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1. CLOSED LOOP SOLAR CHEMICAL HEAT PIPE

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by

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CHANGED RECORD

The system used for the closed loop operation of the solar chemical heat pipe comprises a reformer, heated by the solar furnace, a methanator and a storage assembly containing a compressor and storage cylinders.

1. The Reformer

The reformer, described in detail in the previous report consisted of a 1", inconel 600, U-tube, filled with catalyst to a length of 115 cm. The catalyst was made of 1/8" alumina pellets, coated with 0.5% w/w Rhodium metal. The space above the catalyst was filled with inert alumina pellets. The reactor was inserted in a vertical aluminum box receiver, insulated with a 5 cm thick Fiberfrax alumina blanket. The opening on the front wall, facing the concentrator, was 10 cm in diameter. The gas and wall temperatures were measured along the reactor, and samples of the feed and product gases were automatically withdrawn and analyzed by gas chromatography.

2. The Methanation System

The flow sheet of the methanation system is shown in Figure 1. Its main components are: the methanator M; the gas preheater H; two steam generators S1 and S2; a mass flow controller for the feed and a metering pump for the water.

The feed is preheated in H, which is a 0.5" SS tube, packed with ceramic rings, and electrically heated. The temperature is controlled at the exit, as shown, and not more than 325° are allowed (to prevent carbon formation). The hot feed gas is combined in an insulated and heated line with superheated steam. The methanator used in the present work was designed as a 4-stage reactor, with 3 equal adiabatic stages and one isothermal stage (Figure 2). The adiabatic stages were insulated by vacuum mantles and by additional alumina blanket material. Cooling of the sections between the stages and of the isothermal stage was provided by compressed air. A water cooled condenser was installed at the exit of the last stage. The cooling system was only manually controlled by adjusting the flow of air through a valve. As the amounts of compressed air available were not always sufficient, the gas flow rate through the methanator had to be kept low enough, in order to prevent overheating in the first stage.

The reactor was made of a SS tube, ID = 35 mm. The catalyst was 0.5% Rhodium on alumina 1/8" pellets (the same catalyst as the one used in the reformer). The sections between the reacting stages were filled with 1/8" alumina pellets. Temperatures were measured at the inlet and outlet of each stage. Samples for GC analysis were withdrawn from the feed, after each adiabatic stage, and from the product line.

A six stage adiabatic methanator, with a larger capacity and better control of the cooling system, was constructed and will be operated shortly. A detailed description of this methanator is given in section 8.

3. The storage system.

The feed and product gas containers and the compressor are located in an open shed, for safety reasons. CO_2 is stored in 12 cylinders, most of them containing CO_2 gas at 40-50 atm. Three of the cylinders are replaced, when necessary, by new cylinders containing liquid CO_2 and gas at 60 atm; in this way the pressure in the storage is kept always around 50 atm. The gas is transferred to the feed control system through a 1/2" copper tube. CH_4 is stored in 30 cylinders, each 5 of them connected through a valve to the main manifold. The product-feed system uses 5 rows of 4 cylinders each, connected in two groups. Every cylinder has its own valve, and product can be compressed into any row, by adjusting the position of the valves on the manifold. The methane storage, the product-feed storage and the compressor, are connected to the reactors and the feed-control systems through 1/2" stainless steel pressure tubes. The gas compressor is located near the CO_2-storage, at a safe distance from the flammable gases.

The feed control system is shown in Figure 3. The inlet pressure to the system is regulated by PR1 and PR2. Separate sets are installed for flow control of CO_2 and CH_4. When the feed is a mixture, the CH_4 set is used, because it has the safety device AV. On the CH_4 line, a pneumatic ON-OFF valve AV is installed. This valve is operated by an air solenoid valve. It is controlled from the computer keyboard, but also manually through a switch located in the control room, so that the methane or feed flow can be immediately stopped in case of emergency. FM1 and FM2 are the mass flow meters, which transfer the mass flow rate measurements to the electronic controllers FC1 and FC2, where the flow rate set point has been stored. FC1 and FC2 return the command to the pneumatic control valves PV1 and PV2, which adjust the flow rate according to the set-point. The two flow control systems are connected electronically as "master and slave", meaning that the set point for the CH_4 is always relative to the flow rate of CO_2, thus keeping the molar ratio CO_2/CH_4 constant during the reaction. The gases enter the 5 liter vessel L, which is used as a mixer and is included also in the feed circulation cycle. The feed flow rate can be kept constant, corresponding to an initial set point. Another method is to use the flow rate as a process variable which controls the temperature in the reactor when fluctuations in input power occur.

