improvements which offer the potential for an additional 15% RISP reduction are identified.

INTRODUCTION

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

At the Wilsonville facility, both the thermal processing and the hydrotreating have generally been of longer duration than at Lummus. The critical solvent deashing system has been more efficient at recovering coal extract and has thus rejected less soluble material than the Lummus anti-solvent process. The ITSL concept itself, where the thermal first stage and catalytic second stage have been separated by the deashing step, has been modified so that the topped thermal effluent is hydrotreated before deashing. This configuration is called the Reconfigured ITSL (RITSL) mode of operation. More recently the RITSL mode has been modified so that the first and second stage reactors are directly coupled together and the entire thermal effluent is hydrotreated. This is the close-coupled operation (CC-ITSL). A vent separator is often used between the two stages to let down the first stage products. In even more recent tests a portion of the ash-containing effluent from the hydrotreater is recycled to the first stage, the so called ash-recycle mode. Catalytic-catalytic configurations have also been tested at Wilsonville.

The overall objectives of these modifications in two stage processing is to continually increase the yield of high quality distillate while trying to reduce the cost of production.

The U.S. Department of Energy and Sandia National Laboratories have asked MITRE to develop a method to quantify the impact of these modifications on the cost of coal liquids. In response, MITRE has developed a computerized coal liquefaction cost model that simulates the technical and economic performances of conceptual commercial scale coal liquefaction plants that incorporate the R&D improvements under study at Wilsonville.

This paper describes the methodology employed in developing the model and shows the results obtained when the model is used to simulate the process improvements currently underway at Wilsonville. The model is also used as an R&D guidance tool to predict RSP reductions that can be expected by incorporation of future process improvements.

DEVELOPMENT OF THE MITRE COAL LIQUEFACTION COST MODEL

The analysis methodology employed in the MITRE Coal Liquefaction cost Model has been developed by MITRE over the past several years as a part of our contract support to the United States Department of Energy (DOE) and Sandia National Laboratories. The objective of the methodology is to estimate the outputs and required selling price of products from a commercial scale plant. During 1986, the methodology was refined and computerized to permit rapid evaluation of the impact of variations in process performance on the required selling price of product liquids. The analysis is programmed in LOTUS 1.2.3 (Issue 2), and can be readily modified and expanded as refinements in the analysis methodology are developed.

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

Table 1 shows the data input and adjustments as they appear on the LOTUS spreadsheet for Wilsonville Run 250G. In this example, run data was corrected for the % MAF + 850°F resid produced in the test run. Soluble reject was adjusted to a 70% solid reject from the 68.8% achieved in the run. There is also a slight adjustment in ash from 11.58 to 11.4 wt. % MAF coal.

The bottoms rejected from the liquefaction plant are gasified to produce hydrogen. Additional coal is gasified when bottoms are not adequate to meet hydrogen requirements. Texaco gasification is assumed. Steam driven air separation equipment is used to produce oxygen for gasification. The model performs preliminary steam and fuel gas balances in order to obtain a thermally balanced plant and determine the required capacities for auxiliary equipment. Cl-C3 products from liquefaction are used for fuel gas if plant fuel requirements cannot be met from lower quality sources. The Cl-C3 gases are sold as by-products if not required for plant fuel. Natural gas is purchased if in-plant fuel gas sources (including Cl-C3) are not sufficient to meet plant fuel requirements.

EXPERIMENTAL TEST DATA INPUTS TO COAL LIQUEFACTION COST MODEL

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	EXPERIMENTAL	COMPUTER
	TEST DATA	RUN DATA
RUN NUMBER	RAR 250G	
	#/# MAF	#/# MAF
H2 Stage 1	0.0185	0.0185
H2 Stage 2	0.0457	0.0478
Heteroatoms,inc.H20	0.1569	0.1573
C1-C3 Gases	0.0767	0.0781
Naphtha (C4-350F)	0.1534	0.1534
Lt Mdl Dst(350-450F)	0.0775	0.0775
Hv Mdl Dst(450-650F)	0.2359	0.2359
Hvy Dist (650-850F)	Ø.1621	0.2215
Residual (850+)	0.0543	0.0000
Soluble Reject	0.0818	0.0769
Unconverted coal	0.0655	0.0655
Ash	0.1158	0.1140
(Total Check)	0.9999	0.9999
ILU SV, #MAF/Ft3	37.1000	36,4427
ILU Feed, #/# MAF	3.0650	3.2382
HTR Feed, #/# MAF	2.8790	3.0522
HTR Resid, #/# MAF	1.3720	1.4312
Resid Conv. #/# MAF	0.3410	0.4002
HIR WHSV (Reference)	1.0000	0.8352
HTR SV, #MAF/Ft3*	******	******
Deasher Flow, #/#MAF	0.5275	0.7070
% Solids in Reject	70.0000	0.7000
Forced UC, #/# MAF	0.0655	
Forced Ash, #/# MAF	0.1140	
Recycle Solids Conc.	2.1730	
)elta Resid,#/#MAF	0.0592	
JC Factor	1.0000	
lesid Conversion	0.2485	0.2796
/(1-Resid Conv)	1.3307	1.3881
.n(1/1-Resid Conv)	0.2857	0.3280
lesid Conv., #/Hr/F3	6.0562	5.9360
itr Res.+UC+Ash,#/#MAF		1.8212

