

SAND95-1989C
CONF-9508133-7

1995 Coal Liquefaction and Gas Conversion

Contractors Review Conference

August 29-31, 1995

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

at

RECEIVED
SEP 26 1995
OSTI

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

ADVANCED PROCESS CONCEPTS FOR DIRECT COAL LIQUEFACTION

Richard Anderson¹, Frank Derbyshire¹, Ed Givens¹, Todd Hager¹,
Geoff Kimber¹, James Lim¹, Frank Burke², Mike Lancet², Gary Robbins²,
Dick Winschel², Howard Stephens³, Richard Kottenstette³, Mike Peluso⁴

¹ University of Kentucky Center for Applied Energy Research, 3572 Iron Works Pike, Lexington, KY 40511-8433;

² CONSOL Inc., Research & Development, 4000 Brownsville Road, Library, PA 15129-9566;

³ Sandia National Laboratories, Department 6212, Albuquerque, NM 87185-0709;

⁴ LDP Associates, 32 Albert E. Bonacci Drive, Hamilton Square, NJ 08690.

This project is funded by the U. S. Department of Energy under Contract Numbers DE-AC04-94AL85000 and DE-AC22-91PC91040.

Introduction

The Advanced Concepts Program was initiated by the Department of Energy in 1991, to promote the development of new and emerging technology concepts that have the potential, alone or in combination, to significantly reduce the cost of producing liquid fuels by the direct liquefaction of coal. Among other efforts, the advanced 2-stage liquefaction technologies that were developed at Wilsonville over the past 10 years and by the former Hydrocarbon Research Inc., HRI (now Hydrocarbon Technology Inc., HTI) have contributed significantly toward decreasing the cost of producing gasoline from coal. However, given the low cost of petroleum crude, direct liquefaction is still not an economically viable process. The DOE objectives are to further reduce the cost of coal liquefaction to a more competitive level. The approach has been to develop a long term strategy in which certain promising liquefaction concepts, which have been identified mainly through fundamental studies, are subjected to technical and economic evaluation on a progressively increasing scale of experimentation, and with progressive integration into a complete process configuration. At each stage, depending upon their merit, research on any particular concept may be continued, modified or abandoned.

One of the contracts awarded under this program has involved a collaborative research and development effort between the University of Kentucky Center for Applied Energy Research (CAER), CONSOL, Inc., LDP Associates and Sandia National Laboratories, beginning in August 1991. The project has involved two principal stages: the evaluation of individual process concepts, followed by the integrated testing of those concepts that were judged to warrant further investigation. The results obtained in each of these stages have been reported (1,2). In both stages, individual and integrated concepts were tested and assessed in small-scale laboratory experiments. In a future phase of the research, it is intended that the more promising concepts will be subjected to more detailed testing in larger-scale continuous units.

In this project, the primary focus is on the use of low-rank coal feedstocks. A particular strength is the use of process-derived liquids rather than model compound solvents. Although this stratagem has created some difficulties in experimental operation and in the interpretation of data, it has lent additional credibility to the results.

The original concepts are illustrated in Figure 1, where they are shown on a schematic of the Wilsonville pilot plant operation. Wilsonville operating data have been used to define a base case scenario using run #263J, and Wilsonville process materials have been used in experimental work. The CAER has investigated: low severity CO pretreatment of coal for oxygen rejection, increasing coal reactivity and inhibiting the propensity for regressive reactions; the application of more active, low-cost, Fe and Mo dispersed catalysts; and the possible use of fluid coking for solids rejection and to generate an overhead product for recycle. CONSOL has investigated: oil agglomeration for coal ash rejection, for the possible rejection of ash in the recycled resid, and for catalyst addition and recovery; and distillate dewaxing to remove naphthenes and paraffins, and to generate an improved quality feed for recycle distillate hydrogenation. At Sandia, research has been concerned with the production of active hydrogen donor distillate solvent fractions produced by the hydrogenation of dewaxed distillates and by fluid coking via low severity reaction with H₂/CO/H₂O mixtures using hydrous metal oxide and other catalysts. The technical and economical evaluation of the experimental data and the impact on liquefaction process economics was made by LDP Associates.

For reasons that have been described in the Final Technical Report for this project, the concepts of low severity coal pretreatment and fluid coking were found not to offer sufficient incentives for continued work. The remaining concepts are still considered to be viable prospects for reducing the cost of coal liquids and have formed the basis of a proposal for continued development in a second phase project. The current status of these concepts is described in this paper.

