

Different Routes for Conversion of Coal into Liquids Comprehensive Study

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Abstract: Increased crude oil prices, will shift the importing countries into other sources of energy. The coal is now being considered by several countries, and although it can be transformed into several chemicals, its use in the production of "Transportation (Liquid) Fuels" in which 47.5% of crude is currently in use, is of prime importance. There are several processes developed for the coal conversion. These processes use either direct or indirect route to produce liquids. This paper will review all different processes available, their operating scheme, and commercial availability. The method used will be comparative analysis, using several scientific and industrial resources. The final conclusion serves as a guideline for industrial decision-makers.

Key Words: Coal to Liquid, DME, Fischer Tropsch Process, Methanol.

1. INTRODUCTION

Increased crude oil prices, will shift the importing countries into other sources of energy. The use of coal could be an appropriate choice, and although coal can be converted into several chemicals, its conversion into "Transportation (Liquid) Fuels" in which 47.5% of crude is currently in use, is of prime importance [1].

Since the coal liquefaction is capital-intensive as will be shown in the following sections, it benefits from the economics of scale. Although it is difficult to assess how much the scale-up can affect the project economics, most studies show that the coal liquefaction plants will be economically feasible, if a full-scale commercial plant would produce 50 000-100 000 bbl/day of liquid products. Such a plant would process 20 000-40 000 tons/day of bituminous coal (3-4 million tons oil equivalent (mtoe)/year).

On the other hand, as a general principle Coal to Liquid (CTL) Plants should be in the country of origin, or preferably at the point of origin. This reduces the feedstock cost, since coal is difficult to transport. Cheap workforce would also reduce the overall costs. In addition, there must be sufficient reserves for a project life time of 25-30 years.

Therefore the CTL projects should be implemented where there is at least 100 mtoe coal (150 Mt and minimum Reserves/Production (R/P) ratio of 25 [2].

This report will review different processes available for Coal-To-Liquid conversion, their operating scheme, and

commercial availability. The method used is comparative analysis, which is based on several scientific and industrial resources.

2. CONVERSION OF COAL TO LIQUIDS

To convert coal into liquids, hydrogen should be added or carbon should be removed, in order to increase the hydrogen content of the coal from 5 wt% (42 mol%) up to the hydrogen content of (gasoline or diesel) fuels which is in the range of 12.5-14.5 wt% (67-80 mol%) [2].

There are two main types of CTL processes:

- 1) Direct Coal Liquefaction (DCL) Processes
- 2) Indirect Coal Liquefaction (ICL) Processes

This section explains the operating scheme of these processes in detail, and their comparative characteristics.

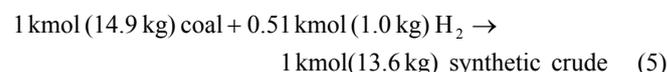
2.1. Direct Coal Liquefaction Processes

This process historically was believed to be the most thermally efficient one among all the CTL processes. CO₂ emissions were also assumed to be lower. These results are now under discussion; although most reliable resources mention this as a fact (as an example see [2]), some life-cycle analysis (from production step until the end-use of products) show almost the same thermal efficiency (of about 59%) [3].

The direct liquefaction in which the coal is first dissolved in high proportion in a solvent in high temperature (about 400°C) and pressure (about 275 bar), followed by the hydrocracking of the solution with H₂ and catalyst, is said to have 60-70% of thermal efficiency by reliable sources [2].

The products - being similar to partially-refined crude oil - can be used directly for stationary fuel applications. However, to be used as transportation fuels, an intensive upgrading is required, by using standard petroleum industry techniques. The products are sent to a nearby refinery and upgraded.

The approximate analytical formula for the coal is CH_{0.81}O_{0.08}S_{0.02}N_{0.01}. Therefore the approximate amount of H₂ required in this process can be found by using (1)-(5) [3].