EXAMPLE OF COST ANALYSIS FROM LOTUS SPREADSHEET

	CAPACITY & CO	ST COMPUTATION	IS 			CALCULATION OF GROSS AND NET OPERATING COST (\$1000 per annum)			
Coal & Ash Handling	Ref. Capacity		Raf. Cost (\$1000)	Est. Cap.	Est. Cost (\$1000)	Coal Cleaning C Electric Power, C Coal. B	\$3.00 /ton AR \$0.04 /kwh \$22.70 /ton AR	\$0 \$90,288 \$329,776	
Cosl Bren & Wandling	35910	Tons/dav(AR)	\$160.759	44023	\$208.570	Hydrotreat Catalyste	\$4.80 /16	\$38,844	
Solide Disposal	3435	Tons/day(dry)	\$6 942	4067	\$8,790	CSD Solvent @	\$0.22 /15	\$6,911	
Coal Dryers	42817	Tons/dav(AR)	\$23.057	41393	\$0	Other Catalyst & Chemi	icals	\$5,000	
Coal Cleaning	35900	Tons/dav(AR)	\$40,500	44023	\$0	Purchased Water	\$500.00 /Nillion Gal.	\$1,476	
Subtotal	00700		\$190.758		\$217.360	Royalties	·	\$3,928	
0000000			,		•	Process Operating Labo	or	\$10,930	
Liquefaction Section						Overhead & GLA	60.0 % Proc. Labor	\$6,558	
						Haintenance E	3.5 \$ TPI	\$128,790	
Shirry Prep & Preheat	6945000	lb/hr	\$303.359	7266992	\$352,279	Local Taxes & Ins. @	2.0 % IPI	\$73,594	
Stage 1 Reactors	14333	ft3	\$38,728	61581	\$120,880	Solids Disposal 🔮	\$6.00 /ton	\$8,053	
Letdown Separation	6945000	lb/hr	\$180,733	7266992	\$52.470				
Stage 1 H2 Purification	389000	lb/hr	\$66.015	439151	\$80,846	Total Gross Annual Op	erating Cost (GADC)	\$704,148	
Stage 7 Parctors	*******	ft3	**********	***********	\$213.894				
Supporting Bracks	4356250	1b/br	\$278.316	6849577	\$429,810	Sulfur. 🔍	\$100.00 /ton	\$50,858	
Latdown/Senaration	4356250	lb/br	\$130,201	6849577	\$201.072	Assonia. E	\$150.00 /ton	\$23,522	
Stage 2 H2 Durification	280000	lb/hr	\$36.677	309624	\$44.271	SNG 🔮	\$5.00 /Hillion Btu	\$76,486	
Solide Separation (ASD)	1000000	lh/br	\$101,758	1586625	\$158,144		• •		
Solids Soparation (HSD)	100000	10/10	•101,100			Total By-Product Crad	its	\$150,866	
Subtatal					\$1.653.666				
Subtotal					*1,000,000	Total Net Operating C	ost	\$553,282	
Hydrogen Production						Areduat Hagrading Par	•-	\$208 RQ1	
			401 404	0/17170	AL17 187	PIDDUCE OPPRATING COS	et 00 (16)	4100,011	
Texaco Gasification	1960700	1D/nr	\$81,090	26//358	\$113,430	207 10 10 12 8	\$1.00 (10)		
Shift, AGR, Methanation	655750	10/11	\$168,701	8/0/93	\$231,470	TOTAL NET OP. COST IN	CLUDING UPGRADING	\$762,173	
Subtotal			\$249,791		\$344,925				
Av Droduct Becovery						CA	PITAL REQUIREMENTS \$1000		
Sulfur Recovery	78762	lb/hr	\$50,204	128425	\$79.529	Construction Cost		\$2,943,774	
Assonia Recovery	71000	lb/hr	\$23.014	43997	\$18,521	Engineering Design &	Project Contingency	\$735,944	
		,	••						
Subtotal			\$73,218		\$98,050	Total Plant Investmen	t, (TPI)	\$3,679,718	
Offeiter & MISC						Paid-up Royalties		\$19,640	
						Allowance for Funds u	sad During Construction	\$621,872	
Syugen Dient	655750	3b/br	\$158,523	B93167	\$221.402		-		
Steps Constitut/FCD	2037000000	Rtu Coal HHV	\$98.530	2233082341	\$118.212	TOTAL DEPRECIABLE CAP	ITAL	\$4,321,230	
Stage Distribution	3383088	h/hr Stern	\$60.269	3476293	\$69,105		-	-	
Noter Elso Eval Svetsa	lesen ac hare	(4258)	\$120.772	•	\$135,869	Start-up Costs		\$140,830	
Hico Offeiter	(can an hace	(ase)	\$75 721		\$85.186	Working Capital		\$176,037	
1120 01121022	(SAND #5 V450	Jabb	413,121		4001100	Initial Charge of Cat	alyst & Chemicals	\$20,412	
Cubbabal			4513 815		\$679.773	THEFTER AND TO ALL AND			
SUDLOLAI			43191013		4027,770	TOTAL NON-DEPRECIABLE	CAPITAL .	\$337,278	
	1000)				\$2.943.774				
Inist cousivoritor cost (\$	1000)					TOTAL CAPITAL REQUIRE	D	\$4,658,509	

