2.2 Direct Liquefaction

Unlike the complete destruction of the coal molecule that takes place in indirect liquefaction, direct liquefaction hydrocracks the coal molecule into suitably small hydrocarbon molecules. Although each process described in this section has its own special features, there are certain features that are common to all the processes. The processes that are being considered today are derived either from the I. G. Farben process of Bergius and Pier or from that of Pott and Broche. Bergius, who obtained the early patents, did so in 1913.

Direct liquefaction processes start with finely divided coal and slurry it with a process-derived liquid. In moving the slurry to the dissolver (reactor) the temperature is increased to about 430°C (800°F) and the pressure to at least 13 MPa (1900 psi). After the coal has been hydrogenated either with the direct injection of hydrogen or the use of a hydrogen donor solvent, the pressure and temperature are reduced. Gases are removed from the product stream and processed into hydrogen, which is recycled, sour gases from which sulfur is recovered, and hydrocarbon gases which can be sold as SNG. The solid material is separated from the liquids distillation, by filtration or deashing techniques and recovered either by gasification or coking. The liquid stream is refined into salable products. Most process configurations have a gasifier to provide a source of makeup hydrogen.

This part of the report deals with the specifics of British and German liquefaction processes for which there is enough information available to give a reasonably detailed description. All of these processes are at the pilot plant stage. As yet there is no foreign commercial direct liquefaction project although there were a number of these facilities in Germany before and during World War II. Some coal liquefaction plants were also operated after WWII. Present indications are that there will not be any of these direct liquefaction facilities built until near the end of this decade or into the 1990's.

2.2.1 Liquid solvent extraction

The Liquid Solvent Extraction (LSE) process, similar in concept to the Solvent Refined Coal (SRC) process, utilizes derived solvent to dissolve the coal at high temperature and moderate pressure. The solvent acts as a mild hydrogen donor. The coal extract is freed from ash and mineral matter by filtration. In a second stage the extract is hydrogenated and cracked to produce clean liquid fuels. The process produces aromatic products as opposed to Fischer-Tropsch synthesis which produces aliphatic materials.

2.2.1.1 History and Status

Development of the Liquid Solvent Extraction (LSE) process has followed some years of work at the Coal Research Establishment (CRE), Stoke Orchard, near Cheltenham, on the extraction of coal by solution in liquid solvents. In the mid-60's, British Coal Utilization Research Laboratories of the National Coal Board worked on extraction of coal with anthracene oil and other tar oils to produce carbon products and electrode coke. A plant with a throughput of 30 kg/h (66 lb/hr) of coal was constructed at the Coal Research Establishment in the early 1970's to make electrode cokes suitable for making into electrodes both for steel-making and aluminum smelting furnaces. The National Coal Board has plans to build a 25 t/day of coal pilot plant which will be the subject of trials over seven-years. Cost of the plant was estimated at $30 million in 1978. The plant is being designed by Matthew Hall Ortech, Ltd. and NCB may tender the construction by year end. The plant would be built at Point of Ayr, North Wales and would be commissioned later than the originally planned mid-1982. Support is now being sought to build a demonstration plant, to be operating before the end of 1980's.[10,11,12,13]

2.2.1.2 Organization Experience

Britain's energy industry is state-controlled and largely state-owned. The National Coal Board (NCB) is the principal developer of synthetic liquid fuels processes. The organization has 20 years of experience in solvent extraction of coal. In the early 1970's, an experimental facility processing 30 kg/h (66 lb/hr) of coal was built at the Coal Research Establishment. The hydrocracking stage relies on petroleum industry techniques and was designed and built at the BP Research Centre under contract to the NCB.[11,12]

2.2.1.3 Plant Location

Experimental facilities are located at CRE, Stoke Orchard near Cheltenham. The 25 t/day pilot plant is to be constructed at Point of Ayr in North Wales.[13]

2.2.1.4 Liquid Solvent Extraction Process Flow Diagram[11,12,13]

The proposed Liquid Solvent Extraction process flow diagrams for the pilot plant are given in Figures 2.4 and 2.5. The process starts with ground coal dissolved initially in anthracene oil but subsequently in the heavy oil fraction delivered by the process. The coal will be dried to the minimum moisture content necessary for pulverizing. The pulverizer will usually provide a feed material of nominally less than 0.2 mm (0.01 in), although it is intended to occasionally attempt to operate with a top size up to 1 mm (0.04 in). Bituminous non-coking coals (middle to low ranking coals) are used because they are in most abundance in Britain. According to CRE, there is no real advantage in using higher quality coals. About 3.5 tons of solvent is used for every ton of coal input.

The coal slurry is initially heated by heat exchange with the hot effluent leaving the digester at 420°C (790°F) and then in a fired preheater. From there it is fed to a digesting reactor. Since no hydrogen is added in the reactor directly, a pressure of about 1.0 MPa (145 psi) is enough to ensure only a small amount of vaporization. This gives a considerable saving in equipment capital cost besides facilitating access, maintenance, and control. Under optimum conditions, extraction levels up to 95% coal material have been achieved.

