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Production of Alternative Liquid Hydrocarbon Transportation Fuels from Natural Gas, Coal, and Coal and Biomass (XTL)

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The NPC believes that these papers will be of interest to the readers of the report and will help them better understand the results. These materials are being made available in the interest of transparency.

Production of Alternative Liquid Hydrocarbon Transportation Fuels from Natural Gas, Coal, and Coal and Biomass

David Gray, Noblis, Inc.; and Harold Schobert, Penn State University

1. Background

With national energy security still being a dominant concern because of increasing dependence on imported oil, there is interest in producing more of our oil from domestic sources. By far the largest single supplier of oil to the U.S. is Canada. But, we must be concerned that an equal amount of imports comes, in total, from four countries wracked by instability or with governments hostile to the U.S.: Algeria, Angola, Iraq, and Venezuela. In addition, the global trade in oil means that, even though the U.S. imports no oil from Iran, and little from Libya, if further unrest in the Middle East should happen to take Iranian and/or Libyan crude off the world market for a time, global oil prices would skyrocket, directly impacting the American economy. Oil is truly the life blood of any industrialized society. Without it, continued and sustained economic growth and social stability would be impossible. Oil provides us with transportation fuels that give us the freedom of personal mobility. About two-thirds of petroleum consumption in the U.S. is in the transportation sector; from the other perspective, some 95-97% of transportation energy derives from petroleum. A second aspect of the vital importance of petroleum is that it provides key petrochemicals for plastics, urethanes, and synthetic fibers. This application accounts for an estimated 16% of petroleum used in the U.S., and over 25% of petroleum processed in the Gulf Coast region.

This drive towards producing more domestic fuels has led to large increases in ethanol production from corn and to increased use of biodiesel fuel from vegetable oils. Using biomass as a feed is considered to be more environmentally acceptable by producing less greenhouse gases (GHG) than fuels from other higher carbon containing fossil sources. Because the biomass has recently extracted carbon dioxide from the atmosphere in order to grow, carbon dioxide emitted from combustion, or use of this biomass, is not counted as a GHG penalty when put back into the atmosphere. Although recently there has been considerable doubt cast on the effectiveness of using biomass for GHG reduction especially when the potential impacts of land use change are considered. Nevertheless, worldwide there is an increasing concern over the potential impacts of climate change and the role of anthropogenic GHG emissions, particularly carbon dioxide from use of fossil fuels.

However, using corn and vegetable oils to produce fuels are ultimately limited by the fact that they are human and animal food sources. R&D is underway to use non-food biomass to produce fuels. These include use of algae-derived fuels and conversion of cellulose and lignin components of biomass to fuels rather than the sugars, starches, and oils. In this way a potentially large domestic resource could be available to produce substitute oil with less impact on food supply.

A potentially large domestic resource that has come into prominence lately is shale gas. Because of recent discoveries of shale gas in the United States and of the success of shale gas production using hydraulic fracturing, natural gas availability in the United States is now considered very robust. A few years ago the United States resource base for natural gas was considered to be very small and there was concern that we were running out of gas. This was because only conventional gas was counted and the expected contribution from unconventional gas (tight and shale gas) was not considered to be very significant. As a result, more gas was imported from Canada and many liquefied natural gas (LNG) regasification facilities were planned and constructed in the United States in an effort to forestall the expected domestic natural gas shortfall. The result was that natural gas prices were very high (around $14/MMBtu).

Now the situation has completely changed. Unconventional shale and tight gas resources in the United States are now estimated to be very large; possibly higher than 2000 trillion cubic feet (TCF). (The United States uses approximately 22 TCF annually). Horizontal well drilling and improved fracturing techniques have opened up this potentially-large resource of domestic gas. This supply abundance has resulted in unexpectedly low natural gas prices (currently around $4/MMBtu).

This large available resource of domestic natural gas will allow gas to be used for purposes other than the traditional uses of industrial processing and heating. For example, more natural gas combined-cycle electric power generating plants can be built that could replace older and dirtier coal power plants. More natural gas can be used to fuel ground transportation fleets as compressed natural gas (CNG) and natural gas could now be used in the United States to produce liquid fuels for ground and air transportation by using Gas-to-Liquids (GTL) technologies.

Another large domestic resource that could be converted into high quality transportation fuels is coal. Coal has advantages of great abundance, relatively low cost and high energy density. Furthermore, the production of synthesis gas from coal (a first step in the process of making fuels) and the subsequent conversion of that synthesis gas to liquid fuels is a proven technology at commercial scale. Coal-to-Liquids (CTL) technology is commercially practiced at Sasol in South Africa. Unfortunately, coal has low hydrogen to carbon ratio and the production and use of transportation fuels from coal produces approximately twice the life cycle greenhouse gas emissions as the production and use of fuels from petroleum. This disadvantage can theoretically be managed by the capture and sequestration of the carbon dioxide produced during the conversion of the coal into fuels. If carbon capture and storage (CCS) can be successfully demonstrated and commercialized the life cycle greenhouse gas emissions would be essentially the same as from petroleum-derived fuels.

Another potentially promising approach that could succeed in meeting both an increase in domestic supply at reasonable cost and a reduction in GHG emissions, is to produce liquid hydrocarbon transportation fuels derived from a combination of coal and biomass in a Coal/Biomass-to-Liquids (CBTL) plant with carbon capture and sequestration. In this way, GHG emissions could be significantly less than petroleum. The carbon contained in the biomass is not counted as a carbon input penalty because the biomass has recently removed this carbon from the atmosphere by photosynthesis. A portion of this biomass carbon is then subsequently captured and sequestered within the CBTL facility during the conversion process. In this way a double benefit accrues to the biomass carbon. The biomass and coal would be converted to fuels together in the same plant. The biomass component would act to reduce the net GHG emissions associated with the production of the fuels and the domestic abundance of high energy density coal would allow greater quantities of fuels to be produced in larger plants thus reducing cost by improving the economies of scale.

These technologies all represent facets of the broad area of XTL, which encompasses the conversion of carbonaceous feedstocks to a mixture of hydrogen and carbon monoxide, called synthesis gas, followed by the separate step of producing liquid hydrocarbon fuels from the gas via Fischer-Tropsch synthesis. In principle, *any* carbonaceous feedstock could be used (given appropriate technology for its conversion to synthesis gas), including biomass, coal, coal/biomass blends, natural gas, municipal solid waste, natural bitumens and heavy oils, and waste tires. Synthesis gas conversion technologies also offer potential routes to hydrogen, substitute natural gas, and various solvents or intermediates such as alcohols and aldehydes.

The principal alternative to XTL is direct coal liquefaction (DCL), which is the conversion of coal to liquids without the intervening step of producing synthesis gas. The primary DCL technology is hydroliquefaction, the reaction of coal with hydrogen and/or a hydrogen-donor solvent, usually in the presence of a catalyst. Liquids can also be obtained from coal by pyrolysis, and by solvent extraction with various solvents in the sub- or supercritical regimes. Some work has been done on the co-liquefaction of coal blended with materials such as scrap plastic, scrap rubber, or heavy oils. A second major difference between DCL and XTL is that usually XTL products are clean liquids that can be used as transportation fuels with minimal refining, whereas the primary liquids from DCL are usually aromatic with nitrogen, oxygen, and/or sulfur incorporated, so will require substantial downstream refining to meet performance and environmental requirements for transportation fuel usage.

2. XTL: Production of Alternative Liquid Hydrocarbon Transportation Fuels from Natural Gas, Coal, and Coal and Biomass

2.1 History and Current Status of XTL

The term XTL in this context refers to the production of liquid hydrocarbon fuels from synthesis gas via Fischer-Tropsch (FT) and methanol synthesis technologies. The synthesis gas can be produced from many carbonaceous feed stocks. This white paper considers the following feed stocks for synthesis gas production: coal, coal/biomass combination, and natural gas.

Production of liquid fuels from coal has a long history and significant advances have been made in the technology over the past several decades. In the early 1900s Bergius reacted coal with hydrogen and process solvent at high temperature and pressure and produced a coal-derived liquid or synthetic crude oil. This direct liquefaction approach was later improved and used in the second world war to fuel the German Luftwaffe with high octane aviation gasoline.

In the 1920s two German scientists, Fischer and Tropsch, passed synthesis gas, consisting of carbon monoxide and hydrogen, over metallic catalysts and produced pure hydrocarbons that they termed "Synthol". These hydrocarbons produced by the Fischer-Tropsch (FT) process proved to be excellent transportation fuels. This Coal-to-Liquids (CTL) process, known as indirect liquefaction because it first involves complete breakdown of the coal to synthesis gas, was used commercially in the 1950s by the South African Synthetic Oil Corporation (Sasol) to produce transportation fuels (gasoline and diesel) using synthesis gas produced by the gasification of coal. This plant, known now as Sasol I, used a combination of fixed-bed and circulating fluid bed FT reactors to produce the fuels. Recently the Sasol I plant was converted from coal to natural gas as feedstock and is now a Gas-to-Liquids (GTL) plant. In the early 1980s Sasol built two large FT facilities that together produce over 160,000 barrels per day of transportation fuels. These plants were designated Sasols II and III. Although these plants are very profitable today, they received government subsidies for several years after start up. They would not have been able to prosper back then in a market economy without this assistance.

CTL technology using FT synthesis is continually being improved and, since the building of the large Sasol plants, there have been significant advances in both coal gasification technologies, that produce the synthesis gas, and in FT processes that produce the clean fuels. At the Sasol II and III plants the circulating fluid bed Synthol reactors were replaced by fixed-fluid bed Sasol Advanced Synthol (SAS) reactors. These are less expensive than the Synthol reactors, are easier to operate, and have a much greater fuels production rate than the Synthol reactors. Sasol R&D started experimenting with slurry-phase distillate (SPD) FT reactors in the early 1980s and built a 2,500 barrels per day prototype reactor at Sasol I. This reactor, that has operated both on iron and cobalt FT catalysts, formed the basis for the huge slurry reactors that have been installed at the

Oryx GTL plant in Qatar. These slurry reactors, with a diameter of about 36 feet, each is capable of producing 17,000 barrels per day of fuels.

Other companies are also developing FT reactor technology. Shell has developed and greatly improved their fixed bed FT process known as the Shell Middle Distillate Synthesis (SMDS) process. Their GTL plant in Bintulu has been operating since the late 1980s and recent improvements to the reactors and catalysts have increased the fuels production rate significantly over the prior design. Conoco Phillips also has developed an FT system that was demonstrated at pilot scale in Oklahoma. Syntroleum, another U.S. company, has also developed an FT process for their GTL system. They have produced large quantities of FT jet fuel for testing by the U.S. Air Force. The U.S. Company Rentech is also developing an FT system based on a slurry bed reactor and are building a pilot facility in Colorado. There are also experimental FT systems under development including a micro channel reactor being tested by Velocys.

In addition to the advances in FT technology, largely motivated by the push to deploy a GTL industry, there have been great advancements in the technology to produce the clean synthesis gas from coal and natural gas. This has been motivated by the push to develop coal conversion into chemicals and fertilizers and for the introduction of Integrated Combined Cycle (IGCC0 power generation. In the case of coal, large entrained flow, oxygen-blown, high pressure gasifiers have been developed by GE (formerly the Texaco gasifier), Shell, Conoco Phillips (E-Gas), and Siemens (formerly Future Energy).

However, no commercial FT CTL plant has been built that integrates advanced coal gasification with advanced FT technologies and the only commercial scale FT CTL plants currently operating in the world are the Sasol plants. China, with an increasingly large appetite for liquid fuels, scarcity of domestic petroleum and large coal resources, appears to be moving towards commercialization of coal to liquids technologies.