DATA INPUTS TO MITRE COAL LIQUEFACTION COST MODEL

RAR 250G

K-M CRITICAL SOLVENT DEASHING

TWO STAGE LIQUEFACTION TECHNO/ECONOMIC MODEL-RUN- RAR 250G

70.0000 %SOL1D REJECT

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REQUIRED INPUT (VALUES)					
COAL PROPERTIES MAF BASIS	I	LLINOIS #6	OPERATING COSIS	,	
Higher Heating Value (HHV)	#/# MAF Coal	14,793	Coal Price, \$/ton As Reciev	ed	22.70
Coal Ash	#/# MAF Coal	0.1140	Coal Cleaning,\$/ton AR	•	3.00
Coal Moisture	#/# MAF Coal	0.1200	Electric Power, MW		285.0
Coal Sulfur	#/# MAF Coal	0.0432	Purchased Elec. Cost, \$/kwh		0.04
Coal Nitrogen	#/# MAF Coal	0.0148	Hydrotreating Catalyst,\$/#		4.80
Coal Carbon	#/# MAF Coal	0.8157	CSD Solvent ,\$/#		0.22
			Other Catalyst & Chemicals	(\$1000/yr) 5000
			Water Required, Million Gal	s./Yr	. 2952
PRUCESS FLAGS			Water Cost, \$/Million Gals.	•	500
			Royalties (\$1000/Yr)		3928
Stage 1 Reactor Type	Cost Fraction	1.00	Operating Labor (\$1000/Yr)		10930
Stage I Let Down Flag	Cost Fraction	0.25	Solids Disposal Cost, \$/ton		6.00
Stage 2 Let Down Flag	Cost Fraction	1.00	Sulfur Value, \$/ton		100.00
Liquefaction Bottoms Type	(1=Solid,0=lig	1.0	Ammonia Value, \$/ton		150.00
Hydrogen Purification Flag	(1=Sep,O=Comb)	1.0	SNG Value, \$/Million Btu		5.00
HIR Catalyst Density	#/ft3 Reactor *	*****	Upgrading Cost, \$/1b H2 Add	ed	1.00
HIR Cat Replacement Rate	#/ton R+UC+ASH	0.50			
	#/ton Coal	0.9106			
PROCESS FLOWS					
Coal to Liquefaction	#/Hr MF Coal	2,500,000	CALCULATED PARAMETERS		
Slurry Catalyst	#/# MAF Coal	0.00	**************		
H2 Feed, Stage 1	#/# MAF Coal	0.10	Coal To Liquefaction	#/hr MAF	2,244,165
H2 Feed, Stage 2	#/# MAF Coal	0.18	Hydrogen Required	#/# MAF	0.0753
			Hydrogen from Coal	#/# MAF	0.0481
COST FACTORS			Coal for Hydrogen Prod.	#/# MAF	0.2456
			Oxygen Required	#/# MAF	0.3980
Eng. Des. & Proj. Contingency	% Const. Cost	25.00	Gasifier Steam	#/# MAF	0.0000
Funds Used During Constr.	%TPI	16.90	Gasifier Water	#/# MAF	0.2650
Maintenance Cost,	%TPI	3.5	Steam Btu Required	Btu/# MAF	995.06
lnsur. & Local Tax Rate,	%TP1	2.0	Steam Coal (maf basıs)	#/# MAF	0.0791
Startup Cost	%GAOC	20.00	Gas Sales (Purchace)	MMBtu/Hr	1931.46
Working Capital	%GAOC	25.00	Tailings Ash	#/# MAF	0.1140
Overhead Rate,	% Op. Labor	60.0	H2 Required for Upgrading	#/Yr	208891028
			lnıtıal Cat. & Chem (Total)	\$1000	20412
			Hydrotreat Cat	\$1000	15671
ECONOMIC FACTORS			CSD Solvent	\$1000	3491
			Other Cat. & Chem	\$1000	1250
Inflation Factor	(1981 Base)	1.1250			
Capital Cost Factor	\$/Yr/\$ Cap.	0.1670			

