

RECENT ADVANCES AND FUTURE PROSPECTS FOR DIRECT COAL LIQUEFACTION PROCESS DEVELOPMENT

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ABSTRACT

Over the last fifteen years, the technology for the direct conversion of coal to liquid fuels has undergone significant development. This has been most evident in improvements in product yields (i.e., barrels per ton of coal), product quality, and, ultimately, in projected product costs. These advances have occurred through the optimization of process conditions and, particularly, a better understanding of the selection and use of catalysts. In addition, engineering and economic evaluations of the liquefaction process alternatives, and macroscopic analysis of global fuel production and consumption have been essential in guiding process development and providing a justification for investment in further R&D. This paper will highlight some of the important technical achievements in reaching the current state of direct liquefaction process development, and provide some speculation on the opportunities and obstacles for future research and commercial implementation.

THE WORLD AND UNITED STATES OIL SITUATION

Petroleum use worldwide is about 65 million barrels per day (MMBPD), and the Energy Information Administration (EIA) predicts that by 2015, worldwide demand will increase to between 89 and 99 MMBPD.¹ Over 55% of world petroleum is used in the transportation sector. Liquid hydrocarbon fuels are ideal for transportation since they are convenient, have high energy density, and a vast infrastructure for production, distribution and end use is already in place. The estimated ultimate world resource of oil and natural gas liquids (NGL) is 2.5 trillion barrels; the sum of 1.2 trillion barrels for OPEC and 1.3 trillion barrels for non-OPEC.¹ Estimates of proven reserves of oil vary over time because more of the oil resource moves into the reserve category as a result of variations in the world oil price (WOP) and available technologies. However, the estimated ultimately recoverable world conventional oil resource (EUR) has been remarkably similar for the last 25 years. James MacKenzie of the World Resources Institute² cites an analysis of 40 estimates of ultimately recoverable oil, for the years 1975 to 1993, conducted by David Woodward of the Abu Dhabi Oil company. In this analysis, Woodward concluded that "there is a fair degree of consistency among the estimates with the average being 2,000 billion barrels (BBO) and 70% falling in the range of 2,000 to 2,400 BBO."

Mitretek has performed analyses of world oil demand and potential supply from the present until 2100.³ The results of these analyses show that when the projected world oil demand is plotted on the ultimate resource curve whose integral is equal to 2.5 trillion barrels, it becomes clear that conventional world oil production will peak in a timeframe from about 2015 to 2020 and then irreversibly decline because of resource limitations.

Because oil is the primary fuel in the transportation sector, Mitretek also examined the potential impact of the above world oil supply scenario on the U.S. transportation sector.³ This analysis concludes that, even with a rapid penetration schedule for alternatively fueled vehicles, there is likely to be a significant shortfall in petroleum supply in the United States before 2015.

THE DEVELOPMENT OF DIRECT COAL LIQUEFACTION TECHNOLOGY

Direct coal liquefaction is the process by which coal is converted to liquids through the addition of hydrogen or the removal of carbon. Hydrogen can be provided directly from the gas phase, through transfer from a chemical source such as a hydrogen donor, or carbon can be removed by a disproportionation reaction in which the coal is converted to (relatively) hydrogen-rich and carbon-rich products. The reaction generally requires temperatures above the softening point of coal (typically around 600 K) to facilitate mass transport and to achieve adequate rates of reaction. Although liquids of some description can be produced by a number of approaches, the objective usually is to produce

transportation grade fuels as substitutes for petroleum-derived gasoline or diesel fuel. The reactions involved include hydrogenation and cracking, and removal of nitrogen, oxygen and sulfur from the coal (primarily as NH_3 , CO , CO_2 , H_2O , and H_2S). The mechanisms of these reactions generally involve both hydrogenation and bond cleavage, although opinions differ as to the reaction sequence.

The cost of producing coal liquids is implicit in these chemical reactions. There is a theoretical minimum amount of hydrogen that is necessary to convert the (empirical) coal structure to liquid products of some specified composition. In practice, the amount of hydrogen consumed (typically 6-7 wt % on a moisture-ash-free coal basis) will be greater than the theoretical minimum because of undesirable side reactions, such as methanation of carbon oxides and C_1 - C_4 gas formation due to cracking. Because hydrogen is expensive, there is a strong incentive to minimize its consumption, but the quality of the product liquid must be known for a comparison of hydrogen consumption values to be meaningful.