The concept of gasifying mixtures of coal and biomass together in the same plant to produce liquid fuels is novel and no such plant currently exists. There are many gasifiers that can gasify biomass but most of these are usually small scale, use air instead of oxygen, operate at lower temperatures thus producing tars, and operate at low or atmospheric pressure. All of those characteristics would make them unsuitable for producing FT liquid fuels. The NUON Shell gasification IGCC facility in the Netherlands has proven that gasification of wood (30% by weight) and coal can be achieved in the same gasifier for the generation of electric power. They have also gasified other biomass feedstocks including chicken litter.

Table 1 lists the status of the commercial XTL plants worldwide

Table 1: Status of Commercial XTL Plants Worldwide

COUNTRY	COMPANY	TYPE	PLANT NAME	SIZE BPD	STATUS
SOUTH AFRICA	PETROSA	GTL	MOSSGAS	40,000	OPERATING
SOUTH AFRICA	SASOL	GTL	SASOL 1	6,000	OPERATING
SOUTH AFRICA	SASOL	CTL	SASOLS II & III	160,000	OPERATING
QATAR	SASOL	GTL	ORYX	34,000	OPERATING
QATAR	SHELL	GTL	PEARL	140,000	IN CONSTRUCTION
MALAYSIA	SHELL	GTL	BINTULU	13,000	OPERATING
NIGERIA	SASOL/CHEVRON	GTL	ESCRAVOS	34,000	DELAYED

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2.2 Technology Overviews

2.2.1 Coal-to-Liquids (CTL) Technology Overview

The only commercial FT CTL plants in the world are the Sasols II and III plants in South Africa. Sasol continues to conduct RD&D in all aspects of CTL including synthesis gas production and synthesis and refining of the FT hydrocarbon fuels and chemicals. Examples of successful RD&D in the area of FT synthesis reactor technology are the development and commercialization of the SAS and SPD reactors.

The U.S. Government through industrial partnerships and international cooperation has also supported R&D for both direct and indirect liquefaction. The government programs, completed by the mid 1990's, resulted in improved processes, catalysts and reactors which contributed to reduced costs and improved product quantity and quality. CTL technologies produce clean, zero sulfur liquid fuels that are compatible with the existing liquid fuels distribution and end use infrastructure. These are essentially refined products and very little refining is needed to produce drop in fuels for civilian or military purposes. CTL technology therefore has a proven track record and is technically viable. However, although Sasol has successful commercial plants in operation, the integration of modern entrained-flow coal gasification with advanced FT synthesis has yet to be demonstrated commercially.

Figure 1 below is a simplified schematic of a conceptual FT CTL plant configuration that integrates entrained flow gasification with advanced FT synthesis. Coal is gasified with oxygen to produce a synthesis gas consisting of carbon monoxide and hydrogen. This gas is shifted to give the required hydrogen to carbon monoxide ratio and cleaned of all impurities including the bulk removal of carbon dioxide. Because this carbon dioxide is a concentrated stream it can readily be dehydrated and compressed for permanent sequestration. The clean synthesis gas is sent to Fischer-Tropsch reactors where most of the clean gas is converted into zero sulfur liquid hydrocarbon fuels. The fuels contain no sulfur because the synthesis gas has less than 30 parts per billion sulfur. Higher sulfur levels would rapidly poison the sensitive FT catalysts. If the major required product is distillate or diesel boiling range fractions then slurry phase reactors would be used. This low temperature FT process produces little hydrocarbon gases and predominately a wax product. This wax can then be selectively hydrocracked into distillate. By using this approach, the overall product distribution can be skewed in favor of diesel. The clean fuels are recovered and the wax is hydrocracked into more diesel fuel and naphtha. The carbon dioxide in the FT tail gas is then removed for subsequent sequestration and the remaining synthesis gas is returned to the FT reactors for additional conversion to liquid fuels. A portion of this tail gas can be combusted in a gas turbine combined cycle power plant or in a boiler to generate all of the electric power necessary for the plant.

The overall very simplified chemistry for the production of hydrocarbons from synthesis gas via FT synthesis can be expressed as:

$$CO + 2H_2 = \text{—}(CH_2)\text{—} + H_2O$$

where $\text{—}(CH_2)\text{—}$ represents the building block for longer chain hydrocarbons.

A variant of this CTL plant can be configured where excess electric power is generated in addition to the liquid fuels. These Coproduction or polygeneration plants would be capable of producing both power and fuels in any proportion consistent with the available markets. In a coproduction configuration the synthesis gas would be passed once through the FT reactors instead of being recycled and the larger quantity of tail gas would be combusted in a combined cycle power plant to generate enough power for the plant needs and excess power for sales.

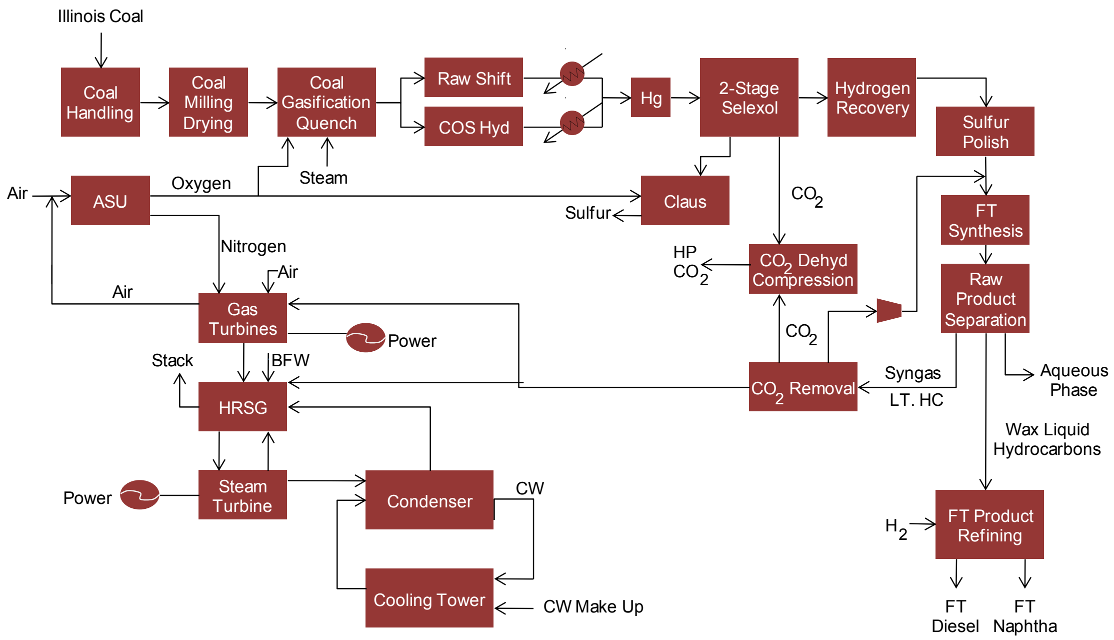

Figure 1: Conceptual CTL Plant Configuration

2.2.2 Coal/Biomass-to-Liquids (CBTL) Technology Overview

Because no commercial or even small scale plants are currently in operation to convert mixtures of coal and biomass to liquid fuels only a conceptual description of the technology can be proffered.

In essence the plant operates just like a CTL plant except that biomass is gasified in addition to the coal (see figure 2). Separate gasifiers could theoretically be used for the biomass and the coal; however it may be more efficient and less costly if the same gasifier could convert both feeds simultaneously. This would be similar to the situation at NUON where the Shell gasifier was able to gasify both wood and biomass.

In this conceptual plant, high pressure, entrained-flow gasification with oxygen is used to convert the coal and biomass into synthesis gas. This synthesis gas is cleaned using conventional gas cleaning technology. Slurry-phase FT reactors are used to convert the clean synthesis gas into raw FT products. Hydrotreating and hydrocracking/hydroisomerization are used to convert the raw FT products into naphtha and diesel. All power required in the plants is generated on-site.

Unfortunately, there is very little data in the literature for the gasification of biomass in entrained high pressure gasifiers. Because of the fibrous nature of most biomass sources, the material is very difficult to pretreat and feed into a high pressure gasifier. Typical problems include clumping and bridging. However, the successful demonstration at the

NUON plant does indicate that co-gasification is technically feasible provided that the biomass receives the appropriate pretreatment and preparation.

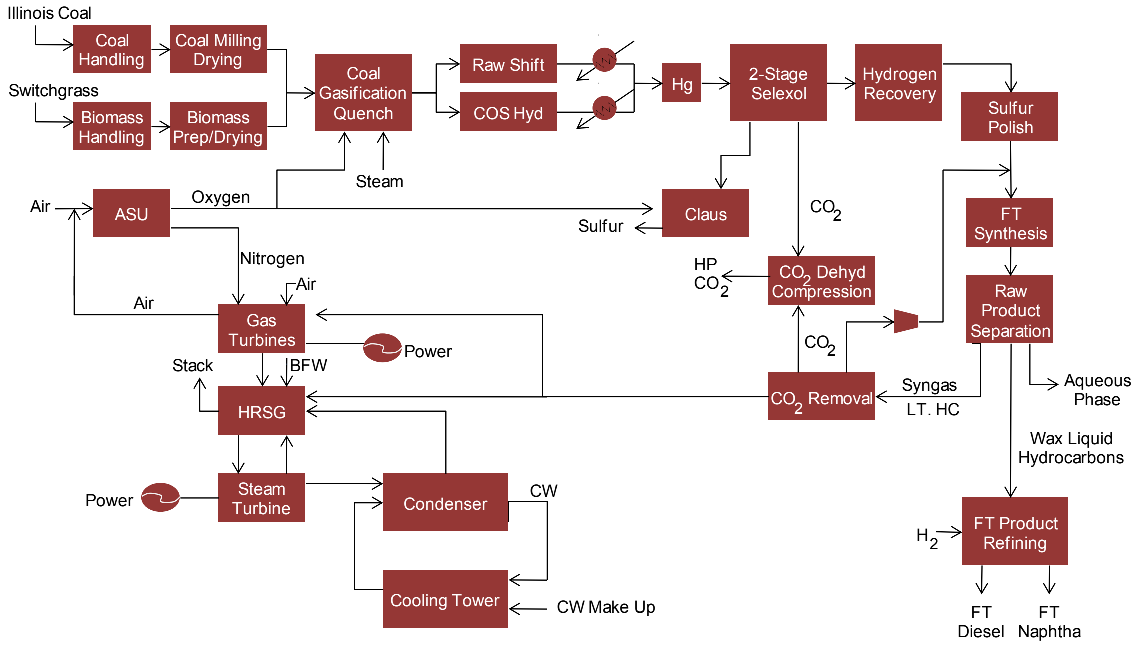

Figure 2: Conceptual CBTL Plant Configuration

2.2.3 Natural Gas-to-Liquids (GTL) Technology Overview

Figure 3 below is a simplified schematic of a conceptual FT GTL plant configuration. Natural gas from conventional wells or from shale formations is purified by removing contaminants like carbon dioxide, hydrogen sulfide etc. and this clean gas consisting predominantly of methane is converted into synthesis gas consisting of carbon monoxide and hydrogen. To accomplish this, natural gas is sent to steam methane reforming (SMR) and to autothermal reforming (ATR) technologies. In SMR the methane is reacted with steam over nickel catalysts and in ATR the methane reacts with oxygen and steam. Using the combination of SMR and ATR can produce a synthesis gas with the correct carbon monoxide to hydrogen ratio for the FT synthesis. For cobalt FT catalysts this ratio is just over 2:1. At this point in the configuration carbon dioxide produced in the ATR could be removed so that overall GHG emissions from the plant would be reduced. Because this carbon dioxide is a concentrated stream it can be readily be dehydrated and compressed for permanent sequestration. The clean synthesis gas is sent to Fischer-Tropsch reactors where most of the clean gas is converted into zero sulfur liquid hydrocarbon fuels. Typically for natural gas feeds cobalt FT catalysts are used. These are expensive and very sensitive to poisoning by sulfur but they have higher overall activity than iron-based FT catalysts. They also produce water as co-product with the hydrocarbons. Commercially there are two major types of FT reactor for this hydrocarbon synthesis. Shell favors the fixed bed reactor and Sasol favors the slurry bed reactor. There are advantages and disadvantages to both. Both reactor types can operate in a low temperature regime where wax is the primary product. This can be hydrocracked to produce distillate or diesel boiling range fractions and naphtha. The raw FT products are recovered and the wax is hydrocracked into more diesel fuel and naphtha. Unconverted synthesis gas is recycled to the FT reactors for additional conversion to liquid fuels. A portion of this tail gas can be combusted in a gas turbine combined cycle power plant or in a boiler to generate all of the electric power necessary for the plant. Hydrogen for hydrotreating is recovered from the synthesis gas and refinery off gas can be combusted in the gas turbines for power generation.