A coal fired steam plant with flue gas desulfurization is used to superheat steam produced from in-plant heat recovery, and to produce and superheat any additional steam required.

Preliminary designs of commercial plants employing two stage liquefaction were prepared by UOP/SDC in 1981 under DOE contract (2). These designs are used as the baseline for estimating capital and operating costs in the MITRE model.

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

Table 2 shows an example of the cost analysis as it appears on the LOTUS 1.2.3 spread sheet. The table shows the reference cost and capacity of equipment in the baseline plant, the estimated capacity of the plant being analyzed, and the cost estimate which results when the .7 scaling described above is applied. Table 2 also shows the calculation of capital requirements and gross and net operating costs as they appear on the spreadsheet. Pertinent capital and operating cost assumptions are shown for convenience. The inputs for these assumptions, as well as other inputs required to describe the coal and the plant configuration are actually input to the portion of the spreadsheet reproduced in Table 3.

The required selling price per barrel of raw product is computed by dividing the annual costs by the annual output in barrels. Annual costs are the sum of net operating costs and capital recovery costs. The program computes capital recovery factor. The capital recovery factor for any specific set of financial assumptions is calculated by DCF analysis on a separate program. The baseline economic assumptions used in the study are shown in Table 4. These assumptions result in a capital recovery factor of 0.167.

Table 4

BASELINE ECONOMIC ASSUMPTIONS

Equity	25%
Project Life	25 years
Tax Life	16 years
Income Tax Rate	34%
Price Escalation	0
0 and M Escalations	0
Fuel Escalation	0
General Inflation	3%
Discount Rate	15%
Interest on Debt	8%
Construction Period	5 years

There are substantial differences in the quality of products produced by direct liquefaction processes in terms of boiling range, hydrogen content and heteroatoms. These characteristics necessarily influence the degree to which the product must be further processed to produce specification fuels. MITRE accounts for differences in product quality by estimating the cost of additional processing required to produce unleaded motor gasoline. The processing to gasoline is assumed to be performed in two stages in existing refineries. The product is hydrotreated sufficiently to produce a heteroatom free product containing 13% hydrogen. The hydrotreated product is then cracked, distilled and reformed in the same manner as the distillate fraction of petroleum crude to produce a gasoline product. The refining assumptions are based on the extensive work of Sullivan at Chevron (3).

Processing after hydrotreatment would employ conventional refining processes of distillation, cracking and reforming. An all gasoline product is assumed. A 7% volume gain is assumed when a 40° API feed is converted to 60°API unleaded gasoline. This implies a weight loss of 4.3%, and is probably conservative. A refining cost of \$6/bbl of raw crude is assumed.

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

Table 5 is the summary output of the program as it appears on the spreadsheet. Yield structure, output, and summaries of the capital and operating cost analyses are reported, as are required selling prices for raw product, hydrotreated product and gasoline. The equivalent crude price shown is the price of petroleum crude which would permit gasoline to be produced and sold for the same price as gasoline from syncrude. For the run shown (Wilsonville Run 250G, ash recycle mode) the required selling price of raw syncrude is \$34.52. At this price, it would be competitive with a sweet crude selling for \$29.66 per barrel as a feedstock for gasoline production.

