2.2.6 Solvolysis Liquefaction

The solvolysis process for coal liquefaction is being developed under the Japanese Sunshine Project supported by the joint public-private funds. Among the main process features[1.3,2.1] are (a) the use of petroleum heavy oil as solvent instead of process-derived heavy oil and (b) considerably less severe liquefaction process condition (e.g., 350-450°C, and 0.1-2 MPa or about 1-20 atm total pressure) than other processes. The liquefaction step yields solvolysis pitch (presumably a preasphaltene-asphaltene mixure in solvent), gas (mainly methane), and cracked oil (mostly n-paraffins). The liquid products undergo catalytic hydroprocessing to yield desulfurized oil.

2.2.6.1 History and Status. The solvolysis coal liquefaction process is one of the three major processes (hydrogenation) being developed under the Japanese Sunshine Project, and intensive R&D activities have been in progress since the start of the project in April 1974. The process has been undergoing modification in process conditions as well as the feed and product compositions over the years.

A 1-tonne/d process demonstration unit (PDU) has been in operation since the end of FY-1977 and has experienced several equipment and operational problems. These problems include (a) solids deposit in the slurry preparation tank, (b) foaming in the reactor, (c) irregular pumping rates of the two plunger pumps (presumably for transporting coal feed slurry to the preheater), (d) occasional plugging of transfer lines and valves, especially after brief pause in operation, and (e) unsatisfactory performance of the solid/refined pitch separator (anti-solvent type). Some of these problems have been alleviated by design modification of the equipment and piping. For example, problem (a) was overcome by providing a centrifugal recirculation pump. The foaming problem was lessened dramatically by installing a recirculation loop around the preheater, and by adopting a lateral, biaxial multi-disk mixer as the reactor. The performance of the plunger pump improved after the diameter of the check-valve ball for the pump was changed (increased?) and erosion-resistant material was used for the ball.

Development of hydroprocessing technologies for solvolysis pitch had been rather limited. It appears that no PDU studies on hydroprocessing have been carried out thus far. The only published study on this subject uses a laboratory-scale fixed-bed cocurrent upflow reactor for desulfurization and denitrogenation of the solvolysis pitch.[2.1] Scale-up of the 1 tonne/d PDU to a 40 tonne/d pilot plant is being studied.

2.2.6.2 Organization Experience. The major R&D work on the solvolysis coal liquefaction process is being conducted by three Japanese organizations: Industrial Research Institute of Kyushu, Kyushu University, and Mitsubishi Heavy Industries (MHI). The former two orgnizations have been concerned with fundamental studies pertaining to solvolysis. MHI has been involved extensively in different areas of coal liquefaction process development, including those under joint projects with the United States and Australia (see Chap. 1 for detail). In the solvolysis program, MHI is responsible for design, construction and operation of the PDU and pilot plants.

2.2.6.3 Plant Location. The 1 tonne/d PDU is located in Nagasaki, Japan. Location of the 40 tonne/d pilot plant has not been published.

2.2.6.4 Solvolysis Process Flow Diagram[J2.1]. Figure 2.19 shows the schematic flow digram of the 1 tonne/d solvolysis PDU. No detailed operating procedure for the PDU is available. The procedure, however, appears to be straightforward according to the flow diagram.

The feed coal preparation (i.e., size reduction, drying, etc.) is assumed to be based on the conventional method. Crushed coal (30-100 mesh; particle size distribution unclear) is blended with petroleum-derived heavy oil (asphalt) in the slurry preparation tank. The coal slurry (about 33 wt % coal) is fed to the reactor after going through the preheater where it is heated to about 360°C. The major portion of the "solvolysis reaction," including solubilization of coal