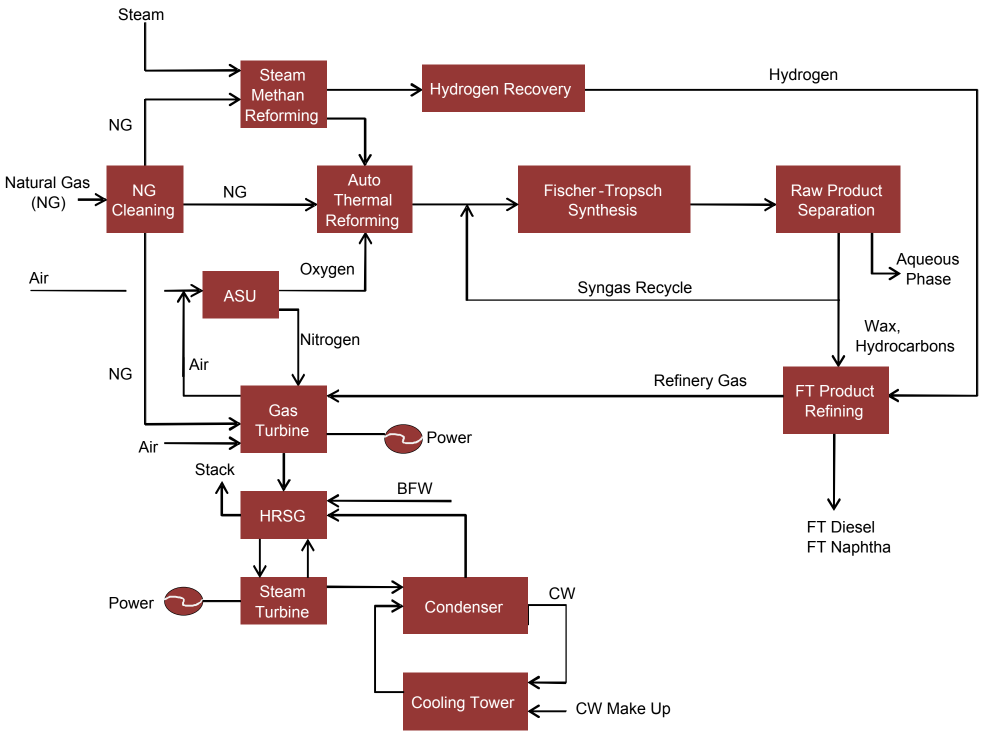

Figure 3: GTL Plant Configuration Schematic

2.2.4 Methanol and Methanol-to-Gasoline (MTG) Technology Overview

Methanol can also be produced from synthesis gas using methanol-specific catalysts via the following reaction:

$$CO + 2H_2 = CH_3OH$$

With modified engines methanol can be used as a neat transportation fuel. It has high octane and could be used in place of gasoline. However it cannot be distributed using the existing hydrocarbon liquid distribution infrastructure. ExxonMobil has developed a process whereby methanol can be converted into high octane gasoline using the MTG process.

In MTG the methanol is first passed to the fixed bed dehydration reactor where methanol is partially dehydrated into an equilibrium mixture of dimethyl ether (DME), methanol, and water. This is then mixed with recycle gas from the second fixed bed reactor and passed into the second fixed bed reactor containing a zeolite catalyst that converts the methanol and DME into hydrocarbons and water.

$$2CH_3OH \leftrightarrows CH_3\text{-}CO\text{-}CH_3 + H_2O$$

$$CH_3OH \leftrightarrows \text{-}CH_2 + H_2O$$

The effluent from the second stage zeolite reactor is cooled and the product is separated into three phases. The gas phase is recycled to the MTG reactor, the liquid water phase containing some oxygenates is sent to wastewater treatment and the liquid hydrocarbon phase is the raw gasoline. This is distilled to produce fuel gas, LPG, and light and heavy gasoline. The heavy gasoline is hydrotreated in a Heavy Gasoline Treatment (HGT) unit to remove durene and then combined with the light gasoline to produce the gasoline product. The gasoline product typically has an intermediate octane number of about 87 and can be used as a direct replacement to conventional gasoline.

2.3 Barriers to XTL Development in the United States

The U.S. is endowed with over 250 billion tons of recoverable coal reserves, has potentially the second largest gas resource in the world (Marcellus shale) and has the potential to provide large quantities of biomass for energy use. Therefore a real opportunity exists to use these domestic resources to enhance U.S. energy security by producing clean transportation fuels to supplement petroleum supply. GTL, CTL, and CBTL technology could be used to produce these fuels.

Although the United States still imports about 11 MMBPD of oil from the unstable Middle East and other potentially hostile countries and world oil prices are currently hovering around \$90 to \$100 per barrel, no commercial U.S. XTL plants are being built. This is because of the considerable number of barriers to deployment of XTL. These barriers can be classified as technical, economic, environmental, commercial, and social.

Under technical barriers, for GTL the technology risks are low because of the demonstrated commercial performance record. For CTL the integration of advanced entrained coal gasification technologies and advanced slurry phase FT synthesis technologies have never been attempted. This poses significant technical risks that may be considered unacceptable by potential process developers. For CBTL again there is significant technical risk. Because of the concerns over climate change another major technical barrier is the successful demonstration that carbon dioxide can be sequestered in geologic formations for extended periods in a safe manner.

Under economic barriers, the uncertainties about future oil prices are a significant barrier. The high capital expenditures needed for large scale CTL plants is a major barrier. It is anticipated that the capital for large (greater than 50,000 BPD) CTL plants will be over \$150,000 -\$160,000 per daily barrel. Therefore, a 50,000 BPD FT CTL plant could cost over \$8 billion. The investment risk for such a large sum is considerable. For GTL the capital cost is lower but a 50,000 BPD plant would still require an investment of over \$3.5 billion. Also for CBTL the cost of delivered biomass is very high.

Under environmental barriers, coal is a carbon rich fossil fuel and when coal is converted into fuels and power large quantities of carbon dioxide are emitted. Typically for a CTL plant with no carbon capture and sequestration the overall life cycle GHG emissions will be double that of the same fuels produced from petroleum. For CTL plants with carbon capture and sequestration the life cycle GHG emissions are about equal to petroleum. If concerns over global climate change continue, then XTL plants will have to capture and sequester carbon dioxide produced during the conversion process. Recent publications have implied that the LCA GHG emissions for natural gas are much greater than previously thought particularly as a result of methane leakage, fracking, and increased GHG forcing value. Concerns over emissions of criteria pollutants and toxics like SOx, NOx, particulates, and mercury should be minimal because CTL plants are clean coal technologies and the removal of these pollutants can be readily accomplished.

Water use in CTL plants is also an important environmental issue particularly in geographical areas of low rainfall. However, use of air cooling in place of water cooling for the major users of water can substantially reduce water requirements to below one barrel of water per barrel of FT product. Generation of large quantities of coal-derived mineral waste also should not be an issue since this waste product is a non-leachable slag suitable for use in aggregate if produced in slagging gasifiers.

Significant deployment of CTL facilities will require the use of large quantities of coal and this will mean an expansion of the coal mining industry. For example, a 50,000 BPD CTL plant will use approximately 7 million tons of coal per annum. There is considerable opposition to increased coal mining.

Another issue concerns actual commercial deployment of CTL. Who would take the lead in commercial deployment of XTL technologies? A polygeneration plant producing liquid fuels and generating power combines elements of both power and petroleum industries.

If many XTL plants were to be built worldwide at the same time then there will be competition for critical process equipment and engineering and labor skills. There is already evidence that this bottleneck is being encountered worldwide because of the large number of simultaneous construction projects.

Finally, there are the issues of permitting and the usual public reluctance to accept the need for new facilities especially coal based plants.

Particular barriers to deployment of CBTL technologies include the high cost of biomass feedstock, the availability of sustainable quantities of biomass feed stock, the GHG and energy penalties associated with the cultivation, harvesting, and preparation of the biomass feed, the high cost of biomass transport, and the technical problems with feeding biomass to high pressure gasification systems.

2.4 Environmental Issues

2.4.1 GHG Emissions from XTL Plants

There are many limited Life Cycle Analyses (LCA) that have been performed for XTL processes. In this white paper the results of the LCA are presented in terms of the "Petroleum Ratio" (PR). This is defined as the ratio of the greenhouse gas (GHG) emissions for the XTL process, estimated from the LCA, and the GHG emissions associated with the same fuel derived from conventional petroleum. For the XTL process the envelope considered for GHG emissions encompasses the following: mining of the coal, recovery of the gas, cultivation of the biomass, transport of the feed stocks to the conversion XTL plant, pretreatment of the feed stocks, emissions associated with the conversion process from feed stock to transportation fuel, transport of the fuel to the end user, and combustion of the fuel. The net GHG emissions estimated from these activities is divided by the heating value of the diesel fuel on an LHV basis to give the effective pounds of carbon equivalent per MMBtu LHV. Assume this is X pounds carbon equivalent/MMBTU.

For the GHG emissions associated with the reference petroleum-derived diesel fuel, data was obtained from the EPA and represents diesel fuel sold or distributed in the United States in the year 2005. This EPA methodology relies heavily on the methodology developed by DOE and described in the NETL report entitled "Development of Baseline Data and Analysis of Life Cycle Greenhouse Gas Emissions of Petroleum-Based Fuels" dated November 2008. The petroleum GHG baseline for conventional diesel fuel sold or distributed in the United States is estimated to be 97.3 kg CO_2E/MMBtu. In U.S. units this is equivalent to 58.5 pounds carbon/MMBtu. To obtain the "petroleum ratio" (PR), X (the LCA emissions for the XTL process) is divided by 58.5. If the PR is 1.0 then both the petroleum and XTL derived diesel fuel have the same GHG emissions based on this LCA. If the PR is less than 1.0 then the XTL diesel has lower GHG emissions than petroleum derived diesel. If the PR is higher than 1.0 then the petroleum diesel has lower GHG emissions than the XTL fuel.

XTL TECHNOLOGY	CTL (NO CCS)	CTL (CCS)	CBTL* (NO CCS)	CBTL* (CCS)	GTL (NO CCS)	GTL (CCS)
PETROLEUM RATIO	**~2.2**	**~0.9-1.0**	**~1.9**	**~O.8-0.9**	**~1.1**	**~0.9**

- CBTL plants co feed 15 weight % biomass

Table 2: Estimated Petroleum Ratios for XTL Processes Bases on LCA

Table 2 summarizes estimates of the PR for XTL plants with and without carbon capture and storage (CCS). For CTL with no CCS the PR is over 2. With CCS the PR for CTL can be about equal to or slightly lower than petroleum. The life cycle GHG emissions from CBTL plants depend on the ratio of coal to biomass used and whether or not the plant captures and sequesters the carbon dioxide. Without carbon capture and sequestration with 15% by mass of biomass the PR is less than 2 but with CCS the PR can be reduced to about 0.8-0.9. For GTL the PR is very dependent on the nature of the natural gas feed but with no CCS the PR is slightly higher than1.0. With CCS this can be reduced to below 1.0.