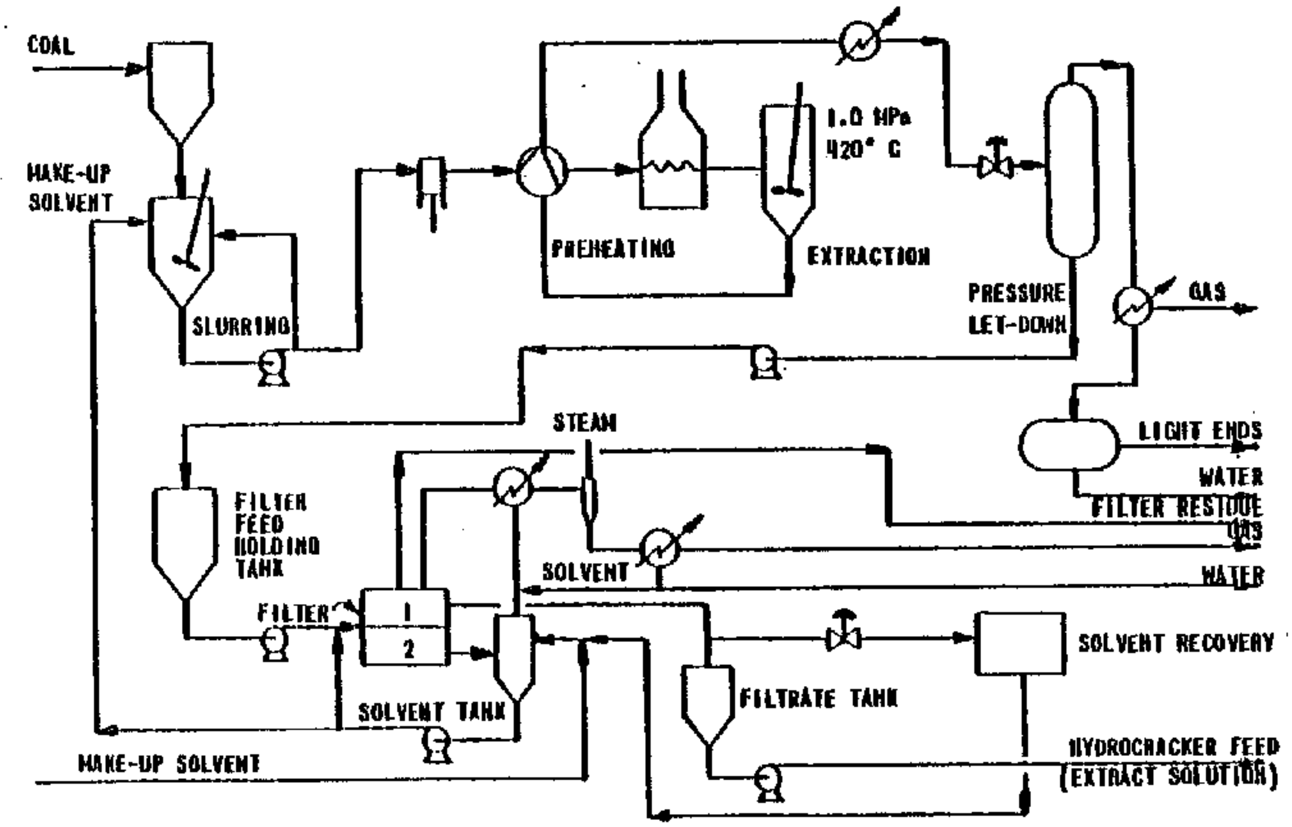

Figure 2.4.
LIQUID SOLVENT EXTRACTION PROCESS

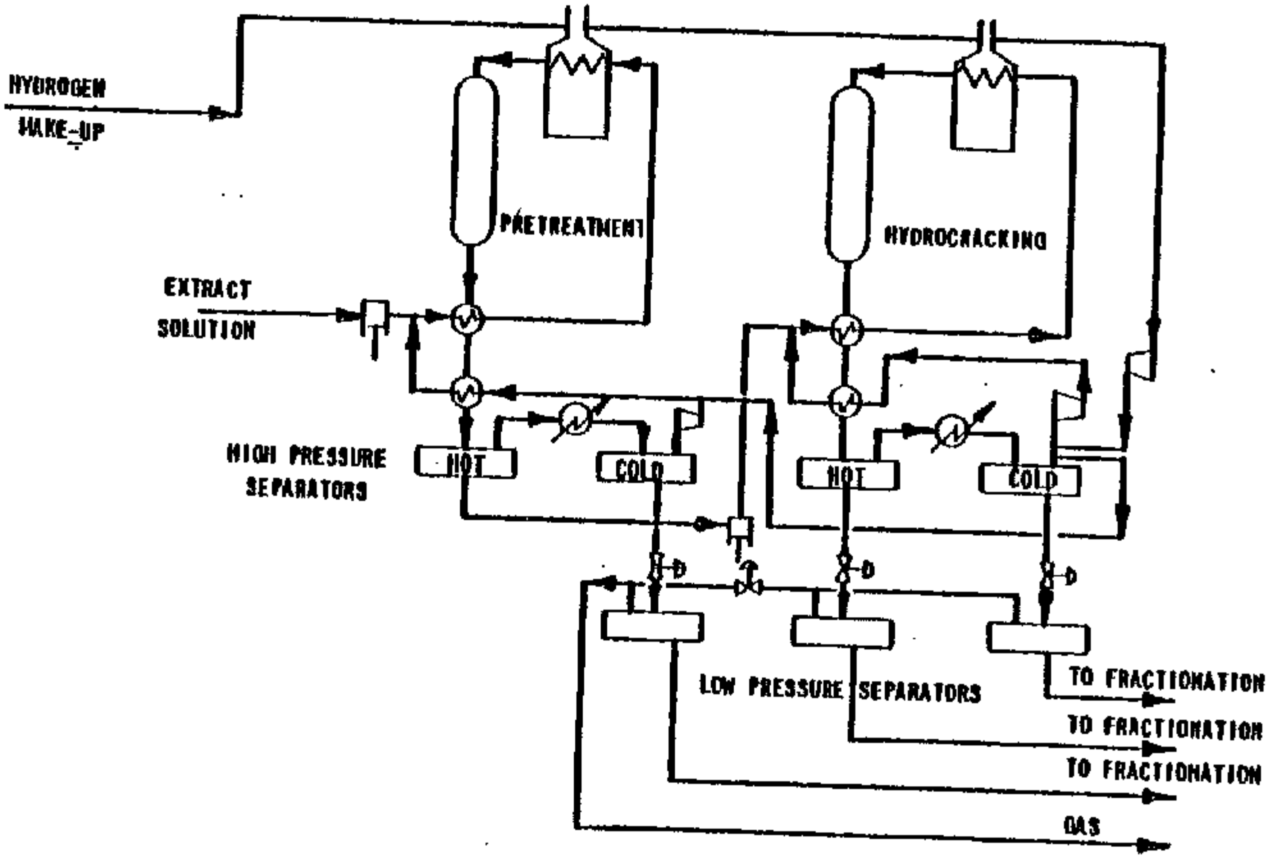

Figure 2.5.
HYDROGENATION UNIT FOR LIQUID SOLVENT EXTRACTION PROCESS

The gases, liquids and residual solids leave the extraction vessels and are cooled in the slurry-digester heat exchanger and then let down to lower pressure. A trim cooler is used to control the temperature of the slurry passing to filtration.

Light liquids and gases produced in the digester are removed overhead in a flash vessel. The overhead stream passes to a vent condenser in which the C_5 - 250°C (480°F) fraction and water are condensed and then separated in a liquid-liquid separator. Slurry from the flash vessel passes to a holding tank. From the holding tank the slurry is presently charged batch-wise into a filter. The filtrate is passed to coal solution storage.

As illustrated in the flowsheet (Figure 2.4), the coal extract solution must be pressurized to greater than 20 MPa (2900 psi) and preheated to 400-450°C (750-840°F) before passing to hydrocracking. Interchangers and a furnace heat the coal solution to reaction temperature.

Recycled impure hydrogen is added to the coal solution on the delivery side of the high pressure pump, resulting in two-phase flow through one of the heat exchangers and the furnace. Hydrogen (make-up) supply would be either by on-site steam reforming of natural gas or may be bought from a hydrogen supplier.

It is intended to recycle the hydrogen stream directly after separating liquids and scrubbing out some heteroatom compounds (i.e., principally compounds of sulfur, nitrogen and chlorine). A facility is provided for purging a proportion of this recycle stream should the hydrogen purity be too low to maintain conversions in the hydrocracker or result in carbon deposition on the hydrocracking catalyst.

Where the pretreatment reactors are used for reduction of heteroatoms in the feedstock, the purge from the main reactor will supply the hydrogen.