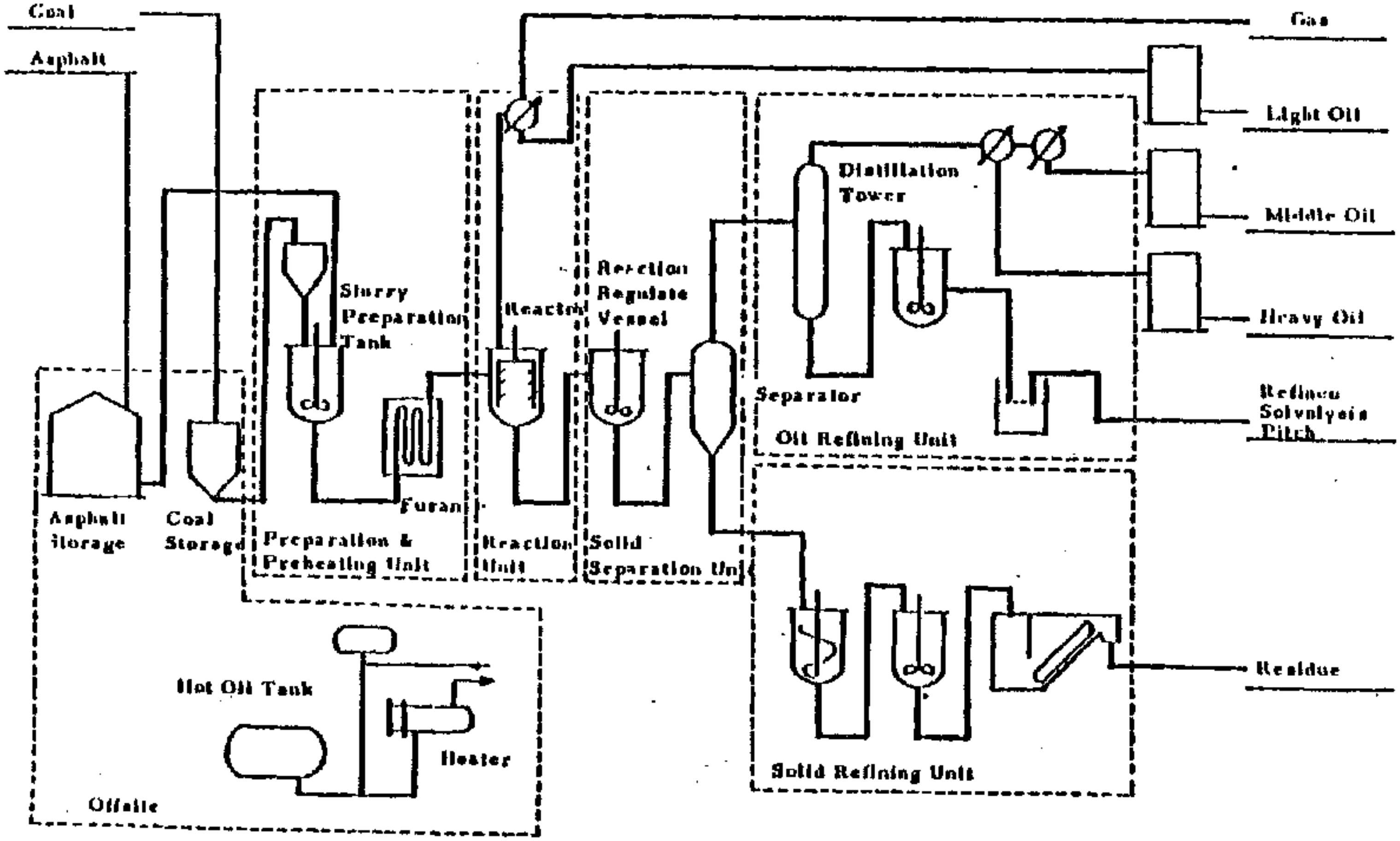

Figure 2.19. Solvolysis coal liquefaction process demonstration unit (1 tonne/d) (From Ref. J.2.1)

and conversion to preasphaltene and alphaltene, takes place in the reactor at about 380 to 450°C and about 0.1 to 2 MPa (about 1 atm-20 kg/cm^2), producing gas (methane-rich), cracked oil (mainly n-paraffins) and "solvolysis pitch."

The liquid product is brought into contact with a "suitable" organic solvent (anti-solvent?) to separate solvolysis residue containing ash and insoluble matter and refined solvolysis pitch is recovered from the extract. The ash-free pitch (a mixture of solubilized coal and petroleum asphalt) is transferred to the distillation tower where it is separated into different fractions of oil.

Since the development of the original solvolysis process, several modifications have been made to the process as well as the equipment. One such modification is the change in solvent for coal slurry from asphalt (petroleum-derived heavy oil) to process-derived, hdyrotreated heavy oil. Other modifications are discussed in Sect. 2.2.4.1.

2.2.7 Extraction Liquefaction

Development of this process - formerly called "solvent extraction coal liquefaction process" - is another major program funded by the Japanese Sunshine Project. The two features of the original process include (a) use of aromatic (hydrogen-donating) solvent (non-process-derived) in coal dissolution and (b) solid-liquid separation by the centrifuge method. The used solvent is rehydrogenated and recycled. The process has since been modified, and the current extractive liquefaction process employs process-derived, rehydrogenated middle distillate as the solvent. The basic process scheme apepars to be similar to that of the EDS process except that heavy oil from the solid-liquid separation centrifugation step is subject to the secondary hydrogenation step before entering the vacuum tower.