Dispersed Catalyst Development

It has been shown that suitable dispersed catalysts can enhance the rate and extent of conversion of both subbituminous and bituminous coals, and that their presence is essential to the continuous processing of low-rank coals. A successful demonstration of the liquefaction of a low-rank coal in a continuous operation was achieved at Wilsonville in Run 263J, when operating in a thermal catalytic mode with the addition of a dispersed Fe + Mo catalyst to the first stage. However, the high cost of the molybdenum catalyst precursor used in that run (Molyvan L), combined with the fact that the catalyst is ultimately purged from the system, creates a considerable incentive to identify lower cost catalysts with comparable activity. In this research, efforts at the CAER have been directed to improving the activity of iron-based catalysts through the co-addition of Mo or other metals, while attempting to minimize catalyst cost. Two basic approaches were employed: the impregnation of the catalyst precursor on the feed coal and the introduction of the catalyst in the form of nanometer size particles.

Development of Standard Microautoclave Tests

To relate the performance of the experimental systems to the base case, it became necessary to develop a standard laboratory scale test that could be used to compare different catalysts and other concepts with the base case. Since the base case operated with a process generated recycle solvent, it was decided to use a similar solvent to closely simulate the conditions in Run 263J. The recycle solvent contained about equal parts of 566°C- distillate and 566°C+ resid, along with about 20% recycled solids consisting of approximately equal parts of unconverted coal and mineral matter. Significant amounts of the iron and molybdenum catalysts had accumulated in this stream and were present as pyrrhotite and molybdenum sulfide, respectively. The first challenge in developing a representative test was to understand how the solvents behaved and affected coal liquefaction.

Liquefaction of Black Thunder Wyodak coal in the microautoclaves consistently gave tetrahydrofuran (THF) conversions in excess of 100%, suggesting that the insoluble organic matter (IOM) in the recycle solvent was solubilized during reaction. It was eventually found that the solvent contained an easily converted THF insoluble fraction, and it became apparent that this same situation also held for other Wilsonville solvents that were evaluated.

Another difficulty with plant-derived recycle solvents was the presence of the recycled catalyst. The contribution of these background catalysts to the overall reaction did not become apparent until other results were obtained using solvents from different Wilsonville runs. The conversion of Black Thunder Wyodak coal in solvents that contained recycled Mo, in addition to the Fe that was present in all these solvents, was always significantly greater than in solvents that contained only iron. The activity of the background Mo was very high and masked the activity of freshly added catalysts, complicating efforts to develop a simulated 1st-stage catalyst screening test.

Standard test conditions to simulate the first stage resid conversion in microautoclaves were defined as 440°C for 22 min. with 1000 psig cold hydrogen. The solvent to coal ration was the same as used in Run 263J, namely 2.33 parts of solvent to 1.0 part of dry coal. However, it is to be noted that the 566°C+ resid conversion was actually higher than observed at Wilsonville. The resid conversion values obtained under the test conditions, with the 1 wt % Fe_2O_3 and 100 ppm Mo (as Molyvan L) base case catalyst, as used in Run 263J, was 30-32 wt %, versus a target value of 24 wt %. The significant activity of the recycled Mo became apparent when using a Mo-free recycle solvent (V-131B from Run 258K) which gave resid conversion of only 17-18 wt %. The same results also showed quite clearly that the activity of the recycled iron (pyrrhotite) was considerably less than that of the Mo component. Further, equivalent resid conversions could only be achieved with fresh Mo catalyst by adding twice the amount of metal that was

present in the recycle solvent. In all these cases, fresh iron as iron oxide was added with the Mo. It was later found that the activity of freshly added Mo was considerably enhanced in the absence of any fresh iron, or as finally realized, was actually less inhibited. Although the inhibiting effect of iron has not been widely studied, the present results suggest that iron oxide, sulfate and nitrate can all inhibit the Mo activity while pyrrhotite has a negligible effect.

Impregnated Catalysts

The development of the base case (see later) showed that the cost of the dispersed Fe + Mo catalyst used in Run 263 is quite substantial. Most of this cost can be attributed to the cost of the Mo precursor, Molyvan L, which is an oil-soluble molybdenum organophosphorodithioate. A considerable amount of effort was thus directed towards identifying lower cost Mo precursors that could be added to the coal by impregnation as water-soluble salts, thereby eliminating the need for expensive oil-soluble catalyst precursors. A range of catalyst impregnated coals was prepared with impregnated Fe and Mo salts, alone and in combination. The outcome of this research showed that, for the Fe-Mo system, the catalyst concentration is the most important variable with respect to determining catalyst activity. It was also found that the metals could be impregnated on as little as 10% of the coal and perform just as well as if they were dispersed over the whole coal. This approach has been referred to as the Vector impregnation method, and it can offer a number of economical and technical advantages: less water is added with consequently less of an energy burden for subsequent drying; the amount of coal handling for the catalyst impregnation step is greatly reduced; and the technique allows more flexibility in plant design. The effectiveness of the Vector method also points to the fact that the catalyst must function primarily through the solvent phase, rather than act directly on the coal.