The coal solution and hydrogen mixture leaving the hydrocracker furnace at 400-450°C (750-840°F) is passed through a guard catalyst which removes catalyst poisons from the feedstock. It is envisaged that there will be two or more of these units operating in parallel so that they can be operated sequentially while the main hydrocrackers are kept on line.

The main reactors will be conventional trickle bed reactors. A number of catalyst beds will be required in order to limit the temperature rise to a maximum of 25°C (45°F) per bed. Inter-bed cooling is achieved by the injection of recycle hydrogen. Catalyst regeneration and pre-sulfurization facilities will be included.

Materials leaving the hydrocracker are cooled by heat exchange with the hydrocarbon feed and hydrogen and passed to the high pressure separator. The gas stream from this separator will be mostly hydrogen but contains some methane and heteroatom gases. Most of the higher molecular weight hydrocarbon gases produced in the hydrocracker remain in solution at this pressure. After scrubbing to remove heteroatoms, the pressure of the hydrogen rich gas stream is boosted and it is recycled to the hydrocracker.

The plant fractionation system treats the liquid products of hydrocracking, the C_5-250°C (480°F) material produced in the digester, and the liquids and gases produced in the coker when present.

The principal cut points will nominally be as follows:

i) gases
ii) C_5-173°C (345°F)
iii) 173-250°C (345-480°F)
iv) 250+ °C (480°F)

Cuts (ii) and (iii) are the 'product' fractions and the 250+ °C (480+ °F) fraction is used as recycle solvent. Alternatively, a 370+ °C (700+ °F) fraction is produced and a bleed stream is fed to a thermal cracker to produce a premium coke.

In order to achieve the required cuts it is necessary to have a vacuum column as well as the equivalent of a normal atmospheric pressure crude fractionation unit. A separate column is included for fractionation of the products from the coker when it is in use. The overall block diagram and material balance are shown in Figure 2. 6.