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Table I Different DCL Processes [4]

Stage Processes				
Process name	Phase of Development	Operating Conditions		Distillate Yield*
Kohleoeel	Feasibility study for China in 1997	T = 470°C P = 300 bar $\tau = 2.1-2.7$ hr		50-60
NEDOL	Feasibility study for China in 1997	T = 430-465°C P = 150-200 bar $\tau = 1$ hr		50-55
H-Coal	Basis of CTSL process	T = 425-455°C P = 200 bar		50
Exxon Donor Solvent (EDS)	Abandoned	T = 425-450°C P = 175 bar		36-46
SRC-I and II	Abandoned			
Imhausen high-pressure	Abandoned	T = 470-505°C P = 600-1000bar		
Conoco Zinc Chloride	Abandoned			
Two-stage Processes				
Catalytic Two-Stage Liquefaction (CTSL)	License for 1st China CTL Project	1 st Stage	T = 400-410°C P = 170 bar	65
		2 nd Stage	T = 430-440°C P = 170 bar	
Liquid Solvent Extraction (LSE)	No more development	1 st Stage	T = 410-440°C P = 10-20 bar $\tau = 50$ min	60-65
		2 nd Stage	T = 400-440°C P = 200 bar $\tau = 1.3$ hr	
Brown Coal Liquefaction (BCL)	No more development			52
Consol Synthetic Fuel (CSF)	Abandoned			
Lummus ITSL	Abandoned			
Chevron Coal Liquefaction (CCLP)	Abandoned			
Kerr-McGee ITSL	Abandoned			
Mitsubishi Solvolysis	Abandoned			
Pyrosol	Abandoned			
Amoco CC-TSL	Abandoned			
Supercritical Gas Extraction (SGE)	Abandoned			

*On Dry Ash Free (daf) Basis

There are generally two types of direct processes: single-stage, and two-stage processes.

The general characteristics of different ICL processes are given in table I.

One of the advantage of DCL processes over ICL ones is that they can co-process coal and petroleum coke (petcoke) or biomass at the same time. This could be economically interesting, because of the increase in the plant throughput.

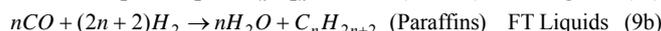
2.2. Indirect Coal Liquefaction Processes

These processes convert the coal into liquids in two steps:

1) Coal conversion into synthesis gas (syngas) by gasification, followed by water-gas shift (WGS) reaction that adjusts the H₂:CO ratio, to meet the requirements of synthesis reactor:



2) Conversion of syngas (after the acid gas removal) into liquids which are typically methanol, dimethyl ether (DME), or Fischer Tropsch liquids (gasoline, diesel, and chemicals). The optimum H₂:CO ratio required for the synthesis of both methanol, and Fischer Tropsch (FT) liquids is 2:1, whereas the ratio of 1:1 is recommended for DME direct synthesis according to the stoichiometric ratios.



Sasol, Shell, and ExxonMobil are the major companies developing the ICL processes.

In this section a brief overview of the indirect processes is given, followed by a detailed study of methanol and DME synthesis.

2.2.1. Sasol Process

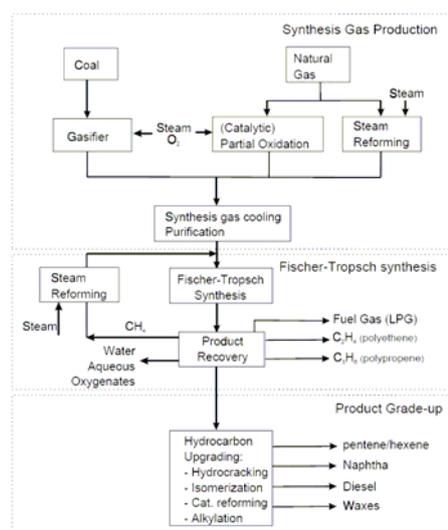


Figure 1 The Sasol Process [5]

The Sasol process converts coal into FT liquids, so that over 33% of South Africa fuel consumption (8 billion liter/year) and a large portion of chemicals production (2 billion liter/year) are produced by the three Sasol plants, which consume 45 Mt of coal at Sasol I, II, III plants [6].

The incoming coal is wet-screened and goes to the Lurgi gasifier after clean-up at Lurgi Rectisol using cold methanol as a physical absorbent. The clean syngas is then directly sent into FT reactor.