The pressure transducer P is connected to the pressure control valve located on the exit line, and can be used to indicate and control the inlet pressure into the reactor. But this method was rarely used, the valve to P was closed and the transducer was connected to the product line, to control the outlet pressure in the system. The inlet pressure was monitored by a pressure gauge.

4. Operation of the Closed Loops

Two methods of operation were applied to the closed loop system.

A. Separate, alternate, operation of the reformer and methanator.

B. On line operation of the 2 reactors.

A. In the first run the solar reformer was operated with CO_2 + CH_4 feed from separate CO_2 and CH_4 storage containers; the flow rate of each gas was controlled by a mass flow controller, to give a mixture having a molar ratio of $CO_2/CH_4=1.3$ at any required flow rate. The product gas rich in CO and H_2, was compressed to 24 atm. and stored in a group of cylinders. The methanation was carried out separately, using the stored CO/H_2 mixture from the reformer as feed. The methanation product gas was also compressed to 24 atm. and stored in a second group of cylinders. This mixture was used as feed for the next reforming cycle.

In the 9 loops operated in this mode, the same gas mixture was used, without addition of fresh make-up gas. As some gas had to be vented to the atmosphere at the beginning of each run, there was a loss in material and the pressure in the storage dropped. Some change in the composition also occurred, because of contamination with CO_2, that was introduced into the system at the end of each run. We later solved this problem by circulating the gases when the reaction is stopped for any reason. This will be described in section 7.

B. A mixture of CO_2/CH_4 (methanation product) from a CO_2/CH_4 storage No 1 is fed to the reformer through a mass flow controller. The flow rate of the feed is so adjusted, that the amount of product from the reformer will be within the capacity of the methanator. The flow rate to the reformer was in this way lower than the rate possible for the reformer in the prevailing solar conditions, and we had to adjust the door openings in order to prevent overheating of the reformer wall. At the resulting gas temperatures (around 820-850°), high conversions of methane were obtained.

The product gas from the reformer was cooled and water (formed by the reverse water gas shift reaction) was condensed. Before entering the methanator, the gas was heated and combined with the necessary amount of superheated steam.

The product of the methanator was compressed and stored in the storage cylinders No. 2. Four cylinders were used as storage. When the pressure in storage No.1 dropped to 5 atmospheres, the "loop" was ended. Without stopping the reactions, storage 2 was changed with storage 1 by changing the position of 4 valves. This starts the second "loop", the feed to the reformer being the mixture in storage 2, which has just been produced in the methanator in the previous "loop".

The duration of a loop was about one hour, so that 5-6 loops could be run in one day (if the solar radiation level allowed continuous operation).

5. Results

5.1 Alternate operation.

As previously mentioned, in the first experiments for the evaluation of the closed loop CHP operation, the reforming and the methanation reactions were run consecutively, and the products from each reactor were compressed into separate storage tanks. The product from each reactor was, of course, used as feed to the second one. Good stability of the reaction mixture was obtained in the 9 loops performed, and no side reactions, such as carbon deposition, were detected. From the experience gained from these preliminary experiments, several improvements in the performance of the system could be introduced (f.i. in the gas sampling method, in the operation of the compressor and in the pressure control in the system) before starting the "on line" closed loop operation

5.2 On line operation

In this mode of operation, 5 or 6 loops could be run in one day, if the solar radiation was stable. The leak-free performance of the system could also be tested in this way, as no gases were introduced or withdrawn from the system during many hours. The total pressure in the storage cylinders did not change, indicating that the system was leak-free and no carbon deposition occurred. Thus, the 43 loops could serve as an "accelerated test" for the performance of the closed loop SCHP.

The constancy of the wall and exit gas temperatures in the reformer, during 6 hours of operation, is shown in Figure 4. Reactant conversions of 80-90% were obtained in the reformer and in the methanator. The gas composition, symbolized by the ratio O_2/H_4, remained constant, indicating that no side reactions, such as carbon deposition, occurred even when many cycles were run with the same gas mixture (Figure 5).

6. Temperature control by fluid flow rate (PID Control)

One of the major problems in the work with solar energy is the intermittent nature of this energy. Even a cloud lasting a few minutes may cause a drop of temperature in the solar reactor, thus disturbing the process occurring inside. In the Schaeffer Solar Furnace the temperature in the reactor may be controlled by changing the opening of the doors, but this is possible only when a part of the incoming energy is used.