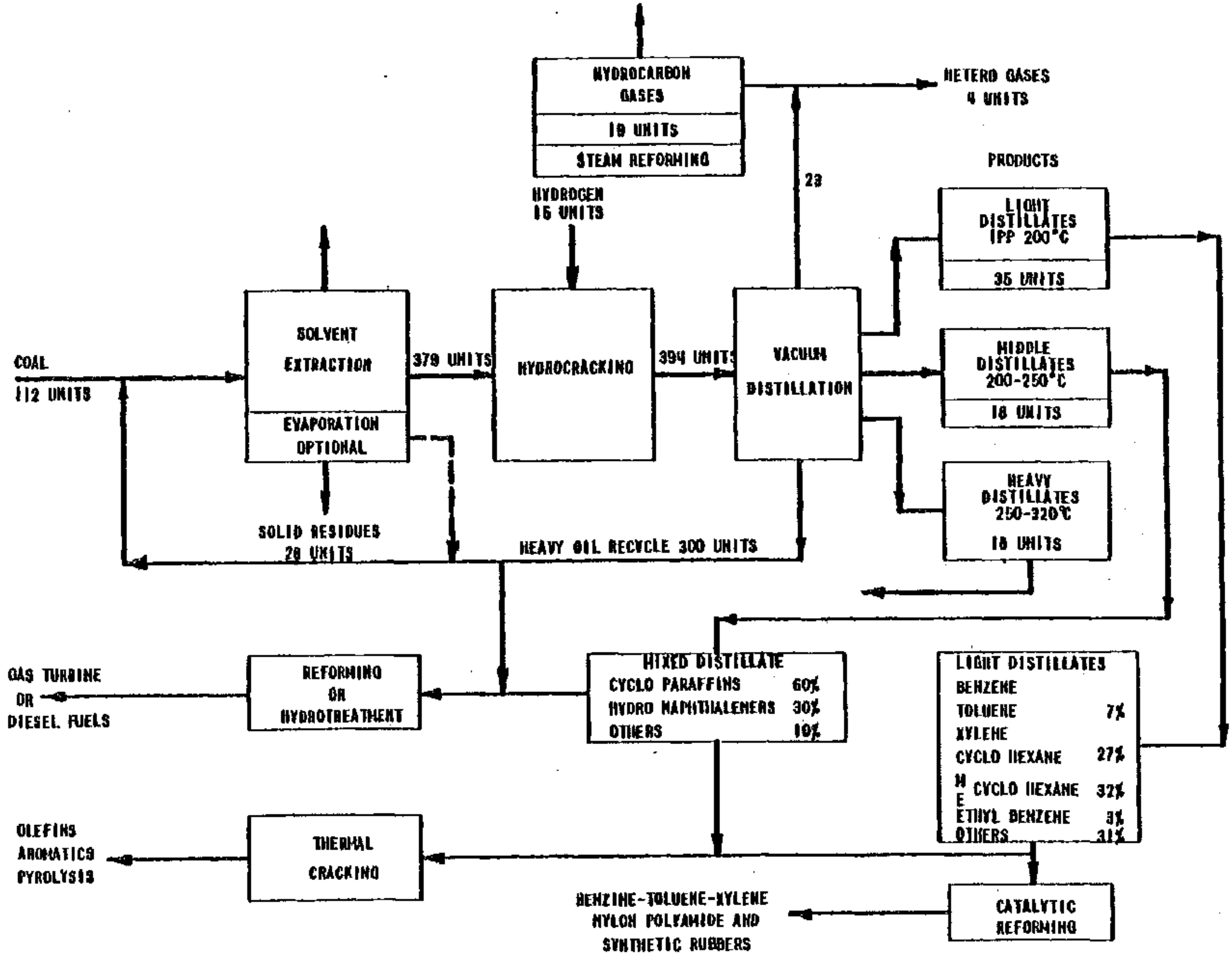

Figure 2.6.

OVERALL FLOW DIAGRAM AND MATERIAL BALANCE FOR LIQUID SOLVENT EXTRACTION PROCESS

2.2.1.5 Equipment Design of Pilot Plant with Key Problems and Points of Emphasis for Development

Two major areas of critical importance for the process to be technically and economically acceptable are solid/liquid separation and catalytic hydrocracking. Problems and improvements related to these areas are discussed below:

Filtration

- Fundamental and pilot plant investigations since 1976 have enabled the NCB to optimize digestion conditions to give fast filtration rates that should make filtration viable on a large scale. Knowledge of this technology could substantially benefit U.S. coal liquefaction development.

- Recent developments in hot filtration of coal are leading to new filters specially designed for this application. Although these filters are expensive, the overall filtration cost is only about 10% of the total processing cost. Further improvements will lead to lower capital costs.[10,14]

Although optimistic that the process could be made commercial, several requirements need to be fulfilled. These are that high yields are obtainable from lower grade coals, hot filtration could be used on a large scale, a long-life catalyst can be developed and that the product proves suitable for use in existing petroleum markets in sufficient quantities and at a price that will ensure continuity of the market.