The addition of Fe and Mo as ferrous sulfate and ammonium molybdate by catalyst impregnation, at the same concentrations as in the base case, can substantially reduce the cost of the dispersed catalyst from ~\$2.60/bbl gasoline to ~\$1.10/bbl gasoline. More than half of the remaining catalyst cost (~\$0.60/bbl gasoline) is attributable to the addition of the ferrous sulfate that was used. For this reason, attention was then given to the possibility of either eliminating or reducing the concentration of iron. As already mentioned, in the first-stage screening test, the activity of freshly added Mo was clearly improved in the absence of added Fe. In fact, the level of activity upon the addition of 500 ppm of impregnated Mo was found to approach that of the highly active recycled Mo at 450 ppm, although it must be stated that the two systems were not strictly comparable. Assuming then that Mo alone will give a performance equivalent to that of the Fe-Mo catalyst at the same Mo concentration, the cost of the dispersed catalyst can be further reduced to about ~\$0.40/bbl gasoline, which is even less than the cost of the iron oxide in the base case.

Another interesting outcome of this project was to establish that the activity of the dispersed Mo catalysts is promoted by the presence of small amounts of nickel, as is already known for supported NiMo catalysts, where the Ni is believed to inhibit the growth of Mo crystallites. Co-impregnating coal with Ni and Mo, both in the presence and absence of Fe, repeatedly gave higher coal conversions while continuing to give resid conversions and distillate yields that were equal to those obtained in the Ni-free system. Since the influence of Ni in increasing conversion is similar to the effect of Fe, it may be possible to substitute Ni for Fe at a considerably lower concentration and reduced cost. For most of the catalysts that were tested, the Mo/Ni molar ratio was 4/1. The cost of adding this level of Ni to 100 ppm Mo, with no added Fe, would be only \$0.03/bbl gasoline, which is still less than the cost of the 1% iron oxide used in the base case.

Sulfated Hematites

The second family of catalysts that was investigated was small particle sulfated hematites that are prepared by the base precipitation of solutions of iron salts. Other researchers have reported that particulate

sulfated-hematites, as well as various metal promoted ones, can be exceptionally active in coal liquefaction. Other potential advantages of using this form of catalyst is that high dispersions can be achieved and maintained during processing. A series of sulfated hematites was prepared and tested in this project. The results were somewhat scattered, with no obvious pattern. Some catalysts exhibited exceptional activity, and others produced resid conversions that were significantly less than obtained in the base case.

A preliminary process and economical evaluation for the preparation of this type of catalyst showed that the cost of a Mo-promoted hematite, used at a level equivalent to the Fe and Mo concentrations in the base case, and with a distillate product yield equal to that of the base case, would cost about ~\$1.90/bbl gasoline. Reducing the Fe content by half while maintaining the same 100 ppm Mo level decreases the cost of the catalyst to ~\$1.20/bbl gasoline. Additional process benefits that could be derived from using this catalyst could further reduce the cost. Based upon the positive results that have been observed in this work and elsewhere, it is considered that this approach deserves further attention.

Solvent Quality Improvement: Distillate Dewaxing/Hydrogenation

Solvent dewaxing was examined by CONSOL as a means of improving coal liquefaction economics through solvent quality upgrading. Coal liquids, and subbituminous coal liquids in particular, contain a paraffinic wax component. Because of their relative inertness, paraffins tend to concentrate in the recycle solvent, and are poor physical solvents for the coal reaction products. Therefore, they can impair the dissolution and upgrading of low rank coals. The purpose of dewaxing is to remove these paraffinic materials from the recycle distillate in the coal liquefaction process, as their presence is detrimental to solvent quality. The removal of the paraffins as a wax stream reduced the burden on the reactors to crack them to light distillate products, with the economical advantage that the reduced reactor burden may translate into higher reactor throughput. The gas production and hydrogen consumption that must accompany the paraffin cracking are thus avoided.

Three dewaxing schemes were evaluated for potential use in removing the wax from the recycle solvent. The features and benefits of each of these dewaxing routes are summarized below.

Ketone Dewaxing

In ketone dewaxing, which is a commercially proven technology, all or part of the heavy distillate stream is dewaxed in a ketone-based solvent. The extent of dewaxing is readily controlled by the choice of conditions. The dewaxed distillate is then recycled, either directly or after hydrogenation, to the first stage liquefaction reactor. The wax product may be purified and sold as a high-value by-product, or it could be converted to product distillate in a fluid catalytic cracking (FCC) unit.

Ketone dewaxing of the Wilsonville Run 262E V-1074 heavy distillate was tested with acetone, methyl ethyl ketone (MEK), toluene and various mixtures of these at temperatures from -35°C to 0°C. The degree of dewaxing was found to be a function of solvent composition and temperature. It was found that the solvent quality of the dewaxed distillate improved rapidly with dewaxing up to ~20 wt % wax removal and then leveled off. The effect of the improved solvent quality on Black Thunder coal liquefaction was to increase the coal conversion from 87 wt % to 90 wt % when dewaxed distillate was substituted for the untreated distillate in the Wilsonville Run 262E solvent (5-min. microautoclave tests at 824°F, 1.5 S/C, 1500 psig of cold H₂). However, some of this increase may be due to the higher proportion of H-donors to coal, since the same overall solvent to coal ratio was used in microautoclave tests with the original and dewaxed solvents. It was also found that hydrogenation of the dewaxed distillate at Sandia further improved coal conversion to 91 wt %.