Another way is to change the flow rate of the reactants. As the process in the reactor is endothermal - heating CO_2 gas or the CO_2 reforming of methane - the temperature of the reacting gases can be controlled by adjusting the gas flow rate through the reactor. The Gould 884 controller was programmed for PID control of the exit gas temperature in the solar reformer. In practice, the process variable, which is, in our case, the exit gas temperature, is monitored by a K-type thermocouple, registered in the controller and compared to the temperature set-point. The output signal of the PID control calculation is sent to the Mass-flow controller to adjust the flow rate of the CO_2 gas. The flow controller for the methane is connected as "Slave" to the CO_2 controller, so that the methane flow rate is adjusted relative to the CO_2 flow, the molar ratio between the two gases being preset in the instrument.

Preliminary experiments of temperature control were carried out with heating CO_2 and CO_2 reforming of methane. The results were promising. However, we still have to find the proper values for P, I and D in order to obtain constant output under realistic working conditions.

7.Internal circulation of reaction gases during short interruptions.

A method for keeping constant temperature in the solar Reformer when the input power decreases (f.i.: clouds) was previously described (PID control of temperature). The principle is: decrease of the feed flow rate until balance is reached between input and absorbed power.

If the input power (and feed flow rate) decreases to a minimum value, and the temperature drops below 600°, the reforming reaction cannot be continued any more, as the conversion will be too low to add the product to the storage. At temperatures under 600° there is a strong tendency for carbon formation from a mixture containing CO and H_2. (f.i.: the equilibrium composition at 450° contains about 30% carbon).

The usual procedure was to stop the feed flow to the reformer when the input power drops to the minimal value, and continue with a flow of CO_2 , which will replace the "dangerous" $CO+H_2$ mixture in the reactor, and thus prevent carbon deposition.

In practical work with a "closed loop" operation, where the product gas from the reformer is compressed and stored for further methanation, the above mentioned method cannot be applied, because a stream of pure CO_2, flowing through the reformer will contaminate the product in the storage containers. The possible variation - to vent the CO_2 stream to the atmosphere, is of course, wasteful. The reformer is, by this method, also contaminated with excess CO_2.

The new method of operation, which was tried out successfully under real solar conditions, uses a circulation pump for the reactants. The system is shown in Figure 6. During reforming, valves 1 and 2 are open and valves 3,4 and 5 are closed. During circulation, valves 1 and 2 are closed, and 3 and 4 are open. Valve 5 is opened just for a short time before starting circulation, in order to relieve the pressure from the pump exit.

When the input power drops so that the temperature in the reactor (exit gas temperature, TRout) cannot be kept over 600°, the feed flow is stopped, and the pump is started to circulate the gases in the reactor and mix them with the gas in a 5 liter vessel, which is installed in the feed line, and contains, of course, the feed mixture. The flow direction is: REF - exit line - pump - feed vessel - REF. In 2-3 minutes the composition of the gas in the reformer approaches the feed composition. During the cooling of the reactor, there might be conditions of "back methanation" in the reformer, a process which also causes decrease in the $CO+H_2$ contents of the mixture. An important role of the circulation is to decrease the residence time of the reactants on the catalyst, thus preventing the slower reactions, leading to carbon deposition. The circulation is continued until the input power increases back. When the temperature reaches 600°, the pump is stopped and feed flow through the reactor is renewed.

During the circulation, there is of course no product flow to the compressor, thus stopping automatically its operation, until the reforming reaction is started again.

Preliminary circulation experiments were performed on a clear day, with high solar radiation. We therefore simulated the drops in input power by closing the doors of the furnace. The results were quite satisfactory. When we finished this set of experiments, we opened the Reformer, and no carbon was found on the catalyst or in the exit lines.

8. An Advanced Six Stage Adiabatic Methanator

A six stage adiabatic methanator was built in the Schaeffer Solar Furnace. The methanator is connected to the Solar Reformer, and its operation will be evaluated, using the Reformer product as feed, as well as by using a $CO+H_2$ mixture from the storage.

The methanator is shown schematically in Figure 7. The system consists of 6 stainless steel reactors, 5 air-cooled heat exchangers after the first 5 reactors, and a water-cooled condenser after the last reactor. The reactors and heat exchangers are well insulated, to ensure adiabatic behavior of the reactors and prevent heat losses from the heat exchangers, so that the total heat balance of the system can be obtained. Steam is supplied from 2 steam-generators (S1 - evaporator and S2 - superheater). The amount of steam is controlled by a Metering pump, which delivers the water to the evaporator. The feed is first preheated in a furnace and then mixed with the steam in the superheater, in order to bring it to the required feed temperature. Compressed air is supplied to the 5 heat exchangers, and the condenser is cooled by tap water or pre-cooled recirculated water.