The coals tested so far have given yields of 83-92 percent dry mineral matter free (dmmf). Some of the product, however, is gaseous, giving actual liquid yields of 82-89 percent dmmf. An actual conversion of 64 percent was obtained for lignite.[EI]

Hot filtration was chosen by the NCB in preference to assisted settling, used by Lummus and Kerr-McGee, and distillation, used in the Exxon Donor Solvent and SRC-II processes, because of the low ash content in the extract solution. The method has been used successfully in a 500 kg/day (1100 lb/day) electrode coke process, where it has regularly achieved an ash content of less than 0.1 percent.

The NCB is in the process of testing prototype designs of continuous filters in the 30 kg/h (66 lb/hr) plant, and is considering designs of filters of 25 t/d pilot plant.

Catalytic Hydrocracking

Kinetic studies using a stirred autoclave system with powdered catalysts have shown that it is possible to increase the amount of coal conversion by the choice of catalyst and by extending the hydrocracking residence time. The NCB has examined 50 catalysts at CRE and more are being studied to find a catalyst with a longer life. Two alternatives are being considered, one by seeking a resistant catalyst and the second by designing the system to remove deactivating agents in the extract before they meet the catalyst.[13]

2.2.2 Supercritical gas extraction

The Supercritical Gas Extraction (SGE) process uses a supercritical organic solvent which extracts the hydrogen-rich, more volatile parts of the coal, leaving a reactive char. In an integrated plant, the char can provide the necessary hydrogen, heat and power for the process. In a second stage, the coal extract is hydrogenated and cracked for producing transport fuels and chemical feedstocks.

2.2.2.1 History and Status

The technique of supercritical gas extraction is based on the ability of substances to vaporize more freely in the presence of compressed gas. The solvent power of a gas increases with its density and the greatest density for a given pressure will be obtained at its critical temperature. The extracting gas chosen is therefore one which has a critical temperature not much below the temperature at which the extraction is to be carried out. This technique was applied to the deasphalting of petroleum fractions even before 1950. In the mid-1960's, tentative experiments were being carried out at the National Coal Board's Coal Research Establishment at Stoke Orchard for the extraction of liquids formed when coal is heated to about 400°C (750°F). These liquids will not distill to any great extent at this temperature, and are not stable at higher temperatures. Gas extraction affords a means of recovering the liquids as they are formed at lower temperature, and thus avoids unnecessary degradation. Toluene has been used in most tests so far as the extracting gas, but the CRE has also tried other gases, including steam.

The SGE process is at present being studied in a pilot plant with a throughput of up to 100 kg/day (220 lb/day). This plant was completed in the late summer of 1977 and is designed to withstand pressures up to 40 MPa (5800 psi) and temperatures up to 500°C (930°F).

The supercritical gas extraction process has been successfully tested in this pilot plant. The coal is initially pulverized, slurried with a light organic solvent such as toluene and pumped through a preheater under a pressure of 1-200 bar (1500-3000 psi). It passes into an extraction vessel, where it forms a fluidized bed and is converted to char by removal of the extract liquids. The char is separated from the solvent and collected in a receiver. The NCB is working on a continuous method to do this to improve the process.

In both cases the product is a mixure of undistillable extract and solvent oil, which can then be hydrocracked. The light product of this has been tested for suitability as a feedstock for both steam cracking and catalytic reforming. The results obtained are shown in Tables 2.8 and 2.9. Although the olefin yield from coal oil naphtha was lower than from petroleum fractions, the yield of byproduct aromatics was considerably higher. Middle distillate cracking performance was poor, but consistent with the high aromatic content. The NCB has been working on secondary catalytic hydrotreatments to improve the cracking pattern.[EJ]

Table 2.8. Catalytic reforming of coal oil naphtha[EJ]

Reformer temperature	480°C (896°F)	510°C (950°F)
Yield (wt % of feed)		
Hydrogen	3.0	3.5
Hydrocarbon gases	1.2	1.7
Benzene	22.3	22.9
Toluene	28.2	28.9
Xylene	11.6	12.0
Ethyl benzene	11.7	14.6
Higher aromatics	4.4	4.6
Total aromatics	81.2	83.0
Non-aromatics	14.6	11.8
Calculated research octane number of reformate	108	108

Table 2.9. Results of cracking tests carried out at 820°C (1508°F)[EJ]

	Coal oil naphtha	Coal oil middle distillate	Petroleum naphtha	Petroleum kerosene
Methane	10.2	7.3	13.9	11.7
Ethylene	16.9	9.0	23.4	25.0
Ethane	2.4	1.6	3.3	2.2
Propyene	7.9	3.2	13.2	10.8
Propane	0.3	0.2	0.5	0.3
Butylene/butane	2.1	0.5	3.5	1.9
Butadiene	5.6	1.3	3.6	3.8
Benzene	14.4	8.0	8.1	7.6
Toluene	13.7	6.2	5.7	3.9
m-&p-xylene	2.1	1.7	1.9	0.2
o-xylene	0.9	0.8	0.8	0.9
Ethylbenzene	2.3	0.6	0.5	0.3

European Chemical News, October 1, 1979, V.33#906, p. 22.

ICI's catalytic reforming processes were carried out with a commercial platinum/aluminum oxide catalyst. Very high yields of BTX products were obtained. The liquid reformate has a research octane number of 108, making it very suitable for use as a gasoline blender.