2.2.7.1 History and Status

The R&D activities on the extractive liquefaction process, commenced in 1978, have been dealing primarily with basic research, and have been conducted by two major contractors, the National Rsearch Institute for Pollution and Resources (NRIPR) and the University of Tokyo. The former is currently testing a small bench-scale (1-2 L/hr) continuous hydrogenation unit to investigate liquefaction of imported and domestic coals. The latter has been studying the mechanism of the coal extract hydrogenation reactions. Other areas of R&D activities include (a) solid-liquid separation technology by Sumitomo Coal Mining Company and (b) hydrogenation catalysts by Sumitomo Metal Mining Company. Construction of 1 tonne/d PDU for the extractive liquefaction process is nearly complete by Sumitomo Metal Industries (SMI) and Chiyoda Chemical Engineering and Construction (CCEC) Company.

2.2.7.2 Organization Experience

The past experiences of NRIPR and the University of Tokyo in coal liquefaction have been largely in fundamental research. Both SMI and CCEC are well known for their expertise in the area of chemical plant construction.

2.2.7.3 Plant Location

The 1 tonne/d extractive liquefaction PDU is located at the Sumitomo Kasaki Research Center in Kasaki, Japan.

2.2.7.4 Process Flow Diagram for Extractive Liquefaction PDU

The schematic flow diagram of the 1 tonne/d PDU is presented in Fig. 2.20. The operating procedure is outlined below based on the limited amount of information from several different sources.

Coal slurry consisting of pulverized coal and rehydrogenated recycle solvent (middle distillate) is prehated to about 450°C (about 840°F) before entering the liquefaction reactor (non-catalytic,