A clean wax by-product, similar to commercial petroleum based waxes, is produced by de-oiling the slack wax that is removed from coal-derived distillate. The slack wax properties indicate that it should be an excellent feedstock to produce high yields of light products in an FCC unit.

There are several advantages of improving the recycle distillate solvent quality. An increase in single pass coal conversion from 87 to 91 wt % could result in about a 6 wt % decrease in rejected organics and similarly improved product yield. Other prospective advantages of improved solvent quality are that it could allow operation at lower severity conditions than in the base case (lower temperature, pressure, residence time) while maintaining current levels of performance. Alternately, it could facilitate operation at higher severity conditions by countering retrograde reactions (increases in coal conversion of ~4 wt % were obtained at reaction temperatures that were ~30°C higher than in the base case) and improve throughput. Economic benefits can also be gained upon cracking the crude wax.

Liquid Extraction Dewaxing

An alternative to ketone dewaxing is the process of liquid extraction using N-methylpyrrolidone (NMP), furfural or similar selective solvents. This is also a commercially proven technology that is used for the removal of aromatics from paraffinic lube oils but not for paraffin removal from aromatic-rich distillates.

In laboratory experiments, NMP and furfural were used at ambient temperatures to extract the aromatics from the heavy distillate fraction of the recycle solvent. It was found that the slack wax yield is greater (>40 wt % vs. ~20 wt %), but the wax is of lower quality than that from ketone dewaxing. The extracted material is also more aromatic than the ketone dewaxed distillate (~30% aromatic hydrogen vs. ~20%), and it is difficult to completely remove the extraction solvent. In terms of solvent quality, the aromatic fraction performs similarly to the feed distillate. However, hydrogenation of the aromatic fraction, which should be facile, is expected to improve solvent quality.

The advantage of liquid extraction is that it can be conducted at moderately elevated temperatures (40 - 90°C) and atmospheric pressure. The process operating costs have been estimated by LDP Associates to be lower than those of ketone dewaxing. It is considered that, with subsequent hydrogenation of the dewaxed distillate, coal conversion improvements should be similar to those obtained by ketone dewaxing plus hydrogenation, with similar associated cost benefits.

Thermal Dewaxing

Thermal dewaxing presents a third possible route to solvent quality improvement. In this process, all or part of a heavy distillate stream is heated to elevated temperatures for a short time to preferentially thermally crack paraffins and naphthenes. The light cracked product is removed as net product and the aromatic-rich heavy distillate is recycled to the liquefaction reactor with or without prior hydrogenation.

Thermal dewaxing was tested by heating the heavy distillate to over 480°C for five minutes. Significant findings are: the dewaxed oil yield was ~75 wt % and the gas yield was <5 wt % at 495°C, and lower; the dewaxed material was more aromatic than most ketone dewaxed distillates (~25% aromatic protons in 490°C dewaxed distillate); and hydrogenating the dewaxed (495°C) distillate produced an improved liquefaction solvent (Black Thunder coal conversion increased by 2 wt % when this hydrogenated thermally dewaxed distillate was substituted for untreated distillate in recycle solvent).

The advantages of this approach are that: it involves a very simple process flow sheet; the process is the same as the “satcracking” process developed by the British Coal Corporation; and it should be easy to demonstrate in a bench-scale continuos unit. The net outcome is that waxes are converted to distillable oils

and gases, and a highly aromatic distillate is produced that should be readily hydrogenated (in a separate hydrogenation reactor or in the first stage liquefaction reactor) to produce a superior donor solvent with similar benefits to those demonstrated for the other dewaxing methods.

Agglomeration and Coal Cleaning

Coal agglomeration has been studied by CONSOL as a potential means of mineral matter rejection and catalyst incorporation with the goal of improving liquefaction economics by increasing yields and lowering catalyst requirements. A specific advantage is that the agglomerating oil is process-derived. Several agglomeration scenarios are presented to summarize this work. These scenarios include: agglomeration at natural pH; agglomeration of low-rank coal at natural pH, after pretreatment; agglomeration of low-rank coal at low pH; and splitting the feed coal, based on ash content, for liquefaction and gasification.

There are three basic issues to be addressed in developing agglomeration as an integrated component of a coal liquefaction process: the agglomeration performance at a given set of conditions; the cost of agglomeration at those conditions; and the liquefaction benefit and economical value of the agglomeration.

Agglomeration at Natural pH

It has been shown that coals ranging in rank from lignite through bituminous can be reduced in ash content by up to two thirds. This performance can be achieved under the following conditions: natural pH or minor adjustment to pH \approx 6-8; and oil dosage of ca. 15 to 35%; 50-65°C; and a coal slurry concentration of 20-43%.