Thermocouples are installed at the inlet and outlet of the catalyst bed in the 6 reactors. The inlet and outlet temperatures of the air in the heat exchangers and of the water in the condenser, are also measured. Temperatures in the preheater, in the evaporator and at the exit of the superheater are controlled by 3 separate temperature controllers. All the temperatures are scanned by the central programmed controller and recorded in the computer.

The feed flow rate to the methanator is controlled by a mass flow controller. In the "on line" operation, previously mentioned, all the products from the Reformer can be supplied to the methanator, and the flow rate is then controlled at the inlet to the Reformer. The amount of water to the steam generator is controlled by a Diaphragm Metering pump. The air flow rate to the heat exchangers and the water to the condenser are controlled manually by valves, as necessary. The amounts of air from each heat exchanger and the amount of water from the condenser are measured by flow-meters.

The pressure in the system is controlled by a membrane pressure regulator ("GROVE") or by an automatic pressure control valve. Inlet and outlet pressures are recorded in the computer.

As the six reactors can be separately disassembled, evaluation of different catalysts will be easy. Each reactor contains 180 ml of catalyst. For the first experiments, reactors 1-4 are filled with Rhodium catalyst (0.5% Rh. on 1/8" Alumina pellets), and reactors 5 and 6 contain a Nickel catalyst. Samples from the feed line and from the exit lines of the 6 reactors are taken through automatic sampling valves to analysis by GC.

The compositions of the gas streams are obtained from the GC results. The conversions of reactants and energy released in the reactors are calculated from the compositions. Total heat balance in the system can be calculated from the amounts and temperatures of the cooling air and cooling water.