2.4.2 Other Criteria Emissions from XTL Plants

Emissions of SOx, NOx, mercury, and particulates would be expected to be very low from XTL plants. This is because gasification and reforming allows for the capture of nearly all of the mercury, particulates and sulfur. The NOx can be controlled by use of low NOx burners in the combustors. Solids effluent from coal and coal/biomass gasification would be a non-leachable slag that could be used as a building material.

2.4.3 Water Usage

The expected water use depends on the degree and type of water management designed into and practiced at the XTL plants. If water availability presents no problems and water cooling is used for all applications the expected use would be in the range 7-10 barrels of water per barrel of liquid fuel product for CTL and CBTL plants. On the other hand, if water is scarce, in Western locations for example, then maximum use of air cooling could be made. This could reduce water usage to about 1-2 barrels of water per barrel of product. GTL can be a water producer depending on the configuration used.

2.5 Estimated Economics for XTL Plants

Because no FT CTL plants have been built since Sasols II and III in South Africa in the early 1980s it is very difficult to accurately estimate the capital costs of new FT CTL plants that would be built in the U.S. in today's economic climate. The tight EPC market has resulted in large escalations of capital costs for major projects. For example, costs for new IGCC plants are estimated to be over $4,000/kW compared to estimates of around $2,500/kW just a few years ago. Likewise, the costs for new Oil Sands projects in Canada have experienced escalations of 70% or more. Costs of GTL plants have escalated sharply since the Sasol Oryx plant was constructed in Qatar.

There is a considerable range of Capex numbers in the open literature based on estimates of costs for the GTL plants that have been built and for those still in construction or in the planning stage. This range is large between about $35,000/DB for the Sasol Oryx plant that was constructed over 5 years ago and about $200,000/DB for the Escravos plant in Nigeria that is still in the planning stage. The large Shell Pearl GTL plant that has almost finished construction in Qatar will produce 140,000 BPD of FT fuels and about 120,000 BPD of natural gas liquids. This plant is expected to cost in the region of $18 billion.

There are many reasons for this large range including plant size, location, project scope, products, gas processing needed, financing assumptions etc. To attempt to address the impact of this range on the required selling price (RSP) of the fuels, a base Capex and a high Capex were used. Tale 3 shows the Capex values used for the XTL plants and the major economic assumptions.

	GTL	CTL	CBTL
BASE CAPEX $/DB	70,000	150,000	157,000
HIGH CAPEX $/DB	180,000	300,000	314,000
CAPITAL RECOVERY FACTOR %	20	20	20
CAPACITY FACTOR %	90	90	90
O&M COST %OF CAPEX	5	5	5
HHV EFFICIENCY %	60	50	50
FEEDSTOCK VALUE RANGE	5-10$/MMBTU NG	$35-$70 /TON COAL	$35-$70 /TON COAL $71/DRY TON BIOMASS

Table 3: Economic Assumptions

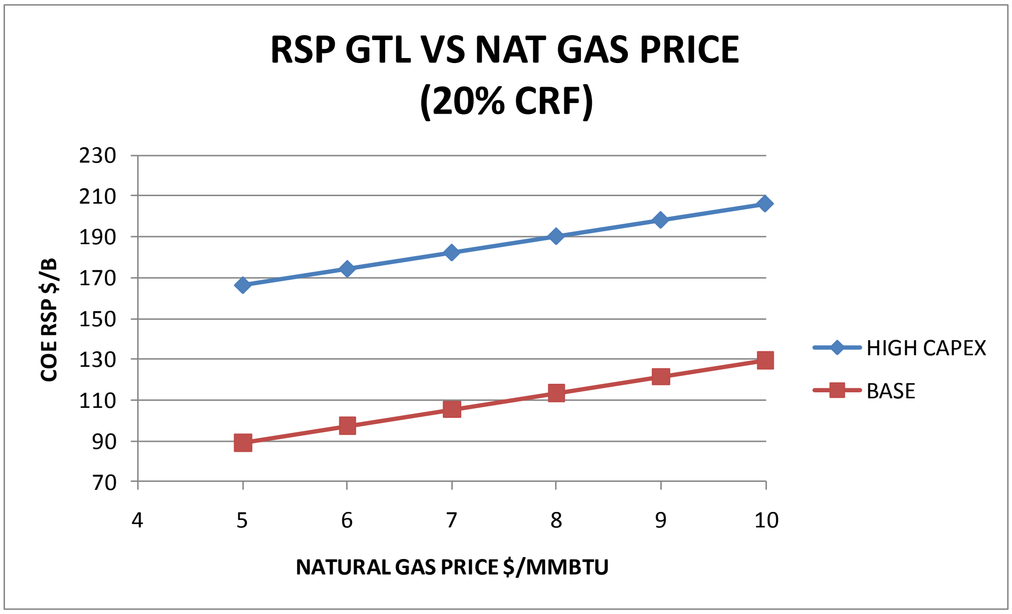

Figure 4: Variation of Required Selling Price (RSP) of Diesel Fuel from GTL with Natural Gas Feed Stock Price

Figure 4 shows estimates of the required selling price (RSP) of diesel fuel produced by GTL as a function of natural gas price at the plant gate for the two capital cost (Capex) assumptions. The GTL plant size is assumed to be 34,000 BPD, equal to the size of the Oryx plant. The base capital cost is assumed to be $70,000 per daily barrel (DB) and the blue line shows the high Capex ($180,000/DB). Economic assumptions are for a capital recovery factor of 20%. If the natural gas price is less than $5/MMBtu the RSP on a crude oil equivalent (COE) basis would be between $80 and $90 per barrel for the base Capex. For the high Capex case it would be over $160/B. The baseline COE RSPs are in the range of the current world oil price (WOP). These economics are based on a capital recovery factor (CRF) of 20%.

Figure 5 shows estimates of the required selling price (RSP) of diesel fuel produced by CTL as a function of coal price at the plant gate for the two capital cost (Capex) assumptions. The CTL plant size is assumed to be 50,000 BPD and CCS is used to capture the carbon dioxide produced during the conversion process. The base capital cost is assumed to be $150,000 per daily barrel (DB) and the high Capex is $300,000/DB. If the coal price is $1.50/MMBtu (equivalent to about $35 per ton) the RSP on a crude oil equivalent (COE) basis would be $120 per barrel for the base Capex. For the high Capex case it would be over $240/B. Clearly the assumptions regarding Capex have a large effect on the RSP and hence on the economic viability of CTL to provide an alternative fuel supplement for petroleum.

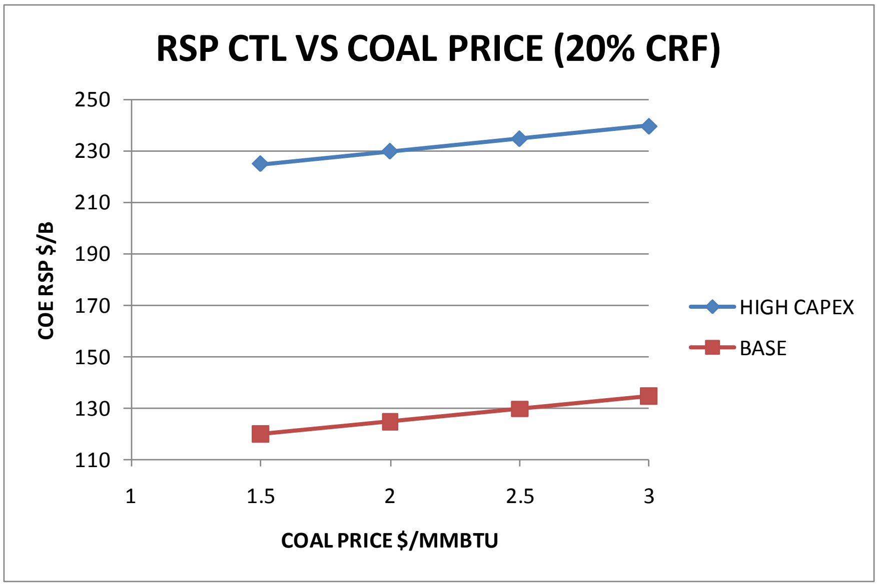

Figure 5: Variation of Required Selling Price (RSP) of Diesel Fuel from CTL with Coal Feed Stock Price

Figure 6 shows estimates of the required selling price (RSP) of diesel fuel produced by CBTL as a function of coal price at the plant gate for two capital cost (Capex) assumptions. The CBTL plant size is assumed to be 50,000 BPD and CCS is used. The base capital cost is assumed to be $157,000 per daily barrel (DB) and the blue line shows the high Capex case ($314,000/DB). If the coal price is $1.50/MMBtu (equivalent to about $35 per ton) the RSP on a crude oil equivalent (COE) basis would be about $130 per barrel for the base Capex. For the high Capex case it would be over $230/B. In all cases the biomass feed stock cost was assumed to be constant at $71/dry ton. Again assumptions regarding Capex have a large effect on the RSP and hence on the economic viability of CBTL.

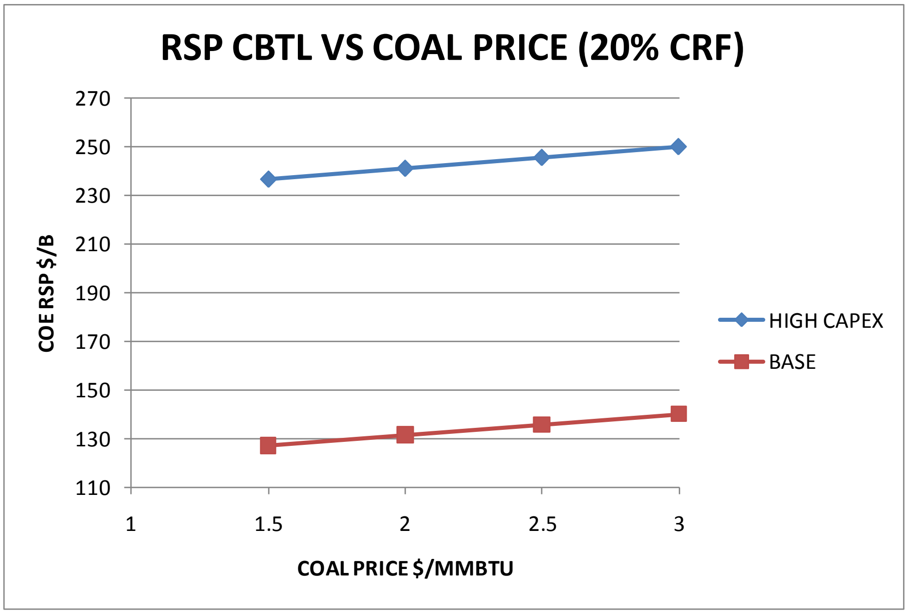

Figure 6: Variation of Required Selling Price (RSP) of Diesel Fuel from CBTL with Coal Feed Stock Price

2.6 Potential Supply Curves for XTL

2.6.1 IEA Reference WOP Scenario

Figure 7 shows one of many potential supply curves for the combined GTL, CTL, and CBTL production until the year 2050 for the EIA reference WOP scenario. To generate these curves it was assumed that an XTL plant would be built three years after the delta between the EIA reference WOP and the COE RSP was zero. The three year delay was assumed to allow time for the plant construction. When the delta became $10/B it was arbitrarily assumed that two plants would be built simultaneously because the risk of the WOP dropping below the XTL RSP was considered less likely. Under these assumptions, for the base case Capex scenario, just over 2 million barrels per day of XTL would be produced by 2050. This would consist of 70% contribution from GTL, 23% from CTL, and 5% from CBTL. In this scenario just over 4 trillion cubic feet (TCF) per annum of natural gas would be used by 2050 to produce 1,428,000 BPD. This is less than 2% of current natural gas consumption. For the production of 500,000 BPD of CTL about 75 million tons per year of coal would be used. This is about 6% of current coal consumption. For the production of all of this XTL a total capital expenditure of about $190 billion would be necessary. This compares to about $360 billion per year that the U.S. pays for imported crude and refined products.