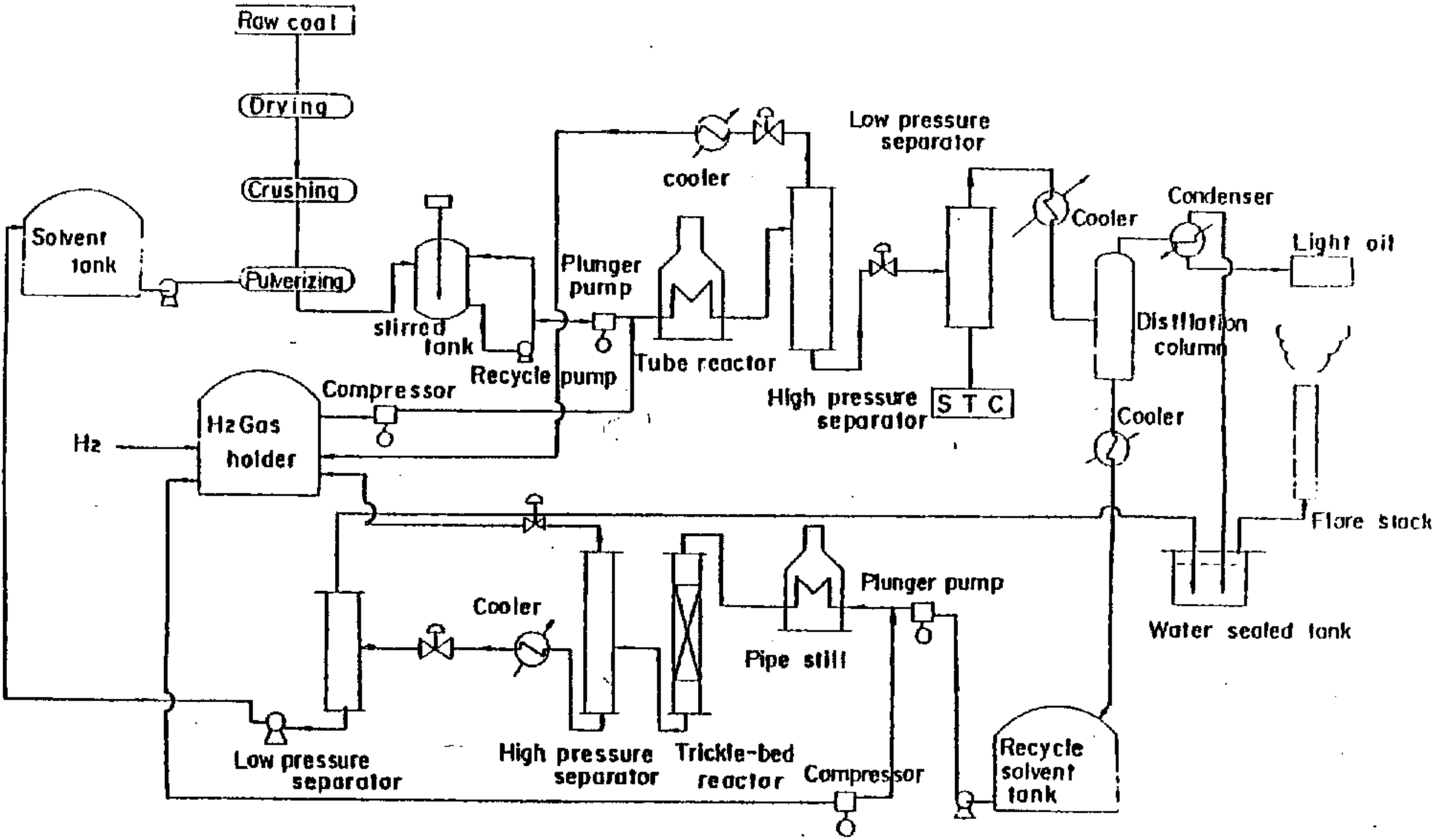

Fig. J2.20 Extraction coal liquefaction process flow (1 tonne/d PDU) tubular type) where reactions take place at about 450-500°C (about 840-930°F) and about 10-15 MPa (about 1420-2130 psia). The residence time of the reacting mass is approximately one hour after which the reactor effluent is separated into two fractions - gas plus light/middle distillates and heavy oil plus residue in high- and low-pressure separators.

The fraction that contains light and middle distillates is further separated in the atmospheric pressure-fractionator, and the middle distillate after rehydrogenation in the catalytic reactor is recycled as the process solvent. Heavy oil separated from the second fraction by means of the solid-liquid separator (a centrifuge system) undergoes a secondary hydrogenation, and is sent to the vacuum tower where middle distillate and heavy oil are produced. The residue is used as the feed to the hydrogen generator/gasifier to produce hydrogen for the process.

2.2.8 Direct Hydrogenation Liquefaction

The direct hydrogenation process for coal liquefaction is the third of the three major processes under the Japanese Sunshine project. The design of the process has placed an emphasis on improving rates of coal liquefaction reaction to achieve high liquid hourly space velocities (LHSV) (i.e., of at least about 10). The design feature to increase both the mass transfer and chemical reaction rates consist of (a) the use of the tubular reactor to obtain turbulent flow, (b) promotion of the "bubble flow" mode, (c) maintenance of high hydrogen concentration in the process stream by use of multistage injection of fresh and recycle hydrogen streams into the reactor system, and (d) application of high reaction temperature (400-500°C or 750-930°F) and pressure (19.6-29.4 MPa or 2840-4270 psia). Another feature of the process is use of the disposable FeS catalyst.

2.2.8.1 History and Status

The development work for the direct hydrogenation process to generate the design data for the 2.4 tonne/d PDU has been in progress since 1975. The data were acquired through autoclave tests as well as tests in a 0.1 tonne/d continuous bench-scale unit. Completion of the PDU construction and start of the shakedown operation are expected by the end of 1981. The initial phase of the PDU tests will be based on domestic coals, and subsequently tests with imported coals will follow. Operation of the PDU will be the responsibility of Mitsui Engineering and Shipbuilding (MESC) Company and Nippon Kokan.

The 0.1 tonne/d bench-scale unit is continuing its operation to conduct the support R&D for the PDU. Main subject areas of studies include (a) evaluation of PDU operating conditions, (b) investigation of liquefaction characteristics of different coal types, (c) determination of properties and material balance of the recycle solvent. Basic studies conducted by Hokkaido and Yamagata Universities, Asahi Chemical Industry Company, Hitachi Ltd., Japan Steel Works, and the National Chemical Laboratory for Industry are: (a) catalyst development, (b) recovery systems for slurry feed and power, (c) reactor materials, and (d) coal pretreatment methods.

2.2.8.2 Organization Experience

MESC and its affiliated Mitsui companies have been active in various coal conversion projects, including joint projects with the United States and Australia.

2.2.8.3 Plant Location

The 2.4 tonne/d direct hydrogenation PDU is located in Kawasaki City, Japan.