The liquefaction reactions require elevated temperatures to proceed at reasonable rates; this requires some pressure containment (~500 psig) to keep the reactants in the liquid phase. If molecular hydrogen is used as the hydrogen source, higher operating pressure (2000-3000 psig) is required for adequate mass transfer. The combination of elevated pressure and temperature is an important factor in determining the capital cost of the liquefaction train, including heat-transfer units, reactors, pumps, pressure let-down systems, etc. Effective catalysts can decrease both the reaction pressure and temperature. Given the heterogeneous nature of coal, the presence of mineral matter, and the variety of functional groups present, it is likely that some form of catalysis occurs, even if an external catalyst is not used. In fact, catalysts are universally employed in practical liquefaction processes, with solid heterogeneous catalysts being the most common. Historically, the first commercial liquefaction plants in Germany used the I. G. Farben process, in which coal was liquefied at 760 K and 10,000 psig in a liquid phase reactor using a relatively inactive iron catalyst. Because of the reaction severity, the German plants produced high hydrocarbon gas yields (30 wt % MAF coal) with a correspondingly high hydrogen consumption (~14 wt % MAF coal).

In the United States, the development of direct liquefaction technology was stimulated by the petroleum shortfalls and price increases of the 1970s. By 1980, three process concepts (SRC-II, EDS and H-Coal) had been sufficiently advanced to merit consideration for commercialization. An interest in producing a substitute fuel oil for electric utility boilers led the Southern Company and Electric Power Research Institute to explore the Solvent Refined Coal (SRC) process on the 6 tpd Wilsonville, Alabama facility. This was a one-stage thermal process in which coal was solubilized in a recycle solvent, and the product was deashed to remove mineral matter and some sulfur. A variant of this was the SRC-II process, developed by Gulf Oil Company and others. In the SRC-II process, coal was hydrogenated in a one-stage reactor with no catalyst addition, but the distillation bottoms were recycled to take advantage of the catalytic activity of the coal mineral matter. The SRC-II process was piloted on a 50 tpd unit at Ft. Lewis, WA. The Exxon Donor Solvent (EDS) process was developed through the 250 tpd pilot plant scale at Baytown, TX. In the EDS process, the coal was fed to a plug-flow reactor in a recycle solvent (the donor solvent) that was hydrogenated catalytically in an external reactor. The donor solvent provided the hydrogen for the liquefaction reaction. In later development, a bottoms recycle stream was added to the EDS feed to provide additional residence time for conversion, and perhaps to utilize the catalytic activity of the mineral matter. One common feature of these processes, and others such as the CONSOL CSF process and the British Coal LSE process, was that the primary coal liquefaction reactions took place in the absence of any added catalyst, ostensibly to avoid the rapid deactivation of the catalyst that was presumed to occur in the presence of the coal mineral matter.

In the HRI H-Coal process, the issue of catalyst deactivation was addressed by utilizing an ebullated bed reactor which allowed a supported catalyst to be added and withdrawn continuously. The ebullated bed reactor also offered superior performance in terms of heat and mass transfer. The H-Coal process was developed at HRI's bench-scale and PDU facilities in Lawrenceville, NJ, and piloted on a 250 tpd unit in Catlettsburg, KY. Representative operating conditions and yields for the H-Coal pilot plant operations with Illinois basin bituminous coal are shown in Table 1. The process made a relatively light product (proportion of naphtha) but also had a sizeable yield of hydrocarbon gases and unconverted resid, which reduced overall liquid yield.

One problem with the single catalytic stage is that hydrogenation reactions are best done at relatively low temperatures where the equilibrium is more favorable, but conversion

(i.e., cracking) reactions are faster at higher temperature. To overcome this, research was conducted on the use of multiple reaction stages, exemplified by work by Lummus and Cities Service in New Brunswick, NJ. In the Lummus/Cities bench unit, the coal was converted to a soluble form in the first stage at relatively high temperature (~720 K) but short contact time (~2 min). The first-stage product was deashed, and converted to distillate liquids at around 670 K in an ebullated bed LC-Finer unit, which simultaneously produced a hydrogenated solvent for recycle to the first stage. A similar configuration was installed at the Wilsonville SRC pilot plant, which employed a Kerr-McGee Critical Solvent Deasher between a thermal first stage and an ebullated bed second stage supplied by HRI.

Lummus first recognized, and Wilsonville later confirmed, that the location of the deashing unit between the two stages had little effect on catalyst life. The most important factor in catalyst deactivation was carbon laydown, not poisoning by metals in the mineral matter. This led to "close coupling" of the two reactor stages, with deashing applied to the second-stage product. It also allowed for "ashy recycle", in which a portion of the second-stage product is recycled directly to the first stage. By concentrating solids in the recycle stream, the amount of material processed by the deasher was significantly reduced, and the unconverted coal was given additional residence time. The Wilsonville unit subsequently was used to explore a variety of staged reactor configurations, including two ebullated bed catalyst stages ("catalytic/catalytic" mode), the use of a dispersed iron oxide as a first-stage catalyst with subbituminous coals ("thermal/catalytic" mode), and alternative temperature staging. As shown in Table 1, this resulted in substantial reductions in hydrocarbon gas and resid production for bituminous coal, with a corresponding increase in distillate liquids, although the product was higher boiling than that of the H-Coal process. Results with subbituminous coal (Table 2) were similar, although a high first-stage temperature was still required to achieve adequate coal conversion. One advantage of the "thermal" first stage is a greater removal of oxygen as carbon oxides. In the single-stage system, carbon oxides are converted catalytically to methane and water, with increased hydrogen consumption.