For the high Capex scenario, no XTL plants would be built and there would be no contribution from this source. The COE RSP for the GTL, CTL and CBTL plants were always higher than the reference WOP for the period up to the year 2050.

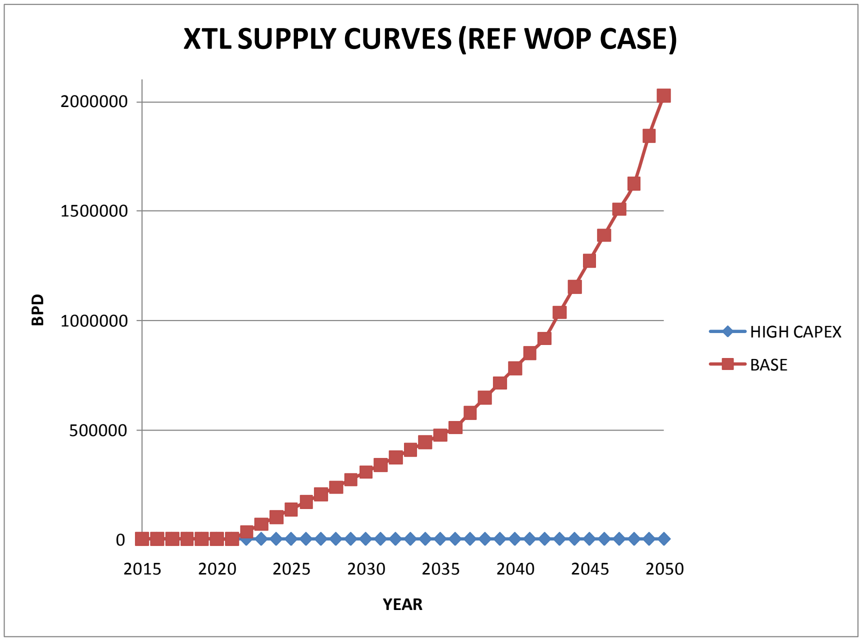

Figure 7: Potential Supply Curves for XTL Assuming EIA Reference WOP and for Base and High Capex Scenarios

2.6.2 IEA High WOP Scenario

Figure 8 shows one of many potential supply curves for the combined GTL, CTL, and CBTL production until the year 2050 for the EIA high WOP scenario. Using the same assumptions as were used above for the EIA reference case, slightly less than 3 million barrels per day of XTL would be produced by 2050 for the base Capex scenario. This would consist of 49% contribution from GTL, 34% from CTL, and 17% from CBTL. In this scenario just over 4 trillion cubic feet (TCF) per annum of natural gas would be used for GTL, and about 166 million tons per year of coal would be used for CTL and CBTL. For the production of all of this XTL a total capital expenditure of about $330 billion would be necessary.

For the high Capex scenario, no XTL plants would be built and there would be no contribution from this source.

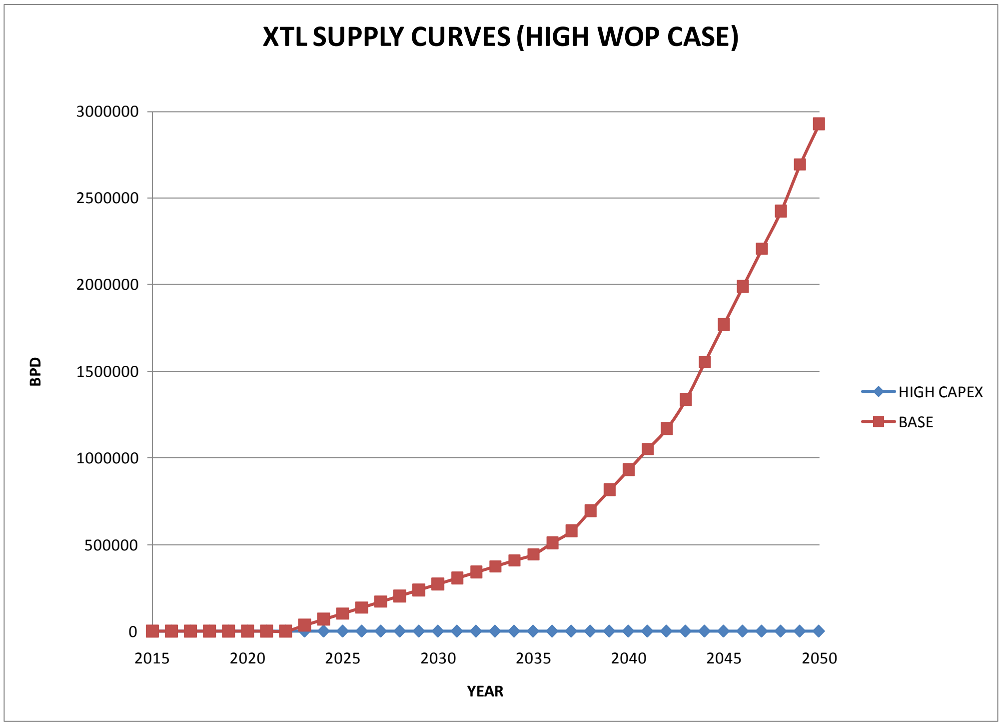

Figure 8: Potential Supply Curves for XTL Assuming EIA High WOP and for Base and High Capex Scenarios

3. DCL: Production of Alternative Liquid Hydrocarbon Transportation Fuels from Coal without Synthesis Gas

3.1 History and Current Status of Direct Coal Liquefaction

Production of liquid fuels from hydrogen and coal is commonly called direct liquefaction of coal, also sometimes known as hydroliquefaction, or as the Bergius process. The adjective "direct" is used to differentiate this process from the totally different process concept that involves gasifying coal to produce synthesis gas followed by conversion of the synthesis gas to liquid hydrocarbons as a separate step. This latter route is sometimes known as indirect liquefaction and was described in the previous sections of the paper.

All direct liquefaction processes aim at increasing the hydrogen-to-carbon ratio, from ≈0.8 in coal to ≈1.8 typical of petroleum liquids. This can be done by adding hydrogen to the coal, i.e., hydroliquefaction, or by removing relatively hydrogen-rich components from the coal and "rejecting" the carbon-rich portion. Chemically, conversion of coal to liquid fuels by reaction with hydrogen is straightforward. The conversion of an Appalachian bituminous coal to cetane, the desired component of diesel fuel, could be written as

$$C_{160}H_{132}N_2O_8S + 116\,H_2 \rightarrow 10\,C_{16}H_{34} + 2\,NH_3 + 8\,H_2O + H_2S$$

Although this equation suggests that the chemistry is relatively straightforward, numerous difficulties have been encountered in converting the chemistry to economically viable engineering practice. There are no known examples of successful commercial-scale operation of direct liquefaction processes in open economies (i.e., economies free of centralized state planning and free of wartime situations where national survival was the issue).

A generic flow chart for coal hydroliquefaction, is presented in Figure 9. This figure is adapted from the 1986 report by Engineering and Economics Research Inc., *Emerging Clean Coal Technologies* (Noyes Data: Park Ridge, NJ).

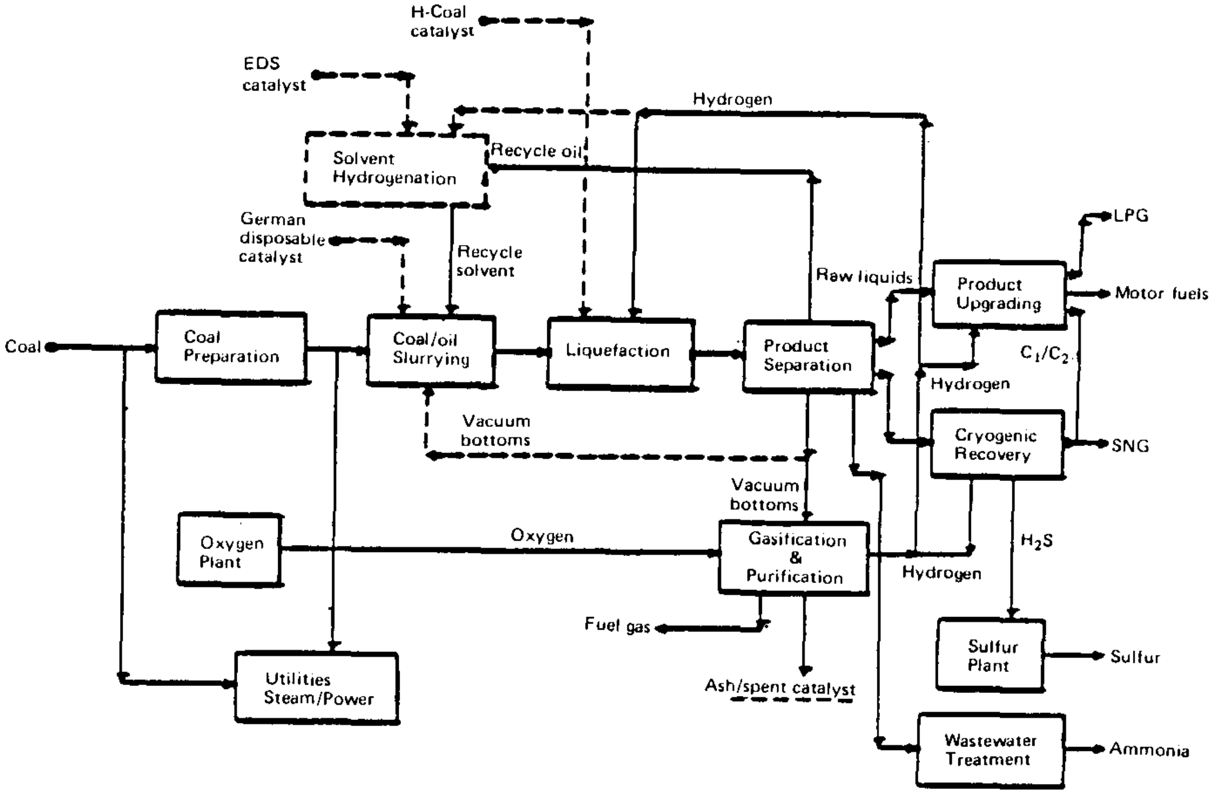

Figure 9. Generic flow chart for liquefaction processes.

Research and development activities around the world have led to a variety of process concepts or configurations for direct liquefaction. Virtually all have several features in common: Coal is pulverized and introduced to a pressurized reaction vessel as a slurry. Liquefaction occurs typically at 400-500°C and pressures of 14 MPa or above. Multiple stages of reaction might be used. The usual intent is to achieve high (e.g. ~90%) conversion of the coal to a liquid roughly similar to crude oil. In many processes the liquid medium is expected to react with the coal itself and not to be a more-or-less inert slurry vehicle. If so, it must be recovered, replenished, and recycled. Unconverted or partially converted coal and mineral matter must be separated from the liquid product stream. If a catalyst was used in the process, normally it would also have to be recovered, re-activated, and recycled. The liquid product, a synthetic crude oil, would be fractionated. Heavy distillation fractions could be recycled through the process (e.g., as the slurry vehicle). Lighter fractions would be upgraded to marketable products similar to (ideally, identical to) ones used in oil refining.

Large-scale operation of Bergius-process plants ended in 1945 or shortly thereafter. Some work on direct liquefaction continued into the mid-1950s. The largest operations in the United States were the pilot plants operated by the U.S. Bureau of Mines in Louisiana, Missouri, and by Union Carbide in Institute, West Virginia. The Louisiana plant was successfully operated on western Kentucky bituminous coal. It ran on a scale of 50-60 tonnes of coal per day (moisture-free basis), with a yield of 690-720 liters per tonne of coal (moisture- and ash-free basis), with coal conversion of 96-97%. The pressure used in the Louisiana reactors, about 58 MPa, very high by current standards. Temperatures were 460-465 °C.