The process can use sour water, whose low pH may enhance ash rejection for some coals. Any dissolved salts in the separated water could be fed to a gasifier of the Texaco type. All organics, most iron, and any pre-impregnated catalyst are retained with the coal. Hence, if this is deemed to be advantageous, catalysts can be added to the coal or part of the coal by impregnation before coal cleaning by oil agglomeration. Also, when using sour water, some silica and \approx 50% of the sodium is rejected from low-rank coals. In no case is there any loss of coal reactivity.

The advantages of coal cleaning by oil agglomeration are: coal can be recovered following any aqueous pretreatment procedure; the lower ash content feed reduces slurry viscosity and can allow a reduction in solvent/coal ratio, or a higher rate of ashy recycle and reduction in the size of the ROSE-SR unit. Increasing the amount of the ashy recycle stream has another advantage in that more of the disposable catalyst will also be recycled, reducing the make-up of fresh catalyst. The dissolution of salts when using sour water may also lower the exposure of the second stage supported catalyst to poisons (especially the Na present in low-rank coals), resulting in lower catalyst replacement rate.

In one process scenario, coal is slurried with waste sour water from liquefaction and recycled water, and agglomerated with process-derived heavy distillate. The agglomerates are rinsed over screens, blown with air to remove surface moisture, and sent to liquefaction. Additional drying prior to liquefaction is optional and depends on other factors (i.e., it is not a requirement of agglomeration). A slipstream of the agglomerate rinse water with ash is used to slurry ash concentrate and coal for Texaco gasification. The remaining agglomerate rinse water with ash is treated to remove solids, and then recycled for slurring coal and rinsing agglomerates. Any additional water requirement would be met by gasification of sour water, and any excess agglomeration waste water would go to water treatment. Because liquefaction is a net producer of water, both from coal drying, and from hydrogenation, it is anticipated that there will be an adequate water supply for agglomeration. The cost of water use and treatment will be minimized by using waste streams wherever possible.

Agglomeration of Coal at Natural pH after Coal Pretreatment

As noted, in addition to cleaning untreated coal, oil agglomeration is well suited to the recovery of coal from any aqueous coal pretreatment step. It has been demonstrated that ash can be rejected following CO-H₂O-pretreatment, and after two types of catalyst impregnation.

This concept differs from that of untreated coal recovery by agglomeration at natural pH in that aqueous coal slurry from a pretreatment step is agglomerated, instead of using sour water to slurry the coal. The concept is not restricted to any particular pretreatment. Sour water might be useable in the pretreatment and agglomeration steps.

Agglomeration of Low-Rank Coal at Low pH

By using low pH conditions, it has been shown that coals ranging in rank from lignite through subbituminous can be reduced in ash content by up to three quarters. This performance can be achieved under the following conditions: pH of 1 or 2 adjusted using H₂SO₄; an oil dosage of 21% to 54%; 50°C; and a coal slurry concentration of 20% to 43%. The use of sour water could be of benefit as its low pH may reduce the acid requirement. As with the process using sour water only, any dissolved salts in the separated water can be fed to a Texaco gasifier. All organics, and most iron are retained with the coal. A pre-impregnated catalyst may also be retained although this has yet to be confirmed. Some silica and ≈90% of the Na, K, Ca, and Mg are rejected from low-rank coals, and there is no loss of coal reactivity due to cleaning.

The advantages of coal cleaning by oil agglomeration at low pH are essentially the same as already described for oil agglomeration at natural pH.

Splitting of Feed Coal Quality for Liquefaction and Gasification

The potential for physical cleaning of several coals (Black Thunder, Burning Star 2, and Martin Lake) was assessed by float/sink tests, and by column flotation (Black Thunder only).

Segregation of the feed coal into a lower ash cleaned coal product that can be fed to liquefaction and a higher ash reject that can be gasified to produce hydrogen was shown to be a potentially attractive option to improve liquefaction economics: both ash and inert macerals are concentrated in the intended gasifier feed, while the lower ash content, more reactive coal is liquefied.

Economic and Technical Assessment

A basis for the technical and economic assessment of the experimental results obtained with the new process concepts was developed from the technical data for the Wilsonville pilot plant operation, material balance period #263J, Figure 1. During Wilsonville Runs #262 & 263, the pilot plant operated in the so-called hybrid ("thermal" - catalytic) mode with Black Thunder subbituminous coal, and with dispersed iron and molybdenum catalysts added to the first reaction stage and a supported nickel-molybdenum catalyst in the second-stage reactor.

An all-distillate product base case was formulated in which resid extinction was achieved in the system via a reduction in reactor space velocities, assuming first order reaction kinetics. It was anticipated that the distillates produced from liquefaction experiments in the present program might differ from those obtained at Wilsonville during Run #263J. As a result, all liquefaction distillates are assumed to be upgraded to a common basis (all-gasoline finished product) so that consistent comparisons are assured.