Sasol uses two types of reactor:

- Low-Temperature Fischer Tropsch (LTFT)
- High-Temperature Fischer Tropsch (HTFT)

The LTFT reactor operates at 220-250°C and 20-30 bar with either a Co-based (Co-LTFT) or Fe-based (Fe-LTFT) catalyst, and produces paraffins and waxes ("distillate" cut with carbon number, n = 12-19) [2].

The HTFT reactor operates at 330-350°C and 20-30 bar with a Fe-based (Fe-HTFT) catalyst, and produces a

lighter, more olefinic product slate including gasoline, petrochemicals, and oxygenated chemicals ("naphtha" cut with n = 5-10) [2].

Development has emphasized making synthetic diesel (i.e. LTFT Process), because the raw "distillate" product is an excellent diesel fuel (Cetane Number, CN = 70-75, aromatic content < 4 wt%), whereas the raw "naphtha" cut (HTFT Process) requires substantial subsequent refining (olefinic content ≈ 24 wt%).

Table II shows detailed characteristics of the products made in Sasol process.

Table II Product Compositions of Sasol Process (wt%) [7]

Product	LTFT Synthesis	HTFT Synthesis
CH ₄	7	4
C ₂₋₄ Olefins	24	4
C ₂₋₄ Paraffins	6	4
Gasoline (C ₅ -C ₁₀)	36	18
Distillate (C ₁₂ -C ₁₉)	12	19
Oils and Waxes (C ₃₅ -C ₁₂₀)	9	48
Oxygenates	6	3

2.2.2. The Mobil MTG Process [8]

The process produces quite pure stream of high quality motor gasoline (RON = 92.0-92.5, aromatic content = 26.5%, S = 0 ppm) from either coal or natural gas in three main steps:

- 1) Syngas Production (gasifier or reformer)
- 2) Methanol Synthesis
- 3) Gasoline Synthesis

The process has been commercialized by a 14 500 bbl/day plant in New Zealand, with the second plant (25 000 bbl/day) being build. The most significant feature of MTG process is that the high quality of the effluents produced, eliminates substantial need for further downstream treatment.

Table III shows the composition of different products in the MTG effluent.

Table III MTG Product Composition [8]

Product	Composition (wt%)
Fuel Gas	1.1
LPG	10
Naphtha	88.8
Distillate	-
Oils and Waxes	-
Oxygenates	0.1

2.2.3. SMDS Process

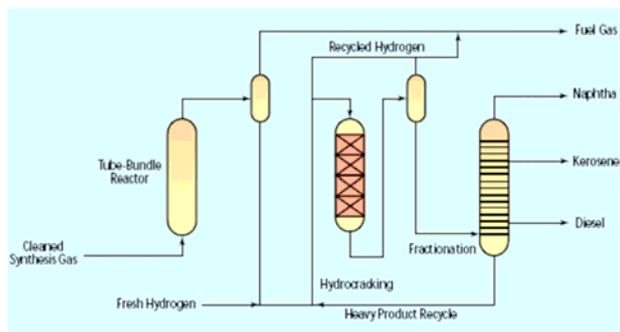


Figure 2 SMDS Process [2]

The Shell Middle Distillate Synthesis Process is based on the syngas produced via methane, but applicable for coal-based syngas after acid gas removal as well. The process is a LTFT process which benefits from lower energy input, complexity and cost; and produces downstream products with higher quality compared to the HTFT process.

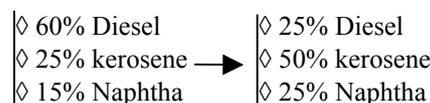
Natural gas is first partially oxidized in an oxygen-blown Shell gasifier to produce syngas. This gasification approach is preferred over steam reforming, despite the considerably higher capital cost and lower thermal efficiency, because it produces syngas with the correct H₂:CO ratio of 2:1. Steam reforming produces excess H₂, which in a stand-alone operation can only be used as fuel.

The clean syngas is then reacted in a fixed-bed tube-bundle reactor that is cooled in boiling water. The product is almost exclusively paraffinic. The catalyst formulation and operating conditions in this step are deliberately chosen to give a much higher-boiling range for products than usual, since this minimizes the production of hydrocarbon gases. The catalyst is typically a Co-based catalyst.