2.2.8.4 Process flow diagram for direct hydrogenation liquefaction

Figure 2.21 illustrates the direct hydrogenation process flow diagram. The key operation steps that are different from other processes include the following: (1) preheated coal slurry/H_2 gas stream containing disposable FeS catalyst is introduced into the

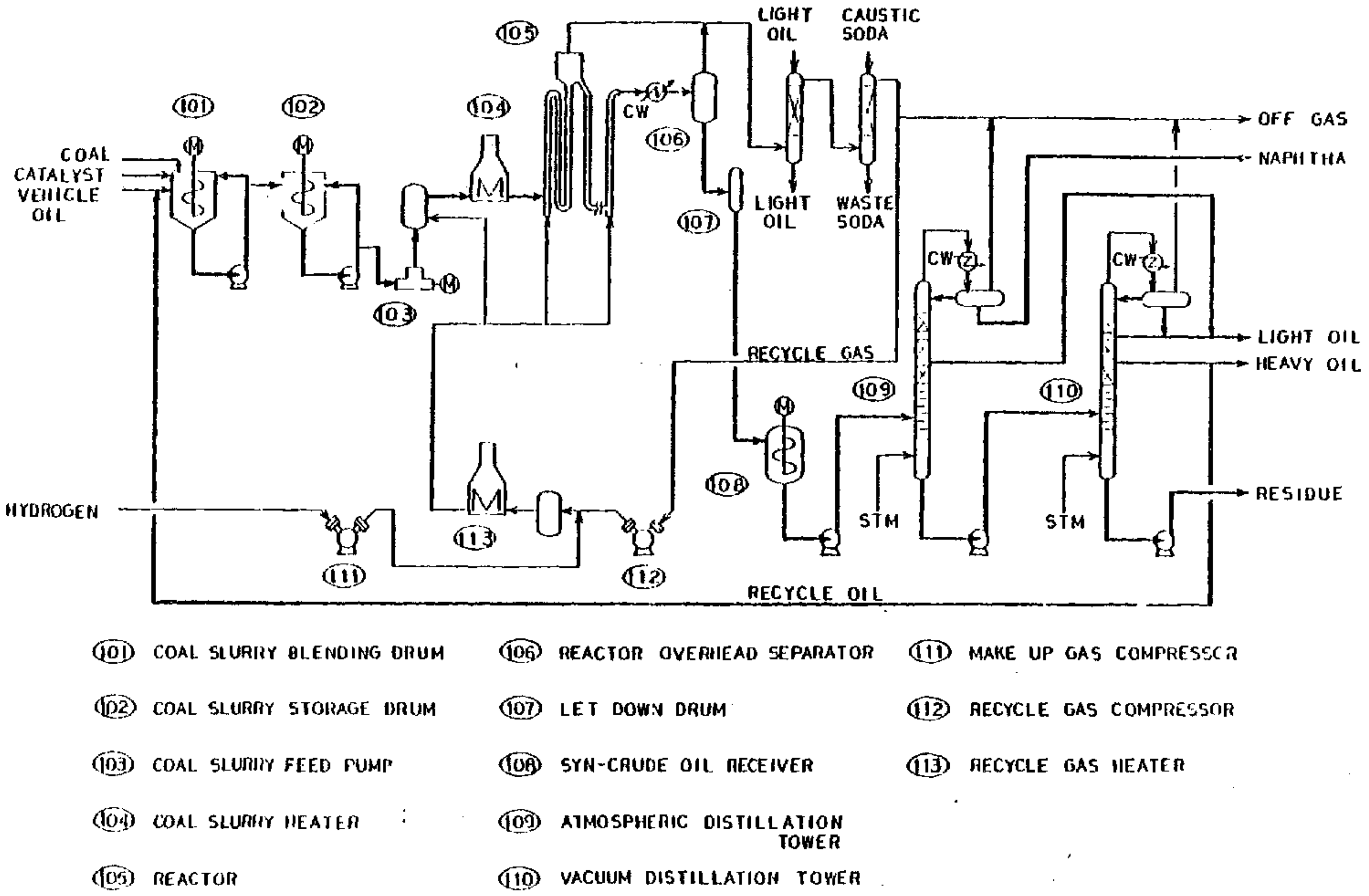

Figure 2.21 Flow diagram of direct hydrogenation coal liquefaction PDU (2.4 tonne/d) (From J.2.1)

tubular liquefaction reactor where additional quantities of H_2 gas are injected at different stages in the reactor system at about 750-930°F and 2840-4270 psia, (2) the slurry phase in the high-pressure separator is separated into solids (unreacted coal, catalyst, ash, etc.) and oil by means of a centrifuge or a hydroclone system, (3) oil thus separated is fractionated into naphtha, light oil, heavy oil and bottoms via the atmospheric and vacuum towers.