Although the first stage in the thermal/catalytic mode did not contain a supported catalyst, the Wilsonville unit was fed a powered iron oxide catalyst to promote coal conversion. This was consistent with research at Mobil R&D showing that solid catalysts promote the conversion of coal to soluble forms. Subsequent work at Wilsonville, HRI, and a number of academic institutions explored the use of dispersed catalysts based on iron, molybdenum, and other metals. In a current collaborative project, CONSOL, the University of Kentucky, LDP Associates, Hydrocarbon Technologies Inc. (HTI), and Sandia National Laboratories have been exploring several advanced concepts for improving direct liquefaction process economics through modifications to the feed coal and recycle solvent and the use of dispersed and impregnated slurry catalysts. This work has progressed through laboratory studies to evaluation of the process concepts in bench-scale continuous unit runs at HTI, the former experimental facilities of HRI. The first run (ALC-1) was made in the all-slurry catalyst mode with molybdenum and iron catalysts. Potential advantages of operation with all-slurry catalysts include: simplified reactor design; simplified operations, constant catalyst activity, more efficient use of reactor volume (no volume needed for catalyst support); and catalyst can be recycled with solids to reduce the fresh catalyst requirements. Raw subbituminous coal was used in condition 1 of Run ALC-1; the same coal cleaned by oil agglomeration was fed in condition 4 (Table 2). In condition 5 (not shown in Table 2), the distillate portion of the recycle solvent was dewaxed and hydrogenated to improve solvent quality. As shown in Table 2, these operations produced exceptional distillate yields of 66% to 69% MAF from subbituminous coal. This was accomplished by near-extinction conversion of residual oils, including unconverted coal. The somewhat higher hydrogen consumptions in these operations resulted, in part, from the higher gas yields due to the higher reaction temperatures, but they also resulted from the use of an in-line gas-phase hydrotreater for the distillate product. These operations produced a low-heteroatom, highly hydrogenated product with low boiling point.

OPPORTUNITIES FOR FUTURE RESEARCH AND DEVELOPMENT

As summarized above, the analysis by Mitretek indicates that the time when worldwide petroleum demand begins to deplete resources may come within the next two decades, even without significant political or economic disruptions. Therefore, it is essential simultaneously to pursue a number of options to mitigate the future shortfall in domestic petroleum. These options are: to continue domestic exploration and production using the best technologies available, to continue to develop and deploy alternatively fueled vehicles, and to continue to improve efficiencies in all sectors of transportation. Yet, even with these steps, this analysis indicates that the domestic demand for liquid fuels will exceed our potential sources of supply. Continuing our reliance on oil imports to alleviate the shortfall is not a long-term solution. Rapidly increasing world oil demand will put ever-increasing pressure on the oil supply and the WOP will rise. The inevitable conclusion is that

additional options will be necessary to ensure that the United States will have the necessary liquid fuels supply to be able to continue economic growth into the 21st century. One of these additional options is to produce liquid fuels from our huge domestic coal resources.

Current direct coal liquefaction technology is technically feasible, but not economically competitive. However, with world oil prices over \$25/bbl at this writing, it is clear that, in the long term, the upward pressure on oil prices persists. Research should be directed toward reducing the cost of liquid products so that these alternative technologies are available as early as possible to have the greatest economic benefit. Several technical issues are pertinent to achieving that objective.

Catalysts. Despite all the research that has been done on catalyst development and testing, improved catalysts still offer the single best opportunity for affecting many of the cost features in a liquefaction process, including yields, selectivity, product quality, hydrogen utilization, and capital cost (through reduced pressure and temperature and increased space velocity). A problem with much catalyst research is that it is done at unrealistic conditions, with results that are not easily translated to a process context. For example, identifying a catalyst that improves coal conversion from 40% to 60% is of little value when the process goal is produce specification products at high yield. On the other hand, identifying a truly improved catalyst could open significant opportunities for redefinition of the basic process concept.

Feedstock Selection. The principal feedstocks are coal and hydrogen. Most coals have been shown to be suitable for most processes. If there is an "opportunity" coal, it will be the result of economic opportunity; for example, the current emphasis on U.S. low-rank coal recognizes its low mine-mouth cost. Reduction in hydrogen cost is problematic. Production of hydrogen from coal involves a large unavoidable capital expenditure for the gasification plant. Production from natural gas is unlikely to be economical in the long term, particularly if petroleum prices have risen. Coprocessing feedstocks, such as waste plastics and heavy resid, may be useful in providing an economic justification for early "pioneer" plants which will demonstrate commercial viability.