Based on the results obtained from this plant, a 25 t/day pilot plant is being designed by Matthew Hall Ortech, Ltd., and the NCB expects to commission the pilot plant by mid-1982 at Point of Ayr in North Wales. Cost of the plant was estimated at $30 million in 1978. The European Economic Community will provide partial funding for the supercritical gas solvent plant.[10,12,13,15,16] The current status of this project is not known.

2.2.2.2. Organization Experience

The NCB is the principal developer of synthetic liquid fuels processes. This organization has performed bench scale experiments on gas extraction for about 15 years.[15]

2.2.2.3 Plant Location

The 100 kg/day (220 lb/day) experimental facility is located at CRE, Stoke Orchard, near Cheltenham. The 25 t/day pilot plant is to be located at the Point of Ayr in North Wales.[13]

2.2.2.4 Supercritical Gas Extraction Process Flow Diagram[11,12,13,16]

Simple flow schematics are given in Figures 2.7 and 2.8 for the extraction and hydrocracking sections of the process respectively. Coal preparation and product fractionation are not shown, being entirely conventional equipment.

Coal will be delivered to the site by road from the washery. The storage capacity of this uncrushed coal on the ground will be 600 tonnes (660 tons) of maf coal [about 750 tonnes (825 tons) as-received.

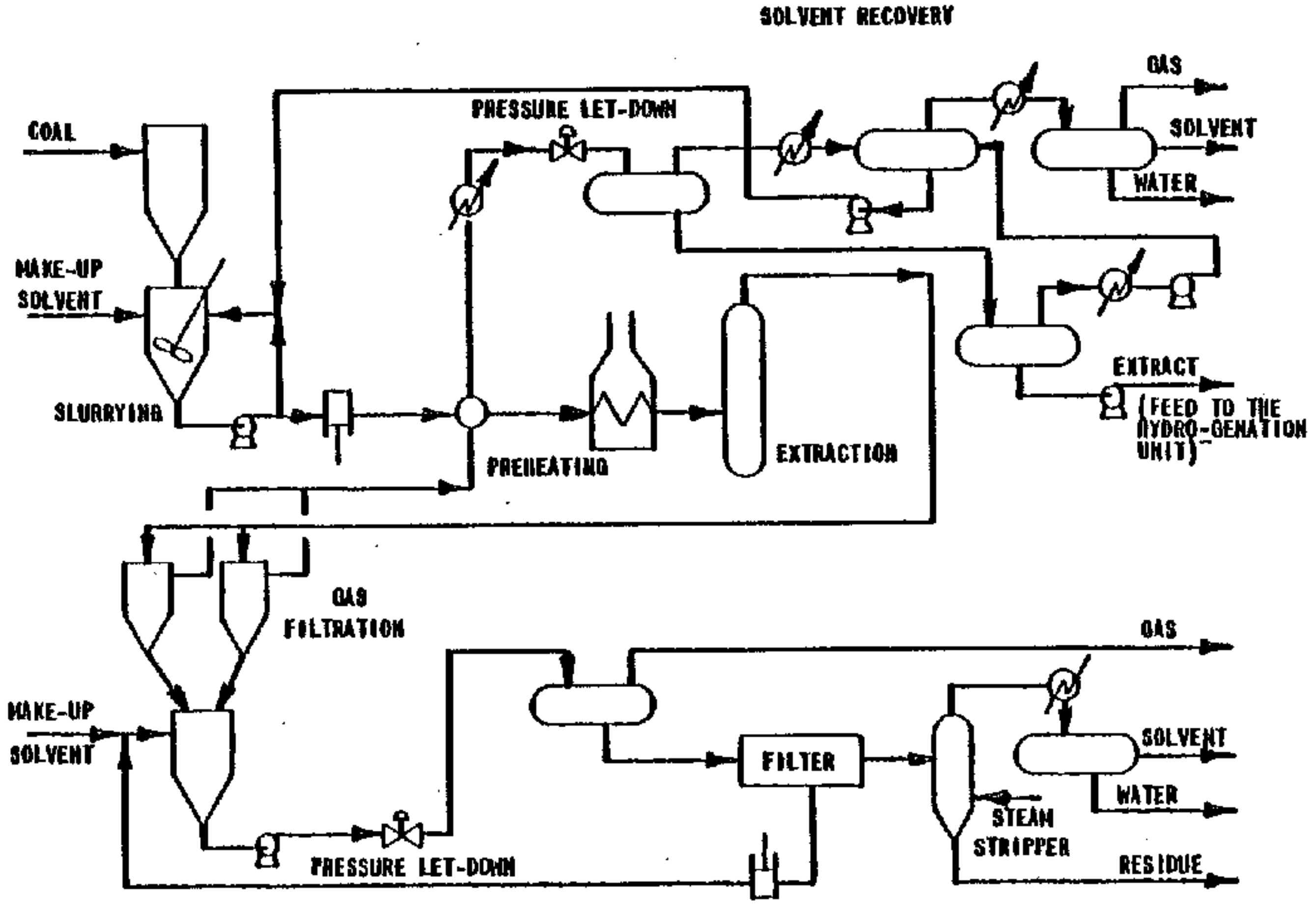

Figure 2.7
SUPERCRITICAL GAS EXTRACTION PROCESS

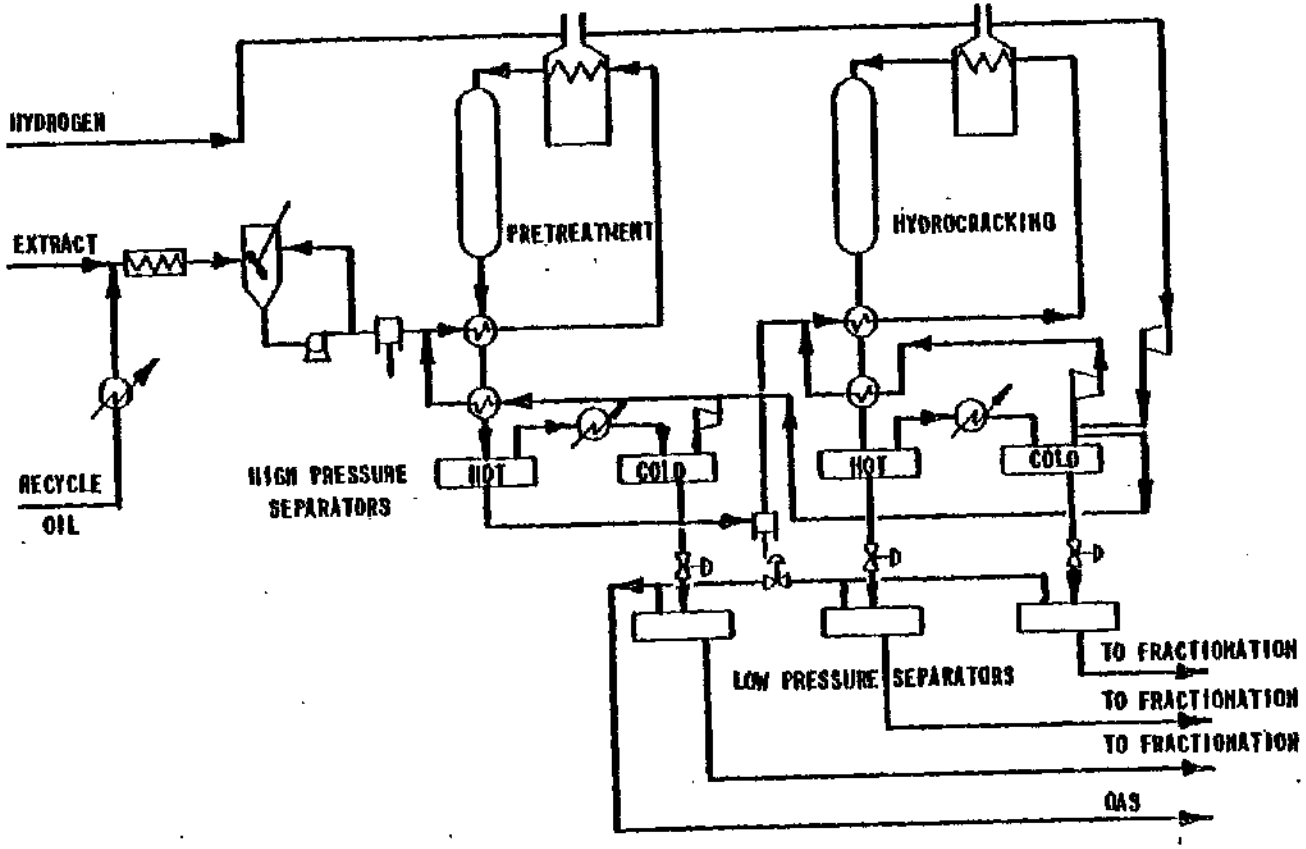

Figure 2.8
HYDROGENATION FOR SUPERCRITICAL GAS EXTRACTION PROCESS