The base case conceptual commercial plant is a facility located at a mine-mouth Wyoming location. The hydrogen needed for liquefaction is generated by water slurry gasification of ash concentrate from the ROSE unit and of fresh coal. Light hydrocarbon gases produced during liquefaction and upgrading are used to close the fuel gas balance. Any excess gas is used to generate hydrogen via the steam reforming process. It is assumed that the electricity needed to operate the plant can be purchased from a nearby utility power plant. The capital and operating cost estimates for the Base case were developed using the relevant portions of previous liquefaction plant studies, as well as in-house information.

The base case plant converts 17,929 t/d of Black Thunder coal (dry basis) into 68,100 bbl/d of gasoline product. An additional 5,204 t/d of coal is gasified to meet hydrogen requirements. Overall coal conversion is 92%. The per pass conversion of resid plus IOM in the first and second stage reactors is approximately 23.5% and 18% respectively. A high process solvent to coal ratio of 2.33 is employed since significant quantities of both IOM and ash are recirculated. Recycled ash is approximately 3.3 times the quantity of ash rejected from the process via the ash concentrate. The ash recirculation rate results in a 3.3 concentration effect for both the Mo and Fe dispersed catalysts. As a result, the effective concentration of Mo on coal to liquefaction is approximately 450 ppm at the Base case fresh addition level of 100 ppm.

A once-through first stage reactor design has been assumed. Four reactor trains in parallel are required to process the 17,929 t/d of coal. The first stage reactor is refractory lined to maximize the cross sectional area per reactor. Reactor gas rates were determined based on the estimated average reactor partial pressures that existed during Wilsonville Run #263J and the recycle hydrogen gas purity. Actual reactor residence times and space velocities were also based on estimates from the Run #263J operation with appropriate corrections for the required resid plus IOM conversion level. Organic rejection (i.e., resid, insoluble organic material or IOM, and de-ashing solvent) from the liquefaction process amounts to 14.5% on a dry coal basis.

Significant investment cost areas include the liquefaction reaction system, vacuum fractionation system, the hydrogen recovery and recycle system, the makeup hydrogen generation system and the upgrading system. The hydrogen production system represents the dominant investment cost. Offsite unit investment costs are widely distributed among the various units. Working capital, start-up costs and the costs of initial catalyst and chemicals adds an additional 10% to the total capital requirement of \$3.842 billion. Assuming a capital charge factor of 15%, the annualized capital costs are \$26.45 per barrel of gasoline product.

Total operating costs are approximately \$20/bbl of gasoline product inclusive of a \$1/bbl credit for ammonia, sulfur and phenol byproducts. The significance of liquefaction system additives and purchased electrical power costs and the relative insignificance of coal cost is noteworthy. Liquefaction additives costs are approximately \$5.20/bbl of gasoline, with the iron and molybdenum dispersed catalysts accounting for more than half of this total. Coal costs are low because of the low \$5/ton, wet mine-mouth price for Black Thunder coal. On this basis, assuming a capital charge factor of 15%, the Base case required gasoline produce selling price is \$46.46/bbl. [Note. The price is quoted for gasoline and not crude oil equivalent.]

Case Analyses of Selected Advanced Concepts

The base case data has been used by LDP Associates to evaluate the impact of three of the concepts that have been under investigation, and to develop a modified base case. Laboratory scale experimental data has been evaluated to determine the prospective gains in terms of increased product yield per unit of coal feed, and reduced solvent recycle rate and liquefaction system additive costs.

Addition of Dispersed Catalyst by Coal Impregnation with Water-Soluble Salts

As pointed out in the base case, the cost of dispersed iron and molybdenum catalysts accounts for almost \$3/bbl of the gasoline produce selling price. A significant portion of this cost results from the use of an expensive molybdenum source, the oil soluble Molyvan L. At \$3.20/lb. and an 8.1 wt % molybdenum concentration, the cost per pound of Mo is \$39.50. By using a molybdenum salt such as ammonium octamolybdate (available in tonnage quantities), the raw material cost per pound of Mo could be reduced to \$7.30. Even with the additional processing costs for preparing the salt solution, impregnating a small portion of the feed coal to liquefaction, and driving off the extra water added to the coal, the cost of the impregnated Mo is still only about 25% of the cost of using Molyvan L. Further, when using a water-soluble Mo source in this way, the cost drops below the cost of using particulate iron oxide at the base case dosage level of 1 wt % Fe on dry coal. Therefore, unless dispersed iron catalysts in conjunction with Mo cover a level of catalytic activity that is not attainable with Mo alone, the use of Fe is questionable. Other advantages can be anticipated if this proves to be the case; using iron at a 1 wt % level adds to the ash in the liquefaction system and increases the organic rejection due to the assumed constant solids content of the ash concentrate. For the purposes of this assessment, the addition of the iron catalyst was assumed to be unnecessary.