DEMONSTRATED IMPROVEMENTS IN TWO STAGE LIQUEFACTION

Figure 1 shows uncorrected experimental two-stage liquefaction data obtained from the Lummus Integrated Two-Stage Liquefaction PDU and the Wilsonville facility. The first bar on Figure 1 is data from Lummus run, Number 2 SCT-12/3LCF-9 and the other three bars are from Wilsonville runs 244-B (Integrated Two-Stage Mode), 250D (Reconfigured ITSL mode) and 250G (Reconfigured Ash Recycle ITSL mode).

The Lummus ITSL process was tested on Illinois #6 Burning Star mine coal from July 1979 to June 1982. The yield structure shown in Table 6 was used as the input to the liquefaction cost model. The soluble reject is high because the Lummus Anti-Solvent Deashing system requires a pumpable underflow, limiting solids content to about 50 wt %. In this case, all of the 850°F+ solids free material is rejected with the IOM (29 wt percent on an MAF coal basis). Total distillate yield is 55 wt percent MAF coal (48.4 wt percent on an MF basis).

Wilsonville run 244 (4) was performed between July and September 1983 using Illinois #6 coal. This run was made in the Integrated Two-Stage Liquefaction (ITSL) mode.

SUMMARY OUTPUT DATA FROM COAL LIQUEFACTION COST MODEL

TWO STAGE LIQUEFACTION T	ECHNO/ECONOMIC N Illinois #6	DDEL-RUN- R K-M CRITICAL	AR 250G Solvent Deashin	70.00 G	PERCENT SOLID F	REJECT		
YIELD STRUCTURE,	LB/LB MAF	COMMERCIAL LBS/HR	PLANT OUTPUT BBLS/DAY		COAL TO LIQUEFA COAL TO STEAM, COAL TO HYDROGE	ACTION, T/ Y/	DAR DAR DAR	33,232 2,630 8,162
H2 Consumed, Stage 1	0.0185				TOTAL COAL	, 1/ 1/	DAR	44.023
H2 Consumed, Stage 2	0.0478					••		
Heteroatoms (inc H2O)	0.1573				PLANT CONSTRUCT	ION COST	(\$1000)	
CIC3 Gases	0.0781				LIQUEFACTIO	N	(*****)	\$1.495.522
C4 - 350F	0.1534	344.255	30,785		SOLIDS REMO	VAL		\$158,144
350F - 450F Product	0.0775	173,923	13.631		HYDROGEN PR	ODUCTION		\$768,298
450F - 650F Product	0.2359	529.399	38.620		BALANCE OF	PLANT		\$521 810
650 - 850F Product	0.2215	497.101	33,815		TOTAL CON	IS COST		\$2 943 774
TOTAL C4-850F PRODUCT	0.6883							
850F+ Product	0.0000				TOTAL CAPITAL R	EQUIRED		\$4 659 509
Solubla Reject	0.0769							
Unconverted Coal	0.0655				OPERATING COSTS	.\$1000/YR		
Ash	0.1140				COAL COST	,,		\$329.776
TOTAL, RAW PRODUCT		1,544,677	116,851		OTHER OPERA	TING COST	5	\$374.372
TOTAL, HYDROTREATED PROL	UCT	1,536,258	127,663		BY-PRODUCT	CREDITS	-	\$150,866
TOTAL, REFINED GASOLINE		1,472,216	136,599		TOTAL .\$1	000/18		\$553,282
BARRELS/TON NAF:	RAW	HYDROTREA	TED			,		****,***
BARRELS/TON MAF:	RAW	40 API PR	GASOLINE		HYDROTREATI	NG COSTS		\$208 891
COAL TO PLANT	3.28	3.58	3.83		TOTAL INC	HYDROTRE	AT .	\$762,173
COAL TO LIQUEFACTION	4.34	4.74	5.07					
					REQUIRED SELLIN	S PRICE		\$/Rarrel
DEASHER COST FACTOR	1.00							4,011.01
COAL CLEANING, \$Btu Recovere	d 100.00 **	F 0 F.	lag.1 or 0		RAM PRODUCT			\$34.52
COAL DRYING FLAG (1 or 0)	0		•••		HYDROTREATE	D 40 API 8	PRODUCT	\$36.56
					GASOLINE			\$39.30
					EQUIVALENT	CRUDE PRIC	ε	\$29.66
	PRODUCT QUALIT	Y DATA:					-	•27700
		SPECIFIC	CARBON	HYDROGEN	NITROGEN	SULFUR	OXYGEN	APT GRAV
		GRAVITY	Wt t	Wt t	Wt t	WE 1	Ht t	Decraes
	C4 - 350F	0.7660	84.8100	13.8300	0.0500	0.1500	1,1600	53.23
	350F - 450F	0.8740	85,7200	11.9300	0.1400	0.1000	2,1100	30.40
	450F - 650F	0.9390	87.4500	11.3200	0,1900	0.0600	0.9800	19 19
	650 - 850F	1.0070	89.1800	10.1900	0.2800	0.0500	0.3000	9.02
	AV RAW PRODUCT	0.915	87.22	11.58	0.18	0.08	0.93	24,76
	HYDROTREATED 4	O API PRODUCT	87.00	13.00	0.00	0.00	0.00	40.00
	GASOLINE (60 A	IPI)	87.00	13.00	0.00	0.00	0.00	60.00