By the mid-50s virtually all activity beyond laboratory investigations was shut down, in large part due to ready availability of inexpensive petroleum. A revival of interest was sparked by the oil price shocks of the 1970s. This led to development of various process concepts sometimes collectively lumped under the term "second-generation processes." In general, the second-generation processes are all derivatives, in some fashion, of the original Bergius process. The modifications embodied in the second-generation processes are aimed at reducing the reaction severity, improving the process efficiency, and improving economics. None of the second generation processes ever progressed beyond the pilot-plant scale, except for a commercial-scale installation of a derivative of the H-Coal process (described below) that is reportedly now under construction in China.

Numerous low-temperature carbonization and solvent extraction processes were operated, some at a commercial scale, prior to World War II. This was mainly done in Europe.

The Pott-Broche extraction process was developed in Germany before the war, and operated in at least one commercial 125 ton/day plant until 1944. It uses a slurry of dried coal in a 4:1 mixture with solvent. Slurry was digested at 415–430 C and pressures of ≈1400–2150 psi for an hour, and passed through a pressure filter to remove partially extracted coal and ash. The yield of liquid was 78–84% based on dry, ash-free coal. In the early years of commercialization, the extract was used as feedstock to a Bergius process, because it was found to be easier to hydrogenate than was the original coal. The primary products were gasoline and diesel fuel. The Ude-Pfirrmann process was similar to Pott-Boche, except in two details. It used gaseous hydrogen in the digester, and extraction time was shortened to thirty minutes.

In the area of low-temperature carbonization, the Karrick process aimed at producing highly combustible, reactive coke for use in power plants. The process gives a liquid yield of about 35 gallons/ton (≈0.8 barrels/ton) from Utah coals. The liquid product provided "motor fuel superior to the average gasoline," but it is important that in Karrick's day gasoline typically had an octane rating of ≈40.

A much greater level of process development and commercialization was undertaken in Europe. The Krupp-Lurgi process consisted of six cells, crudely like a miniature coke-oven battery. Tars from Krupp-Lurgi plants built in Germany in the 1930s were a source of liquid fuels for the Germany military. The yield was about 0.5 bbl/ton. A plant started up in Germany in 1943 produced ≈1300 tons of fuel oil and ≈2100 tons of distillate motor fuels per year, along with 225,000 tons of char. The Lurgi-Ruhrgas process, notable for a very short residence time of the coal (≈3 seconds) was commercialized in Europe, and operated on subbituminous coal. It gave one of the best liquid yields of any of the carbonization processes, ≈32%. It was also applied to the retorting of oil shale. Prior to World War II the Lurgi-Spülgas process was run at a number of sites in Germany, for the primary purpose of making a smokeless char for domestic and industrial fuel use. By-product tars were collected and contributed to motor fuel production during the war. This process, or some close variant of it, was also used in Japan in the same time frame. One of the Japanese plants produced, during the course of the war, 400,000 barrels of liquid fuels. The Koppers process used continuous injection of steam to provide the internal heating for simple rectangular ovens. Ovens could process up to 180 tons per day. A plant based on the Koppers process, and with a design capacity of a million tons per year, was under construction in Germany in 1945. Apparently it was never completed.

Some of the German plants continued in operation after 1945 in what were then East Germany and Czechoslovakia. Lurgi retorts were used in an installation in Dickinson, ND, for the carbonization of lignite to produce briquettes.

The Rexco process originated in Britain in the 1930s. It is an example of several processes developed there with the aim of producing so-called smokeless fuels for domestic and small industrial applications, intended to reduce air pollution. The process yielded ≈20 gallons (approximately 150 lbs.) of light oil and tars per ton of coal, along with 1350 lbs. of char. In the same era, the Wisner process was developed in the United States. A plant operating at Champion, PA produced 7,000 tons of char per month. The yield of tar plus light oil was 0.44 barrels/ton.

A very different approach was used in the Disco process, designed to produce spherical particles of char from caking coals. An 800 ton/day plant near Pittsburgh was designed to convert fine coal from an adjacent bituminous coal preparation plant into lump coal for domestic use. Tar from the Disco process was more viscous and heavier than typical low-temperature carbonization tar. The Disco process is unique in being the only large-scale low-temperature carbonization process to be commercially successful in the United States over a time scale of decades (from the 1930s at least into the 1960s).

3.2 Technology Overviews

3.2.1 The Bergius Process

Direct liquefaction of coal has been practiced, at various scales, for about eighty years. The Bergius process is the archetype of direct liquefaction processes. It operated in two stages: liquid-phase hydrogenation that converted coal into so-called “middle oil” with a boiling range of ≈180-325°C; and vapor-phase hydrogenation of the middle oil gasoline, aviation fuel, and diesel fuel. The Bergius process was used on a large scale in Germany during World War II and is most commonly associated with the German war effort. Some plants based on the Bergius process may have operated in the former Soviet Union and in the former Czechoslovakia for some years after the war. A plant at Billingham, England was built in 1935 and operated on bituminous coal until 1939 or 1940, after which time it was used to process creosote feedstocks.

In German experience, both bituminous and low-rank coals were used as feedstocks. Bituminous coals required very severe reaction conditions, e.g. 475-485°C and 35-70 MPa. Conversion of 60-62% of the coal (moisture- and ash-free basis) to middle oil was achieved. Second-stage vapor-phase hydrogenation was done in fixed-bed catalytic reactors. Under those conditions 50% of the middle oil was converted to 70-75 octane gasoline.

3.2.2 Second-Generation Processes of the 1970s-90s

3.2.2.1 The H-Coal process

The process described in this subsection was originally developed by Hydrocarbon Research Inc. (HRI). This company was acquired by a French company that mainly wanted ownership of HRI's patents. The key employees spun off a new company, Hydrocarbon Technology Inc. (HTI) that continued developing hydroliquefaction. Eventually HTI became part of Headwaters. Therefore, the technology is sometimes described as H-Coal, or as the HTI process, or the Headwaters process. For convenience, the process will be called H-Coal in this white paper.

The H-Coal process relies on an ebullated-bed reactor. Cleaned, sized, and dried coal is mixed with recycle slurry and process-derived solvent. This slurry is preheated to 350°C with recycle hydrogen to begin dissolving the coal, and is then pumped into the bottom of the ebullated-bed reactor at 21 MPa. Preheated hydrogen is also introduced into the bottom of the reactor. Typical temperatures are 450-460°C. The H-Coal process could be configured to produce either a synthetic crude oil or a fuel oil. Operating in the synthetic crude mode requires more extensive hydrogenation than does the fuel oil mode, accomplished by allowing a longer residence time in the reactor. On a moisture- and ash-free coal basis the total liquid yield is 525-700 L/t. Conversion to liquids plus C_1–C_3 gases is >90%.

A pilot plant for the H-Coal process was built and operated at Catlettsburg, Kentucky in the early 1980s. This plant operated at 180-480 tonnes/day. In terms of coal throughput, it was the largest of the various liquefaction pilot plants. There were ambitious plans to build a 16,000 tonne/day plant, which never came to fruition because of termination of government funding support for synthetic fuels in the 1980s. The H-Coal process eventually evolved into the two-stage liquefaction concept, discussed below.

3.2.2.2 SRC II process

Two solvent-refined coal (SRC) processes were developed. The first was intended to dissolve coal, separate the mineral matter and much of the sulfur (which was present as pyrite), and then produce a low-ash, low-sulfur solid boiler fuel by removing the solvent to recover the coal. This process, which came to be known as SRC-I, can be thought of as a coal solidification, or coal-to-solids, process. SRC-I was a reasonable success, as tested at small scale, but evolved into the SRC-II process that was intended to produce liquids.

The SRC-II process was operated in a 50 ton/day pilot plant in Fort Lewis, Washington, until the early 1980s.

In the SRC-II process, reaction begins in a preheater or digestor at 370–400° C with 1500–2500 psi hydrogen. The intent of this step is to initiate the liquefaction reaction. Then, the partially reacted, hot slurry is fed to a dissolver, where the temperature is raised to 440–465° C (820–870° F) and more hydrogen is added. Vapor produced under these conditions is let down to atmospheric pressure and then distilled with a cut point of 205° C, producing light and heavy oils. Liquid coming from the dissolver was subjected to a vacuum distillation. Distillate from vacuum distillation was recycled to the slurry preparation unit upstream of the preheater. Bottoms from the vacuum distillation were sent to a gasifier to make hydrogen.

Middle distillate from SRC-II liquefaction of high-volatile bituminous coals contains 35-50% saturated hydrocarbons, and 50-65% aromatics. It was suggested (based on prevailing environmental regulations of the 1970s) that the SRC-II product could have potential applications in diesel locomotives or marine diesel engines. Nowadays it is likely that substantial downstream hydrogenation and hydrocracking would be needed to produce an acceptable liquid transportation fuels.

A problem with many hydroliquefaction processes is the need for a difficult solid/liquid separation operation downstream of the liquefaction reactor. The SRC-II process avoided this. Any ash, unreacted or partially reacted coal, or other solids were retained in the vacuum bottoms that were sent to the gasifier. Thus solid/liquid separation was avoided entirely.

3.2.2.3 The Exxon Donor Solvent process

The Exxon Donor Solvent (EDS) process relied on transfer of hydrogen from the solvent as the primary reaction step for liquefying the coal. A potential disadvantage of processes in which catalyst is present in the liquefaction reactor is that it is usually not possible to optimize both liquefaction and solvent regeneration. Processes in which these two operations are physically separated do not have this disadvantage. EDS was one application of this strategy. Separating the solvent regeneration step from the liquefaction step allows for separate “fine tuning” of solvent quality and coal hydrogenation.

The EDS process begins with preparing a slurry of crushed, dried, pulverized coal in a recycle process solvent. Pulverized coal was slurried in a hydrogenated, recycled donor solvent. The slurry is mixed with hot hydrogen and pumped through a preheater into a vertical, upward plug- flow reactor. This plug-flow reactor is called a “dissolver” in Exxon’s terminology. Although the gaseous H_2 in the reactor quite possibly participated in reactions with coal or molecular fragments released from the coal, its principal purpose was rehydrogenation of spent donor solvent. The liquid product first goes to a solids-liquid separation and then to atmospheric distillation. Atmospheric distillation removes the light oils; subsequent vacuum distillation provides a heavy distillate. Middle distillate circulates through a catalytic reactor where it is hydrogenated to become the donor solvent for recycling to the main liquefaction reactor as the slurry vehicle. The liquids were hydrotreated and fractionated, to produce a naphtha and a heavy oil. Bottoms from fractionation were sent to a "flexi-coking" operation, which produced some additional heavy liquid and coke. Gasification of the coke could provide a source of hydrogen.

The EDS process operated in a 200-225 tonne/day pilot plant in Baytown, Texas in the early 1980s. The plant operated successfully (the longest continuous run was 57 hours) on several coals. When the pilot-plant campaign ended, the plant had logged over 10,000 operating hours, equivalent to continuous "24/7" operation with a 90% on-stream factor for 15-16 months. Advantages claimed for the EDS process are that it avoids contacting the catalyst with mineral mater from the coal, avoiding rapid catalyst deactivation; and that it offers flexibility in selecting the final product slate.

The Consolidation Synthetic Fuels (CSF) process was somewhat similar to the EDS process**.** The first stage involved extraction of crushed and dried coal with recycle oil. The extract was then filtered while still hot and at pressure to remove unreacted coal and mineral matter. A subsequent step involved catalytic hydrogenation of the extract. Fractionation of the liquid produced recycle solvent for the process and distillate liquids for downstream hydrotreating. The solid was pyrolyzed in a low-pressure reactor to recover additional solvent and distillate. Char was sent to a gasifier for production of hydrogen. Hydrogenation of the liquid product produced naphtha, light oil and make-up solvent. An 18 tonne/day pilot plant for the CSF process was set up in Cresap, West Virginia in the late 1960s.