New Reaction Mechanisms. Despite its variations, current liquefaction technology remains based in the early German technology, i.e., thermal free radical or radical-initiated hydrogen transfer. There are other possible hydrogen transfer chemistries, including carbonium ion, hydride ion and biochemical mechanisms. Although these have been explored, they have yet to yield a promising candidate. As with the catalyst research, much of the problem may lie in a failure to establish exploratory research goals of such a nature that they can be used to justify further development. A realistic candidate must be able to achieve high yields of liquids that meet some minimum standard of quality or upgradability.

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TABLE 1

OPERATING CONDITIONS AND YIELDS FOR H-COAL, ITSL, AND CMSL,
ILLINOIS BASIN COAL

| | H-Coal Pilot Plant Run 8 | ITSL Wilsonville Run 252B1 | ITSL Wilsonville Run 257J | CMSL HTI Run PB-05/2 |
|--|--------------------------------|----------------------------------|---------------------------------|----------------------------|
| Year | 1981 | 1987 | 1989 | 1996 |
| Conditions | | | | |
| <u>Stage 1</u> | | | | |
| T, K | 728 | 705 | 705 | 720 |
| H ₂ Partial pressure, psi, inlet | 2500 | 2500 | 2600 | 2500* |
| Catalyst age, lb coal/lb | 1690 | -1300 | 645 | Dispersed |
| S.V., lb coal/hr/ft ³ reactor, each stage | 29 | - | - | 42 |
| <u>Stage 2</u> | | | | |
| T, K | None | 672 | 678 | 731 |
| Catalyst age, lb coal/lb | None | -470 | 1309 | Dispersed |
| Yields, wt % MAF | | | | |
| H ₂ O | 7.5 | 9.6 | 10.2 | 4.3 |
| H ₂ S, NH ₃ , COx | 3.8 | 5.1 | 5.0 | 6.1 |
| C, x C ₂ Gas | 12.8 | 6.5 | 5.4 | 6.7 |
| Naphtha | 22.9 | 17.5 | 14.5 | 18.4 |
| Middle Distillate | 20.0 | 7.8 | 7.1 | 16.0 |
| Gas Oil | 7.6 | 44.1 | 44.2 | 39.0 |
| Total Distillate | 50.5 | 69.4 | 65.8 | 73.4 |
| Resid | 31.3 | 16.4 | 19.7 | 14.8 |
| H ₂ | -6.0 | -7.1 | -6.0 | -5.2 |
| Coal Conversion | 96.1 | 93.0 | 91.7 | 96.2 |

*Unit back-pressure

TABLE 2

OPERATING CONDITIONS AND YIELDS FOR H-COAL, ITSL, AND CMSL,
POWDER RIVER BASIN COAL

| | H-Coal PDU Run 10 | ITSL Wilsonville Run 262D | CMSL HTI Run ALC-1/1 | CMSL HTI Run ALC-1/4 |
|--|-------------------------|---------------------------------|----------------------------|----------------------------|
| Year | 1980 | 1991 | 1996 | 1996 |
| Conditions | | | | |
| <u>Stage 1</u> | | | | |
| T, K | 719 | 713 | 715 | 716 |
| H ₂ Partial pressure, psi, inlet | 2500 | 2800 | 2500* | 2500* |
| Catalyst age, lb coal/lb | 742 | Dispersed | Dispersed | Dispersed |
| S.V., lb coal/hr/ft ³ reactor, each stage | 25 | - | 42 | 26 |
| <u>Stage 2</u> | | | | |
| T, K | None | 694 | 726 | 726 |
| Catalyst age, lb coal/lb | None | 727 | Dispersed | Dispersed |
| Yields, wt % MAF | | | | |
| H ₂ O | 16.3 | 13.9 | 13.8 | 16.2 |
| H ₂ S, NH ₃ , COx | 3.5 | 6.7 | 5.9 | 5.1 |
| C, x C ₂ Gas | 11.0 | 5.3 | 9.4 | 12.4 |
| Naphtha | 24.3 | 12.9 | 18.6 | 23.0 |
| Middle Distillate | 14.5 | 7.7 | 11.3 | 9.7 |
| Gas Oil | 11.9 | 40.1 | 39.2 | 33.4 |
| Total Distillate | 50.7 | 60.8 | 69.0 | 66.1 |
| Resid | 24.1 | 18.7 | 9.4 | 7.1 |
| H ₂ | -5.6 | -5.5 | -7.5 | -8.8 |
| Coal Conversion | 91.0 | 90.1 | 95.0** | 97.5** |

*Unit back pressure

**SO₂-free ash basis