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Two-Stage Data Corrected For Zero Resid and 70% Solids in Reject

Seven material balance periods were used for detailed product workups. Run 244B was chosen as most representative of this run. Table 6 shows the yield structure obtained during this period. Total distillate yield $(C_4-850^{\circ}F)$ of 55.54 wt percent MAF coal was obtained. The soluble reject in the deasher underflow is only 9.2 wt percent compared to 21 percent for the Lummus ITSL case. The Kerr-McGee Critical Solvent Deashing (CSD) process used at Wilsonville produces a free-flowing dry ash concentrate that contains far less soluble material than does the anti-solvent deashing process used by Lummus. Total distillate quality is inferior to that from Lummus principally because a large proportion (65 percent) of the liquid product is produced in the thermal liquefaction unit in this configuration.

Wilsonville run 250 (5) was performed using Illinois #6 coal (Burning Star Mine). This run was performed from November 1985 to March 1986. The primary objective was to demonstrate Close-Coupled Integrated Two-Stage Liquefaction (CC-ITSL). The resid and ash from the second stage are sent to the CSD unit and the deashed resid is recycled to stage one. In order to implement the CC-ITSL configuration a new reactor was installed at Wilsonville. This reactor is identical to the second stage hydrotreater and can be operated either thermally or catalytically. In run 250, the first stage was thermal and only half the reactor volume was used. Run 250 was divided into several material balance periods each with its own process conditions. Periods A-B, which were conducted for a total of three weeks, used aged Shell 324M catalyst in a true close-coupled configuration. Periods C-H used an interstage separator and Amocat IC catalyst in the second stage. Coal feed rate was also increased from 180 lbs/hr MF (periods A-B) to 280-340 lbs/hr MF. During periods F-H the plant was operated with ash recycle. In this mode, part of the resid, unconverted coal and ash is recycled from the hydrotreater product fractionator to the first stage. The remainder is sent to the CSD unit to be deashed.

Table 6 shows the yield structures for run 250 for material balance periods D and G. Total distillate yields are 63.84 and 62.89 wt percent MAF coal respectively.

Figure 2 shows the Wilsonville experimental data corrected for zero resid and normalized to identical deashing performance. The performance of the Kerr-McGee CSD unit is seen to vary from run to run with respect to the quantity of soluble reject. Generally CSD performance falls within a range of 65-70 percent solids in the ash concentrate (or reject). For example in Run 244B the deasher reject contained 70.6 percent solids, an excellent performance, whereas in Run 250D the performance was considerably poorer with a solids content of only 62.8 percent in the reject. It is expected that if operated with a constant feed at constant process conditions the CSD unit would be operated so that, in a commercial plant, a consistent ash concentrate containing 70 percent solids could be obtained. Additional residual material recovered from the reject is assumed to be recycled to the liquefaction reactors and converted to distillate.

When the test or experimental data is normalized to account for zero resid make and constant deasher performance it is easier to make comparisons between the various test runs based upon true process performance. Thus Figure 2 shows the normalized data for the Wilsonville Runs 244-B, 250-D and 250-G. Note that since the Lummus process uses anti-solvent deashing no normalization of deasher performance was attempted in that case. Based on the normalized Wilsonville data it can be seen that distillate yield (C_4 -850°F) on an MAF coal basis increased from 66.1 for 244-B to 68.83 for 250-G. Table 7 compares the yield structures of the normalized runs and compares them to the Lummus ITSL performance. Total distillate yields have increased by 16 percent in going from Lummus ITSL to Wilsonville 250-G.