3.2.2.4 Catalytic two-stage liquefaction

The catalytic two-stage liquefaction process (CTSL), which was the last major direct liquefaction pilot plant to remain in operation in the United States, was the evolutionary culmination of several predecessors. In the 1970s, several groups showed that conversion of coal to products soluble in a strong solvent is essentially complete in about five minutes. Consumption of gas-phase hydrogen in these first few minutes is essentially nil. Almost all of the hydrogen used for converting the coal to a soluble form comes from the solvent. Provided that the solvent is well hydrogenated, this so-called short-contact-time liquefaction provides a good, non-catalytic way of dissolving coal. Processing the primary liquefaction product in a second, catalytic step provides a hydrogenated process solvent to be recycled to the first stage and the desired liquid products. This tight coupling of the coal dissolution step and the further processing of the liquid is called integrated two-stage liquefaction (ITSL).

ITSL involves the dissolution of coal in one reactor, without catalyst, followed by removal of mineral matter and unconverted coal, and then catalytic hydrogenation of the liquids in a second reactor. A portion of the product from the second reactor is recycled as process solvent. British Coal tested a two-stage liquefaction process in a pilot plant in Point of Ayr, Wales. In the 1980s several companies proposed or developed various schemes for ITSL. The culmination was the Advanced Coal Liquefaction R&D Facility, in Wilsonville, Alabama, Wilsonville pilot plant. By the mid-1980s it was recognized that there were advantages to operating an ITSL process with catalyst in both stages. This process modification is called catalytic two-stage liquefaction (CSTL). By 1985 Wilsonville was converted to operate in the CSTL mode.

CSTL used two ebullated bed reactors with supercritical extraction for solids rejection. The first-stage was run at 400°C, to allow slow dissolution of coal into the recycle solvent, and for catalytic rehydrogenation of the solvent to proceed at a rate matching the rate of coal conversion. Further conversion and improvement of product quality occured in the second stage, where primary liquids from the first stage were hydrocracked into distillable liquids. Products of the second stage are, in principle, able to be upgraded further to clean transportation fuels by standard refinery processes. CSTL was able to achieve yields of distillates of up to 880 L/t; 94% conversion to products lighter than residual oil was achieved. The CTSL pilot plant in Wilsonville was the last of the big liquefaction pilot plants to stay in operation, but was shut down in the mid-1990s.

3.2.2.5 The Conoco zinc chloride process

The Conoco process envisioned a much different approach to selection and use of the liquefaction catalyst. In this process, the catalyst was a bath of molten zinc chloride. Zinc chloride, and related compounds, can be excellent hydrocracking catalysts. Massive amounts of molten zinc chloride can convert coal to gasoline in a single step. Unfortunately, this requires a very high catalyst-to-coal ratio, about 1:1 on a weight basis. Nevertheless, the reaction rapidly yields liquids boiling in the gasoline and naphtha range that would be suitable for further refining to high-octane gasoline. In the Conoco process, crushed and dried coal is slurried with a recycle solvent, and pumped to the reactor where it reacts with hydrogen in the presence of molten zinc chloride at 350-440°C and 10-30 MPa. The liquid is distilled into naphtha, fuel oil, and recycle oil. The yield of gasoline was envisioned to be 770 L/tonne of moisture-free coal, with a hydrogen consumption of 1056 m^3 H_2/m^3 gasoline. This process was tested in a 0.9 tonne/day plant.

The principal perceived disadvantage of the Conoco process is that molten chloride salts, and the hydrochloric acid produced by their exposure to moisture, are voraciously corrosive toward many metals. Chlorides also accelerate stress corrosion cracking of stainless steels. And, although zinc chloride is very good at removing heteroatoms, these readily react to form zinc sulfide, zinc oxide or a zinc-ammonia complex, deactivating some of the catalyst and necessitating its replenishment or regeneration. The difficult solids separation step is eliminated because minerals and unconverted coal leave the reactor with spent zinc chloride. In a separate reactor, zinc chloride is distilled away from the minerals. Zinc sulfide is converted first to zinc oxide, which then reacts with chloride in the reactor atmosphere to produce zinc chloride again.

3.2.3 The Shenhua Process

The world's only commercial-scale hydroliquefaction plant is the so-called Shenhua plant, built by the Shenhua Group Corporation in Majata, Inner Mongolia. The Shenhua process represents evolutionary development of earlier work beginning with the H-Coal process (Hydrocarbon Research, Inc.), with further improvements by Hydrocarbon Technology Inc. and Headwaters. Bituminous coal is slurried with recycle solvent and catalyst. The slurry is fed to a liquefaction reactor (the largest one ever built, with a 6000 ton/day capacity), followed by solid-liquid separation. The primary liquids are hydrotreated to produce primarily diesel fuel and naphtha, in amount of 24,000 barrels per day. On an annual basis, the Shenhua plant expects to utilize about 3.5 million metric tons of coal, producing 715,000 metric tons of diesel fuel, 250,000 metric tons of naphtha, 120,000 metric tons of LPG, and about 3,500 metric tons of phenols. On a dry, ash-free basis, about 57% of the coal is converted to liquids.

Initial development, during 2002-04, involved testing in a 120 kg/h unit. This led to scale-up to a process development unit (PDU), which was completed in 2004. The PDU was operated successfully for a total of 178 days, including one 100-day continuous run. The first steps toward starting up the full-scale plant were taken in late 2007. Gasification for hydrogen production was started in May 2008, followed by solvent hydrogenation and recycle in November 2008 and finally the liquefaction reactor in late 2008. The first plant campaign was for about 300 hours, ending in January 2009.

The total cost of the plant is estimated to be $1.5 billion, and required four years for construction. This cost represents an investment of $62,500 per daily barrel of capacity (in 2008 dollars). The breakeven cost was $35-40 per barrel.

3.2.4 Other Routes to Liquids from Coal

The alternative to forcing hydrogen into coal is to separate coal somehow into a relatively hydrogen-rich set of products, ideally liquids, and leave behind (or “reject”) a very carbon-rich material such as a char. There are several ways to do this. Two that have achieved some measure of commercial success are pyrolysis or carbonization, in which coal is heated in an inert atmosphere to drive off liquids and gases and leave behind a solid char; and solvent extraction, in which coal is treated with various kinds of solvents to dissolve portions of the coal, leaving behind the insoluble, unreactive (and usually carbon-rich) parts of the coal.

3.2.4.1 Solvent Extraction

3.2.4.1.1 The National Coal Board supercritical fluid process

In Britain during the 1970s the National Coal Board developed a process for supercritical fluid extraction of coal. Toluene proved to be an excellent solvent for this process. When Wyodak subbituminous coal was processed in a ≈250 lb/day plant, a 20% yield of extract was obtained. The extract apparently solidified to a low-melting point solid, with no mineral matter and low sulfur and nitrogen.

3.2.4.1.2 The Penn State process

Penn State University has developed a solvent extraction process, so far tested only with bituminous coals. Coal is slurried with solvent in a 1:10 ratio. The solvent is heated at ≈360° C (680° F) for 1 hour in a batch reactor. No hydrogen is used. The pressure in the reactor, about 150–300 psi, is selected to be just adequate to keep most of the contents in the liquid phase at the working temperature. The mixture is sent through a pressure filter to separate unextracted coal. Downsteam of the filter, most of the solvent is recovered for recycle back to slurry preparation. Because solvent recovery for recycle would not be complete, make-up solvent is needed. If this process were co-located with an oil refinery, light cycle oil from the catalytic cracking unit is an ideal solvent. Otherwise, methylnaphthalene oil would be used. Yield of extract depends on the specific coal used, but on a dry, ash-free basis ranges from 40% to about 70%. A coal extract:solvent mixture of nominally 1:1 ratio is then sent to two-stage hydrotreating. In the first stage, the mixture is hydrotreated to knock out sulfur and some nitrogen. This hydrotreated liquid is then sent to a hydrogenation unit for aromatic ring saturation. Hydrotreated and hydrogenated liquid is fractionated using atmospheric distillation. The dominant product (≈80%) is clean middle-distillate fuels. Small amounts of gasoline and heavy fuel oil account for the rest. Products make superb jet fuel, very clean diesel fuel that can be used as-is or blended with petrodiesel, and a liquid that can be fed straight to solid oxide fuel cells.

3.2.4.2 Pyrolysis and Hydropyrolysis

Industrial-scale coal pyrolysis is usually referred to as carbonization. Carbonization processes are usually categorized as low-temperature carbonization, running at <700° C, and high-temperature carbonization, >900° C. Low-temperature carbonization processes have been run for the purpose of making gaseous fuel (e.g., town gas), or for making a solid char (e.g., for use as "smokeless" domestic fuel), or sometimes for obtaining the liquids. The sole purpose of high-temperature carbonization is to make metallurgical coke from bituminous coals.

All low-temperature carbonization processes make solid, carbon-rich char as the dominant product. Yields in the range of 75–80% are not atypical. If markets exist, it has a variety of potential uses, mostly of low value. These include a solid, smokeless fuel; a reducing agent for metallurgical processes, possibly even blending with more expensive metallurgical coke; or a feedstock for making activated carbon. Unless a market can be found for the char, it will otherwise represent a major disposal problem and environmental headache for a plant making coal liquids by low-temperature carbonization. All low-temperature carbonization processes also produce gases, with yields in the range of some 5–10%. It usually has a low to moderate heating value, so in the best case it could be sold as so-called town gas. It could also be used inside the plant for process heat. The liquid yield will be in the range of a few percent up to an optimistic 30%. The liquid, sometimes called low-temperature tar, will be primarily aromatic hydrocarbons and their alkylated derivatives containing oxygen, nitrogen, or sulfur. To produce marketable fuels, low-temperature tar would need significant downstream refining. The tar could be regarded comparable to an aromatic or asphaltic crude oil and processed in oil refinery operations. To some extent this was done in the 1930s and ‘40s, but of course fuel specifications were not so tight then as they are now.

The simplest approach to coal hydrogenation would be to react hydrogen directly with solid coal, at some temperature adequate to give acceptable reaction rates. Since any appreciable reaction is not likely until the coal is undergoing active breakdown of its molecular structure, processes that involve the heating of solid coal in gaseous hydrogen are often called hydropyrolysis. (Occasionally, but less commonly, the term hydrocarbonization is also used.) There are two options for liquids production in hydropyrolysis. One is production of liquids with no net production of char, and the other is liquids produced with no net hydrogen consumption. Hydropyrolysis offers some advantages relative to hydroliquefaction described above. The investment cost for a hydropyrolysis plant should be lower because the plant is less complex (e.g., there is no need to handle and recycle large quantities of liquid vehicle). Hydrogen consumption is low. The by-product is a partially desulfurized char that could be used as boiler fuel or as feed to a gasifier. These apparent advantages aside, hydropyrolysis was never scaled up beyond laboratory or bench equipment.

3.2.4.2.1 Low-temperature carbonization

The Toscoal process is a derivative of the Tosco process that was designed to retort oil shale. As tested with Wyodak subbituminous coal. the process gives a liquid yield of 9% based on as-mined coal.

3.2.4.2.2 Hydropyrolysis

The Coalcon process was originally developed for low-rank western coals but was extended to include Appalachian bituminous coals. Reaction with hydrogen occurs at 560°C and 3.8 MPa. A heavy oil as produced was similar to No. 6 fuel oil. It was considered to be a candidate for refining to gasoline, stationary turbine fuel, or low-sulfur, low nitrogen heating oil. In the mid-1970s there were ambitious plans to build a 2400 tonne/day demonstration plant, which would have made 640,000 liters/day of liquids and 620,000 m^3/day of SNG. A contract was awarded to build this plant at a site to be selected in Ohio or West Virginia. These plans never came to fruition because of what were termed “scale-up troubles”.