Oil Agglomeration at Low pH

The experimental results indicate that the oil agglomeration at low pH can remove approximately 50% of the ash in Black Thunder coal. The reduction of ash in the feed coal will reduce organic rejection during solids separation thereby increasing the potential product yield. It will also reduce the ash recirculation rate within the process while still maintaining the same catalyst recycle enhancement factor as in the base case. In effect, front end ash removal purges useless inerts from the system. Through oil agglomeration at low pH, potential supported catalyst poisons, such as calcium, sodium, magnesium and potassium are also removed. For this assessment, it has been assumed that the second stage reactor supported catalyst replacement rate can be reduced by 30%.

The oil agglomeration process is well-suited for the preparation of the feed coal: distillate recycle solvent can be used as the agglomerating agent; sour water can be used as make-up water to the system; and the slurry reject of solids and dissolved salts can be utilized in the gasification process. Of course, the use of oil agglomeration will add capital and operating costs to the overall process. The capital cost for low pH oil agglomeration is expected to be approximately \$60 million, and the cost of the sulfuric acid could also be significant.

Distillate Solvent Quality Improvement

It is proposed that three process steps will be used to treat the waxy distillate recycle solvent: solvent extraction, solvent dewaxing and hydrotreating. In combination, these processes effectively remove and recover the waxy material from the distillate solvent and enhance its donor solvent capabilities. Both solvent extraction and solvent dewaxing are commercial processes used in the petroleum refining industry.

The objectives of applying these three processes are: to reduce the distillate solvent recycle while improving its quality; to recover a valuable by-product wax; and to increase the potential product yield via coal conversion improvement. It is estimated that the wax yield is 4 wt % on coal. However, this wax accumulates in the distillate recycle solvent until the rate of its removal by cracking is equal to its production rate. Based on the Wilsonville Run #263J data, the wax concentration in the distillate recycle solvent is estimated to be approximately 24 wt %. Therefore, the removal of a substantial portion of the wax significantly reduces the distillate solvent recycle rate. The wax that is removed and recovered has a

current estimated selling price (34¢/lb.), more than double that of gasoline. The ability of the wax market to absorb the significant quantity of wax produced by a commercial size plant is a key consideration.

The solvent extraction process is used upstream of the solvent dewaxing process as a means of significantly reducing the feed rate to, and therefore the cost of, the much more expensive solvent dewaxing process. In the solvent extraction process, a solvent such as furfural or NMP, is used to absorb aromatics from the feed stream. The paraffinic wax is not absorbed and passes through the unit. For the modified base case, approximately 70% of the distillate solvent feed to the extraction unit is absorbed, thereby reducing the solvent dewaxing unit feed rate by a factor of 3. In the solvent dewaxing process, the paraffinic wax is separated from the feed stream by chilling, precipitation and filtration in the presence of a suitable solvent such as MEK. When wax production is desired, a three stage filtration system is used. In addition, a wax finishing step is also required.

Conventional fixed bed hydrotreating is used to make the final improvement in distillate solvent quality. For the modified base case, a single train system operating at conditions favorable for hydrogenation of the aromatics (340 to 400°C & 1800 psig) is anticipated. It is also assumed that full dewaxing and hydrotreating of the distillate recycle solvent will improve coal conversion by 3 percentage points. Such an improvement further increases the potential product yield and reduces the IOM recycle rate.

Combine Impact of Selected Concepts: Modified Base Case

The benefits of reduced feed ash and improved coal conversion are evident. While the solids concentration in the ash concentrate remains the same, organic rejection is reduced to 8.5% on dry coal. At the same time, the recycle solvent rate is reduced by 20% because of the removal of the wax, lower feed ash and higher coal conversion. The recirculation of the Mo catalyst remains at the same 3.3 factor as in the base case. In order to achieve the higher product yield, the required per pass resid plus IOM conversion increases in both reaction stages. Since reaction temperatures are not changed, this increased conversion is achieved by reducing the space velocity (predicted by first order kinetics) by approximately 15% versus the base case. Although reactor space velocities are lower, this is partially offset by the lower recycle rate, such that the reactor volume, and hence cost, is only slightly increased.

In this configuration, the gasoline production rate increases by 4.5%, while a significant quantity of the valuable wax by-product is also produced, and the C4+ product yield increases to greater than 65 wt % on dry coal. Hydrogen consumption increases in proportion to the increased production rate. Because of the significant decrease in organic rejection, additional gasification of coal is required to close the hydrogen balance. The total electrical power requirement for the modified base case increases by approximately 12% due to increased gasification quantities and the requirements of the added units.

Process unit investment increases by \$432 million due to the added units and the increased gasification requirements, and total capital required increases by \$520 million over the base case. The net operating costs drop by approximately \$140 million/year due to the lower liquefaction system additive costs and the significant impact of by-produce wax revenue. If a 15% capital charge factor is used, the required gasoline product selling price is \$41.82/bbl or \$4.64/bbl lower than in the base case.