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TWO STAGE	LIQUEF	ACTION	TEST	DATA
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<u>Net Yield (Wt % MAF Coal)</u>	LUMMUS	<u>244B</u>	<u>250D</u>	<u>250G</u>
Heterogases inc. H ₂ 0	14.84	13.90	14.76	15.69
$C_1 - C_3$	5.79	5.00	6.98	7.67
$C_{A}^{-} - 350^{\circ}F$	13.05	9.65	13.30	15.34
350 - 450°F	15.04	7.30	7.08	7.75
450 - 650°F	20.18	21.03	21.30	23.59
650 - 850°F	7.17	17.56	22.16	16.21
850°F + Resid	-	10.66	-1.28	5.43
Total C ₄ - 850°F	55.44	55.54	63.84	62.89
Hydrogen Consumption	5.35	4.74	6.10	6.42
Soluble Reject	21.12	9.22	12.94	8.18
IOM	8.16	10.42	8.86	6.55

Table 7

NORMALIZED YIELD STRUCTURES FOR WILSONVILLE RUNS COMPARED TO LUMMUS

<u>Yields (MAF Coal Basis</u>)	LUMMUS	<u>244B</u>	<u>250D</u>	<u>250G</u>
Heterogases inc. H ₂ 0 C ₁ -C ₃ C ₄ -350°F 350-450°F 450-650°F 650-850°F	14.84 5.79 13.05 15.04 20.18 7.17	13.97 5.25 9.65 7.30 21.03 28.13	14.78 7.05 13.30 7.08 21.30 25.15	15.73 7.81 15.34 7.75 23.59 22.15
Total C ₄ -850°F	55.44	66.11	66.83	68.83
Hydrogen Consumption	5.35	5.11	6.20	6.63
Soluble Reject	21.12	9.35	8.68	7.69

The yield structures from the normalized Wilsonville runs and the uncorrected yield structure from Lummus ITSL have been used as the basis for the commercial plant performance. Conceptual commercial plants processing 30,000 TPD of moisture free coal to liquefaction have been developed from the normalized yield data. The capital and operating costs of these plants have been estimated together with the output of products. Products from the plants can be raw distillate products, hydrotreated distillate or gasoline. The required selling price of these products have been computed based on the consistent economic assumptions used in these analyses.

Table 8 summarizes the conceptual commercial plant data for these four cases. The table shows that significant advances have been made in two-stage coal liquefaction since the Lummus ITSL experience. Product outputs have increased from 92,400 BPD to 116,900 BPD for the ash recycle close coupled ITSL configuration represented by Run 250-G. This represents an increase in raw output of over 20 percent. For hydrotreated products and gasoline the increase is over 18 percent. These increases in output correspond to the greater C4-850°F product output between Lummus and Wilsonville 250-G: an increase of 19 weight percent MAF coal. Much of this increase is certainly due to the improvements in deashing technology brought about by the Kerr-McGee CSD process compared to the Anti-Solvent Deashing system used by Lummus. Soluble reject has been reduced by a factor of 2.7. The additional residual material that has been recovered is now available for upgrading to distillate in the liquefaction reactors. Had the Lummus system been able to recover more during deashing the performance of the system using Illinois #6 coal would have been much improved. Reactive coals like Illinois #6 seem to convert well using short contact time (SCT) thermal first stage reactors. Making too much distillate product thermally as was done in Wilsonville Run 244-B is detrimental to overall product quality and can be the cause of excessive hydrocarbon gas make.

The additional improvements in two-stage processing demonstrated by the Wilsonville operations are in the areas of increased space velocity for processing, decreased material flows to the deasher, and thus decreased equipment costs. Thermal stage space velocity has increased 24 percent from Run 244-B to 250-G and hydrotreater space velocity increased 29 percent. Flows to the deasher have been substantially decreased by using ash recycle (by a factor of 3). Table 8 shows that capital cost has been reduced by over 4 percent from 244B to 250G and raw product output has increased by 9 percent. Hydrotreated product show a smaller increase (4 percent) since higher quality of the raw 250G product results in a lower volume gain during hydrotreating. This improvement in quality is accounted for in the economic analysis. As can be seen from Table 8, the costs of hydrotreatment of Run 250 products are considerably less than for Run 244-B.

Table 8 also shows the required selling price (RSP) for raw products, hydrotreated products and gasoline. Reductions in RSP of about 20 percent can be realized from Lummus ITSL to Wilsonville 250G. The equivalent crude value for Run 250G products is calculated to be \$29.66/barrel.