Flash hydropyrolysis uses a reaction temperature is about 700-1000°C and reaction time, 0-200 ms. The process was being developed by Rockwell, and basically relied on rocket engine technology for the reactor design. About 30-40% of the carbon in the coal is converted to liquids of which in turn some 30% is low-sulfur, low nitrogen naphtha that consists largely of BTX. In principle, this could be an attractive product, but even the xylenes boil below the diesel range, and these aromatic compounds would have extremely low cetane numbers.

At least until World War II, oils from low-temperature carbonization processes were of no commercial importance in the United States. The oil embargoes and price shocks of the 1970s led to interest in the U.S. in producing liquids from low-temperature carbonization. The COED process (char-oil-energy development) produced an oil yield comparable to the Karrick and Lurgi-Ruhrgas processes, about 1 barrel/ton. Subsequent evolution of COED led to the development of the COGas process, designed to produce synthesis gas by gasifying the char, rather than retaining it for use as a solid fuel. The COED and related COGas processes were, from a mechanical perspective, about the most complicated of the various low-temperature carbonization processes. Even so, it was felt in the 1970s that COED could be commercialized quickly because all of the mechanical equipment and process know-how were already in existence, if the economics were right. Likely the same would be true today, with the same caveat.

In recent years low-temperature carbonization has been considered a variant of clean coal technology in the European Union, with the notion that sulfur, chlorine, and mercury could be removed from the coal during processing, and used in conjunction with production of relatively clean electric power. A 2008 web posting claimed that China "has announced high volume commercial coal liquefaction production by this [i.e, Karrick] method." No details were made available.

3.2.5 Combining DCL and XCL

3.2.5.1 The Accelergy MCL Process

Accelergy Corporation has licensed technology from ExxonMobil for conversion of coal and biomass using ExxonMobil's microcatalytic direct coal liquefaction (MCL) approach. The intent is to combine the MCL process for converting coal with biomass conversion, to reduce the carbon footprint and other environmental impacts. The biomass feedstock is crambe (*Crambe abyssinica)*, which does not compete with food crops and which can flourish in the northern Great Plains. Products would be clean liquids primarily in the gasoline, jet, and diesel ranges. The liquid yield would be four barrels of crude oil equivalent per ton, with a CO_2 emission of 0.38 tons. The CO_2 emission is about half that of other processes. In addition, MCL should be more thermally efficient than CBTL. A collaborative effort with the University of North Dakota Energy and Environmental Research Center envisions establishing a demonstration facility at EERC, and possible further scale-up at the Tesoro refinery in Mandan, ND.

A venture with Great Plains Oil and Exploration was also announced in 2010. The biomass feedstock would be camelina (*Camelinia sativa*), another crop well-suited to the relatively dry, cold climate of the northern wheat belt. The intent is to produce synthetic jet fuel.

3.2.5.2 The ISFuel Process

An on-going research and development effort for an alternative liquid fuel production process that combines DCL (low temperature carbonization) and XTL (gasification / FT synthesis) is producing interesting results. The initial step utilizes pyrolysis to separate carbon char and organic volatile compounds, primarily single ring and double ring compounds. The carbon char is then gasified with an increased residence time to increase the production of hydrogen and carbon dioxide. The additional hydrogen is utilized to upgrade the organic volatile compounds into a high-density synthetic fuel that is thermally stable, i.e., would be capable of being used as a heat sink in addition to being a source of propulsion energy. The additional hydrogen is used in FT synthesis of the producer gases to make low-density synthetic fuels that have excellent cetane properties similar to typical FT-derived diesel fuels. All remaining hydrogen is then utilized to convert the carbon dioxide into methanol and water, thus reducing the carbon footprint and creating two additional desirable and marketable products. A flow diagram is given as Figure 10.

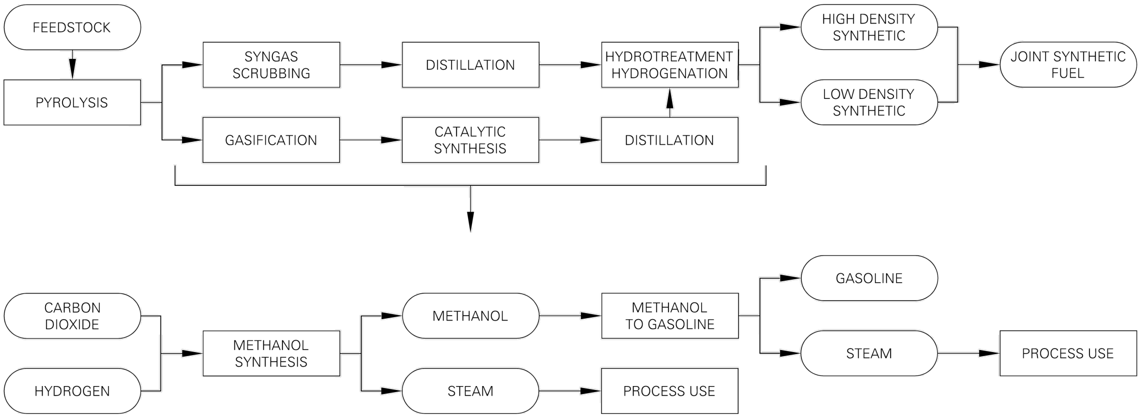

Figure 10. Flow Chart for ISFuel Combined DCL-XTL Process (Courtesy R.C. Knight, ISFuel Inc.)

Analysis of blended fuels that contain both low-density synthetic fuels and high-density synthetic fuels produced in this way have been shown to pass all property requirements for jet fuel as a fully synthetic blend. These prototype fuels also exhibit properties similar to the diesel fuel specification requirements, superior to JP-8 jet fuel that is currently used as a diesel alternative. Current studies with new additives to make a fully synthetic fuel that can pass both jet and diesel fuel are being finalized by Integrated Synthetic Fuel Incorporated, the company working on this emerging process method and fuel blend. Presently prototype fuels are very close to meeting both diesel and jet specifications with a single fuel formulation. This blend already shows a higher testing score than that of JP-8 for use as a diesel fuel. The remaining challenge is meeting HFRR diesel fuel lubricity requirements.

Additional research and development into these hybrid production methods may result in a feedstock-versatile, economically viable plant with a reduced carbon footprint. Increased product yield from co-processing, while achieving cost savings from feedstock by-product looping, should enhance economic viability while also reducing the net carbon emissions. The resulting fuel is fully synthetic, and has potential both as a battlefield multiple-use fuel and civilian-use fuel as a single fuel blend that can be used in multiple roles.

3.3 Barriers to DCL Development in the United States

DCL deployment faces many of the same barriers that have already been identified and discussed in the XTL section of this white paper. These include the significant technical risks (especially given only one commercial-scale DCL plant running in the world, and that only for about two years) with the attendant question of who would take the lead in building the first plant(s); the very high capital expense, at least for hydroliquefaction, and the related investment risk; questions of permitting, which will be made all the more complicated by the antipathy of the public and many NGOs to coal; likely shortages of process equipment and skilled labor; the need for substantial expansion of the mining industry; and a need to deal with CO_2 and other environmental issues.

The primary liquid from hydroliquefaction, carbonization, or solvent extraction is likely to be highly aromatic, also containing various compounds of oxygen, nitrogen, and sulfur. It will require significant downstream refining to produce liquid fuels that meet market and environmental specifications. These additional downstream processes will add capital and operating costs.

These processes, especially hydroliquefaction, will consume substantial amounts of hydrogen. The likely way of obtaining hydrogen is via coal gasification. Not only does this also add to capex and opex, it implies that all of the various operations of a gasification plant must be embedded inside a hydroliquefaction plant. If one needs to install gasifiers and ancillary equipment anyway, perhaps XTL would be a better choice.

Especially with low-temperature carbonization, and somewhat will solvent extraction, inevitably there will be a solid product containing unreacted or partially reacted coal and ash. Unless a use exists for the solid, it will be a major cost to collect and dispose of in an environmentally acceptable manner.

Many additional issues have been cited as real, or at least perceived, barriers to economically successful, commercial-scale direct liquefaction of coal. These include:

- Selection of materials of construction for reactor vessels and ancillary equipment, to withstand high-temperature, high-pressure hydrogen environments and abrasive coal or mineral slurries.
- Finding an inexpensive and convenient source of process heat.
- Finding an inexpensive source of hydrogen, ideally one that does not contribute to the carbon footprint..
- Separation of coal mineral matter and unreacted or partially reacted coal particles from the process stream.
- Subsequent post-liquefaction upgrading and refining of the “synthetic crude oil” from liquefaction into commercial-quality, marketable liquid fuels. It has been

presumed that the primary liquids would be treated in the standard unit operations of an oil refinery, but there seems to be little verification of this.

- A related issue is that the final, upgraded products of DCL have been assumed to be fungible with the comparable petroleum-derived products. This point does not seem to be fully demonstrated either.

3.4 Environmental Issues

3.4.1 GHG Emissions from DCL Plants

Estimated CO_2 emission from a hydroliquefaction plant is 360 kg per barrel of finished product. This is considered to be lower than emissions from a CTL plant. A hydroliquefaction plant has more fired heaters than a CTL plant, making CO_2 more difficult to capture because of the multiplicity of relatively small sources of flue-gas CO_2 (i.e., ≈10-15% CO_2 in the gas stream) relative to fewer and more concentrated sources in a CTL plant.

Some efforts are underway to develop, at least conceptually, a zero-emission DCL plant. Major components of emission reduction would be the use of non-carbon routes to hydrogen production, such as water electrolysis using solar, wind, or nuclear energy for the electricity, and use of algae photobioreactors for CO_2 capture. Presumably bio-oils from algae would be blended with the coal-derived liquids. Non-carbon sources of process heat would reduce potential GHG emissions even further.

3.4.2 Other Criteria Emissions from DCL Plants

With adequate design for capture of potential emissions, a DCL plant should have very low emissions of SOx, NOx, mercury, and other hazardous materials. Assuming that unconverted coal and ash would be fed to gasifiers for hydrogen production, most of the potentially hazardous trace and minor elements (mercury, selenium, arsenic, etc.) would be handled exactly as in CTL plants. The primary liquids from DCL contain known and suspect carcinogens.

3.4.3 Water Usage

The major water requirements would be for hydrogen generation (via gasification) and for cooling. For solvent extraction or carbonization processes in which the primary liquid would be upgraded elsewhere, the on-site hydrogen requirement would be very low to nil. Water usage is also impacted heavily by factors of plant design, such as the extent to which air cooling could replace water cooling. Potentially, therefore, water requirement could vary over a substantial range, from a low of approximately one barrel of water per barrel of product to a high that would be an order of magnitude higher. The estimate of two barrels of water per barrel of product would be consistent with water requirements in CTL.

3.5 Estimated Economics for DCL Plants

It has been nearly twenty years since a detailed economic analysis was done for hydroliquefaction, and possibly much longer for solvent extraction or carbonization. A hydroliquefaction plant capital cost, for coal being converted to clean, specification-grade transportation fuels, is likely in the range of $120,000 per daily barrel of capacity. Estimated cost of the finished liquid products is $0.20 per gallon higher than from a CTL plant.

It should be noted that the estimated cost of $120,000 per daily barrel is about double of the claimed cost of the Shenhua plant ($62,500). The figure for the Shenhua plant was based on 2008 dollars; the world has seen significant increases in capital equipment prices since then. In addition, it is not clear what basis was used for conversion of yuan to US dollars. Therefore, this is not to say that one figure or the other is grossly in error, but they probably can be taken as “bookends” for the cost of a plant.