In the final step, the waxy heavy paraffin is catalytically hydrogenated, isomerizes and hydrocracked in a single trickle-bed reactor to give products that are mainly middle distillates.

A high degree of product recycle is used to minimize the production of light products.

By varying the hydrocracking severity and the extent of recycle, the product distribution can be adjusted:



2.2.4. Methanol and DME Synthesis [3]

Methanol as a substitute for gasoline, and especially a blend of MeOH/gasoline (85-90% MeOH/15-10% gasoline, M85 or M90) is recommended by several researches as a compromise of price/performance.

DME is also a potential substitute for transportation fuel (diesel), or cooking fuel (LPG). DME is gaseous at normal conditions (25°C, 1 atm) but could be easily liquefied by mildly pressurized canisters.

In addition, there is currently a trend towards using MeOH and DME as a feedstock for petrochemical plants as a substitute for naphtha. Currently Mobil MTG process uses DME to produce gasoline, and UOP/HYDRO MTO (Methanol To Olefins) and Lurgi MTP (Methanol To Propylene) processes convert MeOH to light olefins (ethylene and propylene).

The processes used for DME, MeOH (and even FT liquids) synthesis are either *ONCE-THROUGH CONFIGURATION* or *RECYCLE CONFIGURATION*. The difference is that in first case the only output from the facility is a liquid fuel. In the second case, electricity is a major co-product. The two configurations are essentially identical through the first few process steps.

The operating principle of DME and MeOH Synthesis is

described in this section.

Coal Gasification

The coal is fed into the gasifier either in a dry form or in a water slurry form, depending on the type of gasifier used. The slurry gasifier has two important advantages: Feeding can be done at high pressures (about 40-60 bar), which provides cost benefits, and the additional hydrogen (in the slurry water) promotes a larger H₂ fraction in the syngas. However, the oxygen required by slurry-feed gasifier is higher than that of dry-feed gasifier. The final selection therefore is a compromise.

WGS Reaction

Following gasification, the raw syngas is cooled and cleaned of contaminants. A water-gas shift (WGS) reactor is incorporated after the initial cooling to adjust the ratio of H₂:CO. Sulfur-tolerant water-gas shift catalysts are available (e.g., a CoMo catalyst made by Haldor Topsoe), so that sulfur removal can be done after the shift.

Syngas Purification

Low sulfur levels are required to guarantee long catalyst life. The final sulfur content depends on catalyst type; it should be less than 1 ppmv for Co-based catalyst, whereas higher values are still acceptable for Fe-based catalyst. Several technologies are commercially available that can achieve such levels, including physical absorption into organic fluids (e.g. Selexol® [UOP] or Rectisol® [Lurgi, Linde]) and chemical reaction of amines with the sulfur compounds.

Since the syngas is available at elevated pressure (> 60 bar), physical absorption is preferred. The captured H₂S is typically converted to elemental sulfur using the Claus process, with tail gas clean-up in a SCOT plant

Selexol solvent absorbs CO₂ in addition to H₂S. The CO₂ may be vented or captured for sale as a by-product. The idea of co-capture and co-storage of H₂S and CO₂ has also been proposed. This would have significant cost advantages for coping with sulfur, since no Claus/SCOT plant would be needed to convert the H₂S into elemental sulfur, and separate systems for desorbing H₂S and CO₂ from the Selexol solvent would not be needed.

MeOH/DME Synthesis

The gas is preheated (to about 260 °C) before feeding into the reactor. In a single pass of gas through the reactor, only a portion of the CO and H₂ will be converted into desired fuel. After synthesis, purification of the raw synthesized product by flash tanks/distillation steps produces the final fuel.

Although DME was historically produced via MeOH, there is trend toward direct DME synthesis, with JFE as a pioneer. The operating scheme of JFE process is described in [12]. A pilot plant (in which Total is a partner) was built in Shiranuka-cho, Hokkaido, and produced 100 ton/day of DME in 2004.