POTENTIAL IMPROVEMENTS IN TWO-STAGE LIQUEFACTION

The MITRE coal liquefaction cost model allows sensitivity studies to be performed to estimate the economic impact of changes in various parameters on the required selling price of liquid products.

Sensitivity studies can be performed for numerous parameters, as required, but in this paper only the potential economic effects of the following are specifically assessed:

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CONCEPTUAL	COMMERCIAL	PLANT	SUMMARY	DATA

	LUMMUS ITSL	244-B ITSL	250-D CC-ITSL	250-G-RAR
Economic Data (Million \$)			······	
Plant Capital Cost	4,418	4,859	4,670	4.658
Coal Cost	271	290	314	330
Other Operating Cost	337	389	380	374
Byproduct Cost	79	69	126	151
Hydrotreating Cost	227	330	190	209
Total Operating Cost	756	939	758	762
Plant Coal Requirements TPD (A	R)			
Coal to Liquefaction	33,232	33,232	33,232	33.232
Coal to Steam Plant	2,564	1.980	2.433	2.626
Coal to Gasification Plant	371	3,441	6.276	8,162
otal Coal to Plant	36,166	38,652	41,941	44,019
Plant Product Outputs (BPD)				
Raw Product	92,400	106,900	112,200	116.900
lydrotreated Product	103,800	122,800	124,400	127.700
asoline	111,100	131,400	133,100	136,600
Required Selling Price (\$/bbl)				
Raw Product	41.52	40.27	36.40	34.5
lydrotreated Product	43.61	43.21	37.46	36.56
asoline	45.75	45.26	40.07	39.30
Quivalent Crude Value (\$/bbl)	35.82	35.36	30.40	29.66



Figure 3

Potentail Reductions in Required Selling Prices

- coal beneficiated to varying degrees
- improved deasher performance
- elimination of deasher
- increasing coal concentration in liquefaction slurry
- increased space velocity in the hydrotreater
- improved selectivity to distillate during liquefaction
- improved catalyst life (i.e., decreased catalyst deactivation rate)
- catalyst cost variations

When the incremental benefits of each of the above changes are combined then the cumulative benefit of these changes can be used to predict the potential future improvements in two-stage coal liquefaction using a Wilsonville type configuration. The effect of this type of analysis is shown in Figure 3.

Figure 3 shows the cumulative effects of five sensitivity cases on the cost of liquid products. The baseline case 250G represents the cost of products for test data corrected to zero resid and a deasher performance of 70 percent solid in reject. The bar labeled "clean ND" represents a case where the input coal to liquefaction is cleaned to produce a beneficiated product containing 4 percent ash at a Btu recovery of 80 percent. It is assumed that the coal cleaning preferentially removes the inertinite macerals in the float so that the IOM is reduced to 2 percent MAF coal after liquefaction. Because of the low solid content brought about by the low input coal ash and the low residual IOM, the deasher is eliminated and the coal liquids final separation is accomplished by vacuum distillation. The act of coal cleaning (i.e., ash removal) increases the quantity of MAF coal going to the liquefaction reactors for a given reactor volume, thus conceptual plants employing coal cleaning for fixed reactor sizes are larger product producers. It is additionally assumed that the reject and middlings streams from the coal benefication plant are used for hydrogen production.

The third bar on Figure 3 labeled "36 percent slurry" represents a case where the percent coal in the slurry to liquefaction is increased to 36 wt percent. This effectively reduces the size and hence costs of the liquefaction reactors. The fourth bar labeled "2X HTR SV" assumes that the hydrotreating catalyst activity is increased such that the space velocity through the hydrotreater can be doubled and still maintain the same overall levels of conversion and selectivity for otherwise identical processing conditions. The fifth bar represents the case whereby the selectivity of the catalyst is improved to the extent that hydrocarbon gas make is reduced to 3 percent and only distillate boiling below 650°F is produced. Carbon now not reporting to gases is assumed to increase the distillate yield. This is labeled "IMP Select."

The final bar on Figure 3, labeled "2X CAT LIFE" represents the case where catalyst deactivation can be reduced such that the life of the catalyst is doubled for the same level of activity and selectivity. The effect of this is to halve the catalyst replacement rate, thus operating costs are reduced for the same level of product output.

The additional potential improvements cumulatively decrease the capital cost and further increase the product output. The net result of these improvements is a reduction in required selling price of about 17 percent. Similarly the equivalent crude value is reduced from \$29.66 per barrel to \$24.82, a savings of 19 percent.

ACKNOWLEDGMENT:

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