Raw coal is fed into a crusher which will produce a distribution of sizes below 3 mm (0.12 in). The crushed coal is dried with hot flue gas from a fired heater, the water vapor being vented to atmosphere. The dried coal is classified to remove and recycle any oversize particles before passing into a surge bin from where it is pneumatically conveyed to the storage silo. The silo will contain enough coal for three days of normal operation.

The preferred mode of operation will be to continuously feed coal and hot solvent to the slurry tanks. Facilities are also included for batch weighing or using cold solvent. Hot coal slurry is fed to metering pumps from a tank circulation loop. The metering pumps pressurize the material to about 20 MPa (2900 psi). Vessels are included to give mean particle residence times of the order of minutes at the appropriate conditions of temperature and pressure. Two types of reactor (fluidized-bed and entrained-bed) have been tested on a 5 kg/hr (11 lb/hr) scale, and both are included in the design of the pilot plant.

During contacting, the coal decomposes to form a lower molecular weight fraction (coal extract) and a solid particulate residue. The coal extract material dissolves completely in the supercritical solvent phase. Extraction efficiency will be around 40% by weight of the dry mineral-matter-free coal.

The mixture leaving the reactor is passed through a filtration system. The cleaned fluid passes on to the solvent extract pressure let-down valve via a heat exchanger where it heats the feed slurry.

The solid residue which collects in the lower part of the filter vessel is free-flowing in character and is continuously removed to a slurry vessel before being depressurized. The residue will be steam stripped to remove much of the remaining solvent before stock-piling. Recovered solvent is returned to storage.