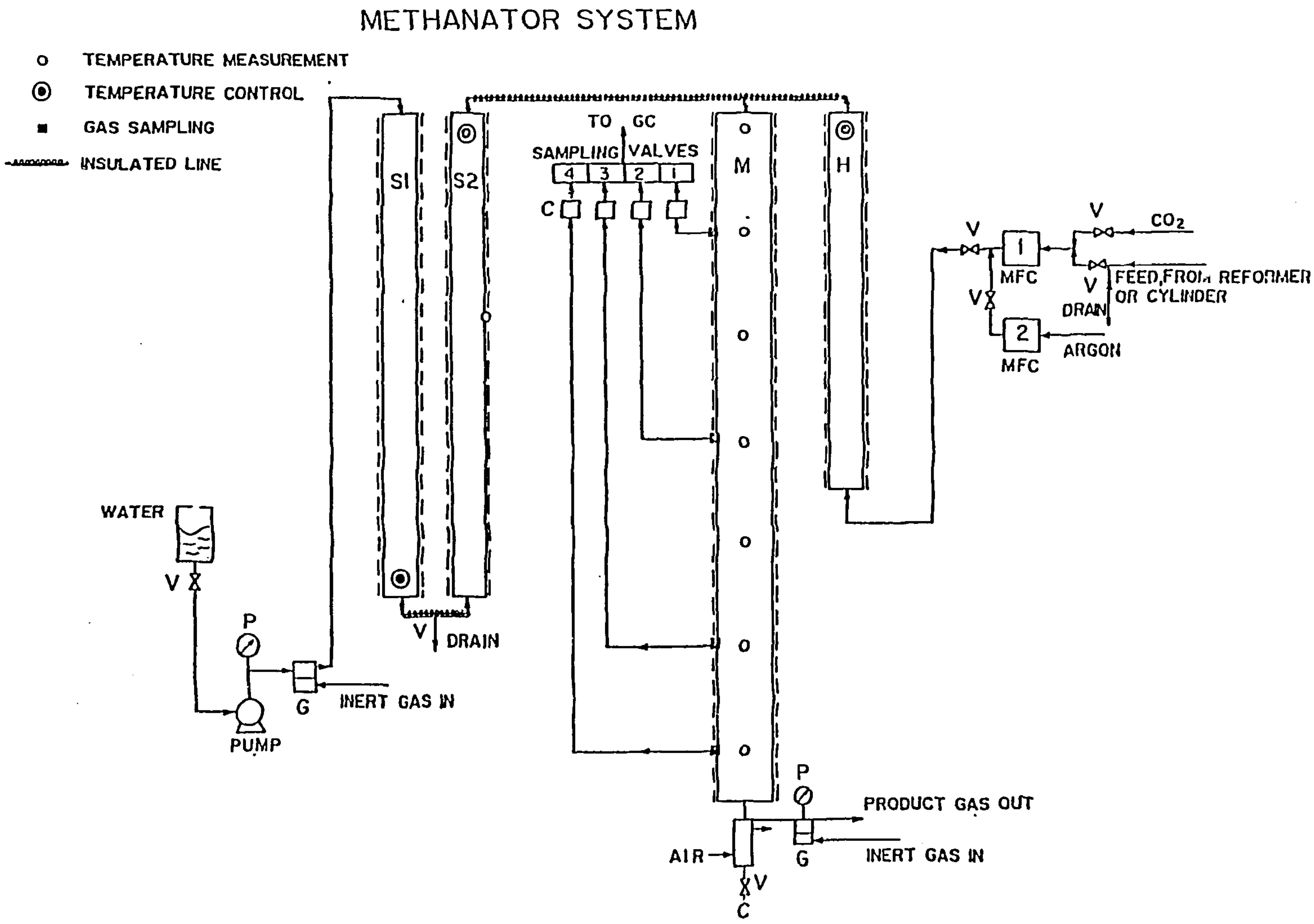
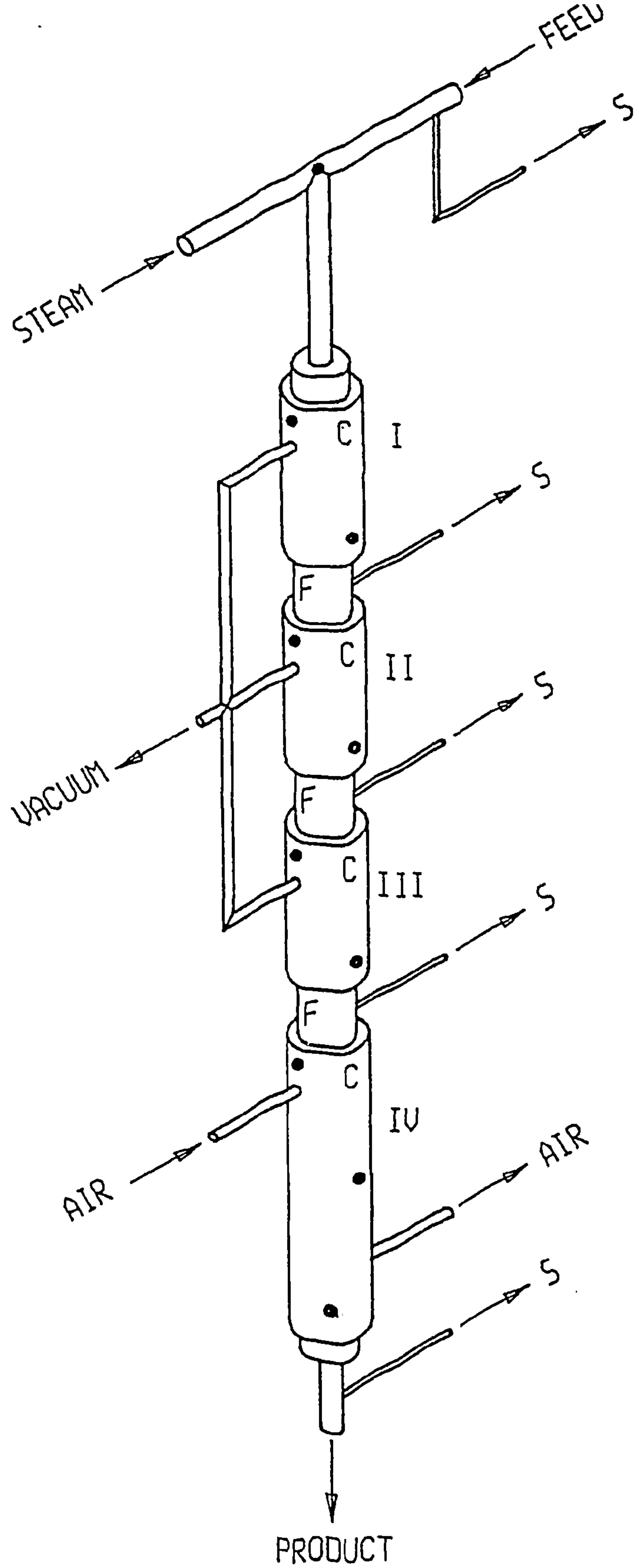


Figure 1

The Methanator System

M - Methanator; H - Gas preheater; S1 - Steam generator; S2 - steam superheater; G - Pressure regulator; P - Pressure indicator; C - Condensor; V - Valve; MFC - Mass flow controller; GC - Gas chromatograph.