References

1. Derbyshire, F; Givens, E; Burke, F; Winschel, R; Lancet, M; Stephens, H; Kottenstette, R; Peluso, M; "Improved Coal Liquefaction through Enhanced Recycle Distillate Quality," DOE Contractors' Review Conference, Pittsburgh, PA, 28-29 September, 1993.
2. Anderson, R; Derbyshire, F; Givens, E; Hager, T; Kimber, G; Lim, J; Burke, F; Lancet, M; Robbins, G; Winschel, R; Stephens, H; Kottenstette, R; Peluso, M; "Advanced Process Concepts for Coal Liquefaction: Process Simulation Testing," DOE Coal Liquefaction and Gas Conversion Contractors' Review Conference, Pittsburgh, PA, 7-8 September, 1994.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

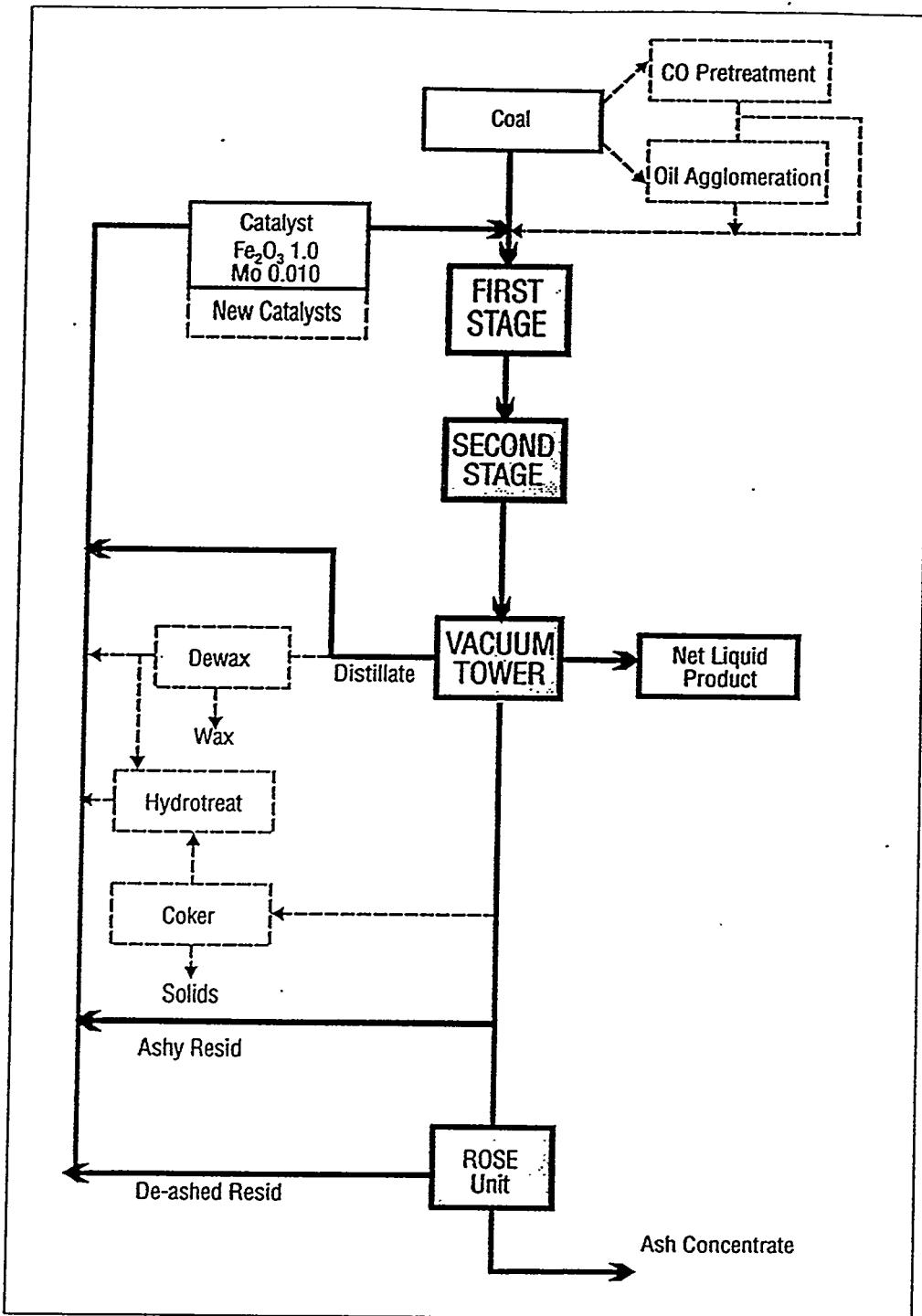


Figure 1. Advanced Concepts Shown on Schematic of All-Distillate Mode Operation, Wilsonville Pilot Plant Operation