The hot extract/solvent mixture is flashed to a low pressure; the majority of the solvent passes out of the flash drum as an overhead vapor stream, while extract containing residual solvent constitutes the underflow.

The overheads are condensed at a temperature a little below the solvent boiling point in order to recycle this solvent directly to slurry preparation. The non-condensed vapor is passed to a cold water condenser, effluents from which are flared (if gaseous) or sent to a waste solvent tank and/or to waste water treatment. The underflow from the primary flash drum may be passed to a vacuum unit for separation of residual solvent.

After solvent recovery, extract would normally be passed to a tank for mixing with recycle oil before being repressurized for feeding to the hydrogenation system. The principles regarding preheating this feed are the same as described for the liquid solvent extraction (LSE) process.

The principles involved and the flowsheet for the SGE process are also identical to those discussed for the LSE process, although some operating ranges with respect to flow rates, temperatures, pressures, and residence time may be somewhat different. The requirements of this unit are similar to those for the LSE process. In addition to the two main product cuts described in LSE process, a solvent cut will be required to make up process losses. Unlike the LSE process, no additional equipment has been included for 'coking' the heaviest fraction.[11,13]

The overall plant block diagram and material balance[12] are shown in Figure 2.9.

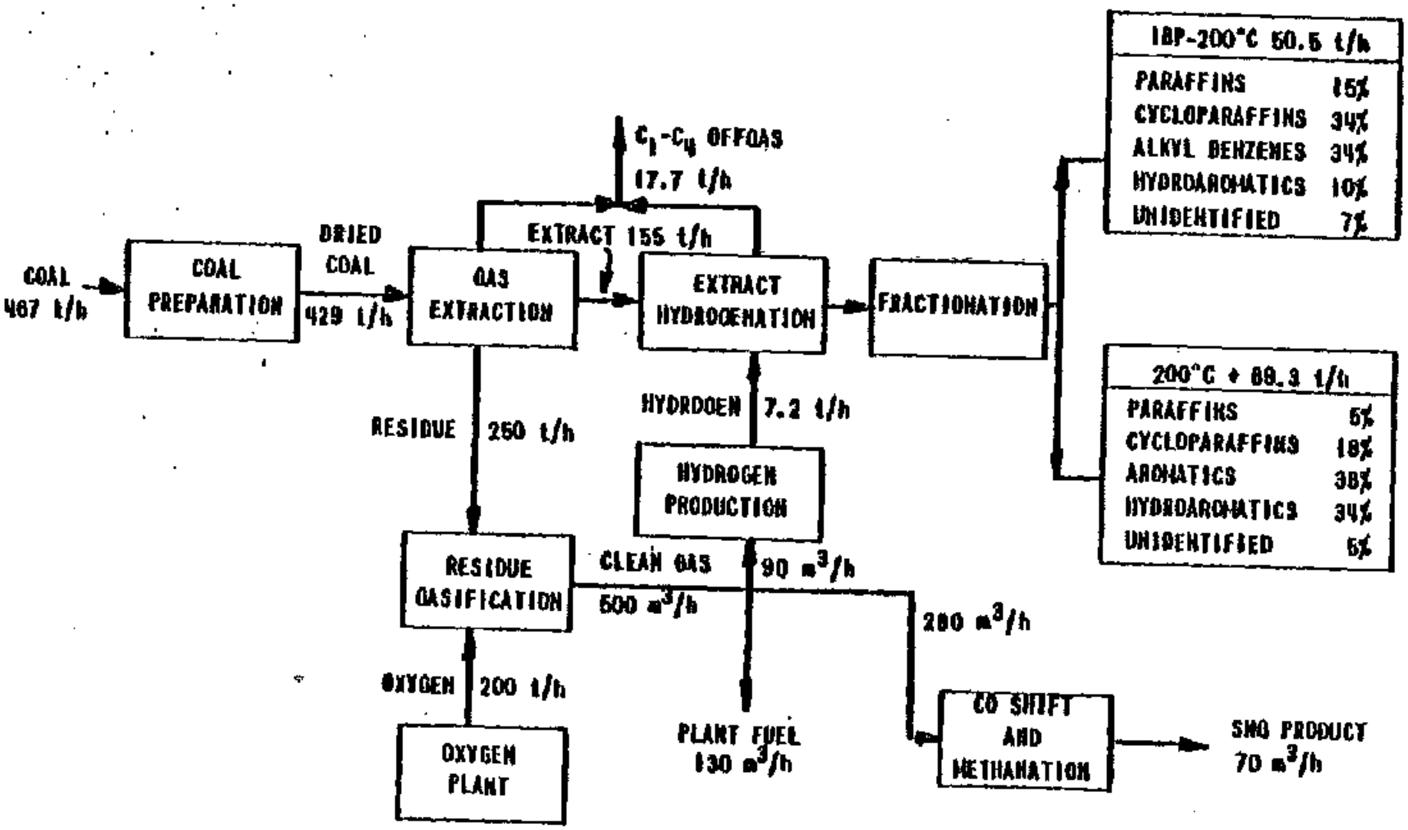

Figure 2.9
OVERALL FLOW DIAGRAM AND MATERIAL BALANCE FOR SUPERCRITICAL GAS EXTRACTION PROCESS