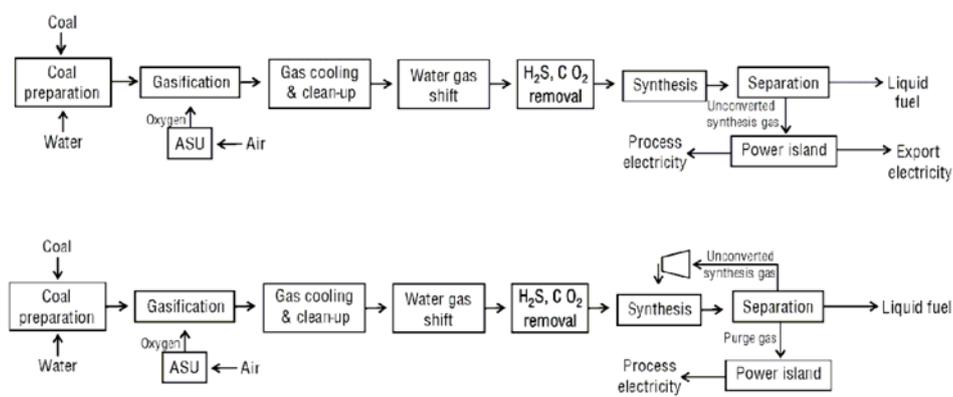


Figure 3 Different Configurations for DME/MeOH Synthesis [3]

Power Co-Production

In “once-through” configuration (Fig. 3, upper), the unconverted gas is used as fuel for a gas turbine. The hot exhaust of the turbine is used, to raise steam to drive a steam turbine. The power generated by the gas turbine/steam turbine combined cycle is sufficient to provide the power needed to operate the plant, plus a significant amount of power for export to the grid.

In “recycle” configuration (Fig. 3, lower), most of the unconverted gas is returned to the synthesis reactor to generate additional liquid fuel. The remainder of the unconverted gas fuels a power cycle making only enough power to meet the process needs.

3. CONCLUSION: COMPARATIVE ANALYSIS OF ICL AND DCL PROCESSES

Commercial Feasibility

The ICL Processes have been commercialized by the Sasol CTL and Shell GTL Plants, whereas the DCL processes are scaled up to Process Development Units (PDUs) or Pilot Plants. The first commercial DCL is being built by China Shenhua Liquefaction Corporation using the ebulliated reactors. The first train is being started with a capacity of 20 000 bbl/day upgraded distillates (naphtha, jet fuel, and diesel) in 2008 with a scheduled extension up to 50 - 60 000 bbl/day. The technology has been industrially proven with the Catletsburgh demo plant in US in the 80's [12].

Product Quality

The DCL processes produce semi-refined crude oil, which requires more intensive upgrading than the ICL products. This increases the cost and complexity. In addition, the upgraded DCL products are still highly aromatic with low cetane number of about 30 compared to typical values of 40-55 for crude-derived diesel.

The ICL processes on the other hand produce better products, especially with LTFT process making paraffinic distillates (with < 4% aromatic content) and high cetane number of about 70.

However it should be kept in mind that although the DCL products require severe upgrading, the product yield is typically higher than the ICL processes.

The upgraded products obtained by both processes have low (<1 ppm) sulfur content.

Energy Consumption and Thermal Efficiency

The DCL processes are carried out at about 400°C and 150-300 bar. The hydrogen compression introduces high investment cost and the effluent upgrading requires high energy consumption¹. This energy could not be recovered easily.

The ICL processes are carried out in three steps: gasification, syngas purification and synthesis. The gasifier operates at 1400-1600°C and 40-60 bar. This requires high energy input, but part the heat input could be recovered by HP steam production.

The synthesis reactors operate at 200-350°C and 20-30 bar. The heat input could be easily recovered to produce either MP steam/electricity as a co-product, or to preheat the clean syngas.

As said before, the exact value of thermal efficiency for both processes is now under some uncertainties. According to industrial resources, the ICL process is said to have slightly lower efficiency (55-60%) than DCL process (65-70%) [2].

Water Consumption

Since the CTL projects are mainly implemented in water-scarce locations, the water consumption should be kept as low as possible. There are three major requirements for water: process water, boiler feed water, and cooling water. Cooling water loss is often the most significant factor.

The ICL processes are considered to have low water consumption. Assuming a yield of 2 barrels of product per ton of sub-bituminous coal, the water use could vary from 1-1.5 bbl/bbl of product for a zero-discharge air-cooled plant to 5-7 bbl/bbl of product for a plant with water cooling and less use of waste heat for process heat or cogeneration as indicated in [9]. However, the results given here, are for theoretical studies, and the actual water usage in water-cooled plants are about 15-20 bbl/bbl of product.

The use of DCL technologies requires more water consumption. According to Headwaters Inc., the water usage for a HTI process is 19 bbl/bbl of product for a 40

000 bbl/day of liquid products [9].

Carbon Emissions

Both processes have higher emissions (2-8 times more) than a crude-refining process if no CO₂ capture/storage is implemented. This is due to high carbon content of the coal.

However, there is room for substantial reduction by CO₂ capture/storage, especially for ICL processes. This is due to the fact that in all ICL configurations, some CO₂ should be removed (together with H₂S) from the syngas before the synthesis reactor, and thus a relatively pure stream of CO₂ is available at ICL facilities.

The CO₂ captured could be used in three main cases [3]:

1) Injection into deep beds of unmineable coal beds and to enhance coal-bed methane recovery. This application is not of economic interest at current situations.

2) Injection into depleted oil reserves as a mean for Enhanced Oil Recovery (EOR).

3) Injection into deep saline aquifers for storage purposes.

There are about 74 EOR projects worldwide, mostly (66) in the United States, where in 2000 oil production via EOR reached 216 000 bbl/day (4 % of total US oil production), a by-product of which is the sequestration of 30 Mt of CO₂ annually. Most of the injected CO₂ comes from natural reservoirs of CO₂, but 5 Mt/year comes from anthropogenic waste CO₂ sources.

Therefore the only large potential remaining is for storage in deep saline aquifers, for which there are no enhanced resource recovery opportunities. The total area of these aquifers amounts to 70 million km² worldwide, leading to a capacity to store 2 700-13 000 GtC. For comparison, estimated remaining recoverable fossil fuel resources (excluding methane hydrates) contain 6 000-7 000 GtC.

This potential is now in the research phase, with several pilot projects like Statoil Aquifer Project (Utsira Formation) which injects CO₂ to an aquifer under the North Sea (Sleipner West). The injection has been done continuously from 1996 and seems to be secure.

However, there still are some technical issues for this type of injection including the insufficient strength of geological structure of the aquifers to store high pressure CO₂. Therefore, several demonstration operations will be required until 2014 to validate the potential, and a commercial use is expected for 2020.

Economic Considerations

Both types of processes require high investment and operating costs. Syngas generation spends about 60- 70% of the total capital investment.

As an order of magnitude, the EPC costs for the synthesis of 10 200 bbl/day of FT liquids and 104 MW of electricity with Rentech ICL once-through process will be about 740 million USD (with a product cost of 41.98 \$/bbl). Such a unit will process 7 650 ton/day of bituminous coal, and requires 48 million USD/year of OPEX [10].

The CAPEX required for the Shenhua DCL plant is also over 2 200 Million USD. This plant is designed to process

¹ Primary energy consumption required for heat and power at US refineries amounted to 13.3% of the heating value of total inputs to the refineries in 1994 [3].

12 800 ton/day coal to produce 50 000 bbl/day of liquid fuels (with a product cost of 40\$/bbl) [11].

However, the economical values mentioned should be handled carefully and be considered as a rough estimate, especially due to the dramatical increase in the equipment cost since 2003-2004. The other factors such as the date in which the cost has been mentioned, should also be taken into consideration if any decision is going to be made.

In addition, it should be considered that the cost reduction can be done by integration with the nearby refineries for further refining of DCL products or export of excess electricity to power network for ICL processes. The overall economics of the project can also become more interesting by scaling up the projects for both cases, or by modular designs of ICL processes.

Other Factors

Although several factors are discussed in this paper in a comparative way for both ICL and DCL processes, the final selection is not usually so easy. It is a matter of specific study for each case, and several factors including the geographical location of plant, product market and specifications, CO₂ regulation, price and availability of feedstock including feedstock to make hydrogen, etc. should be considered.

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