C - CATALYST

F - CERAMIC FILLING

S - SAMPLE TO GC

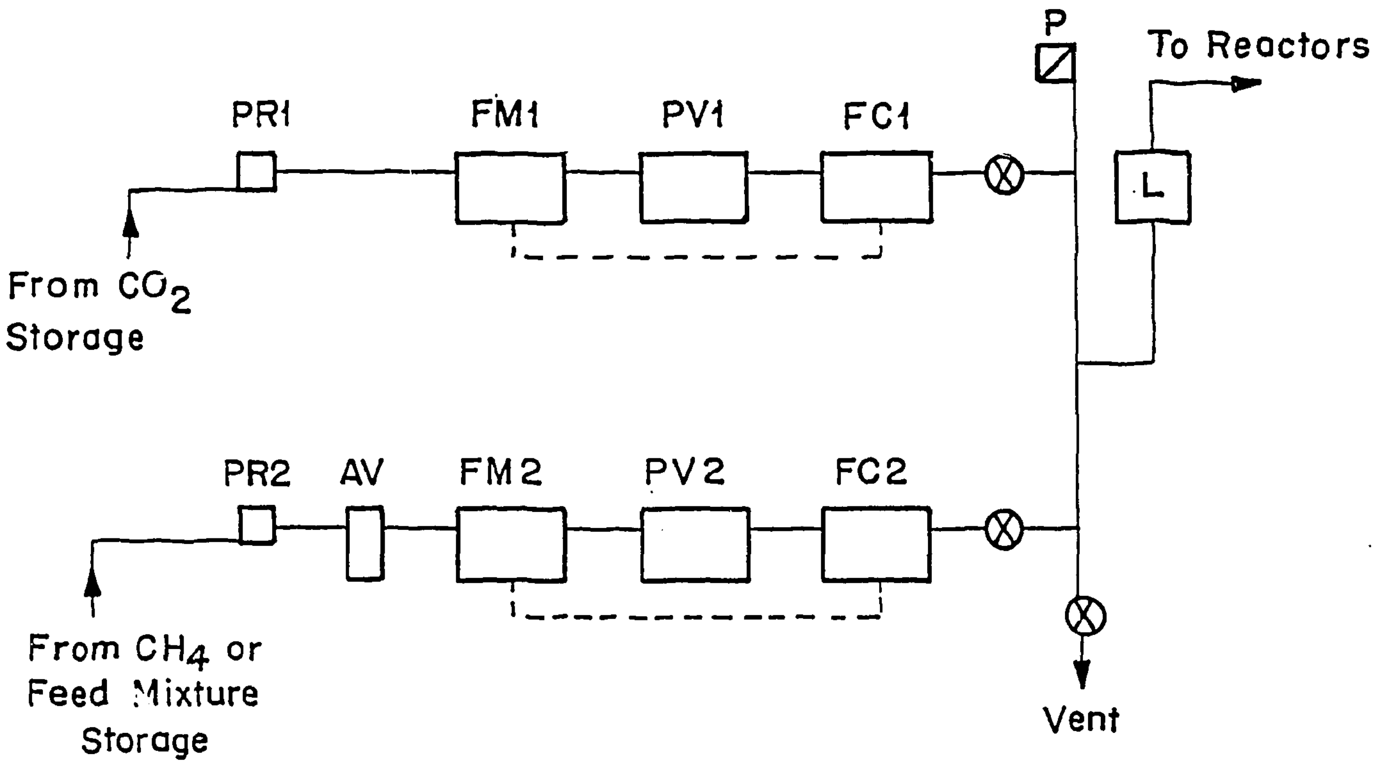
● - THERMOCOUPLE

Figure 2

THE 4-STAGE METHANATOR

CLOSED LOOP OPERATION

3. THE FEED CONTROL SYSTEM



PR - Pressure Regulator

AV - Automatic Valve

FM - Mass Flow Meter

PV - Pneumatic Control Valve

FC - Flow Controller, Electronic system

P - Pressure Transducer

L - 5 liter intermediate vessel

Figure 3

The feed control system

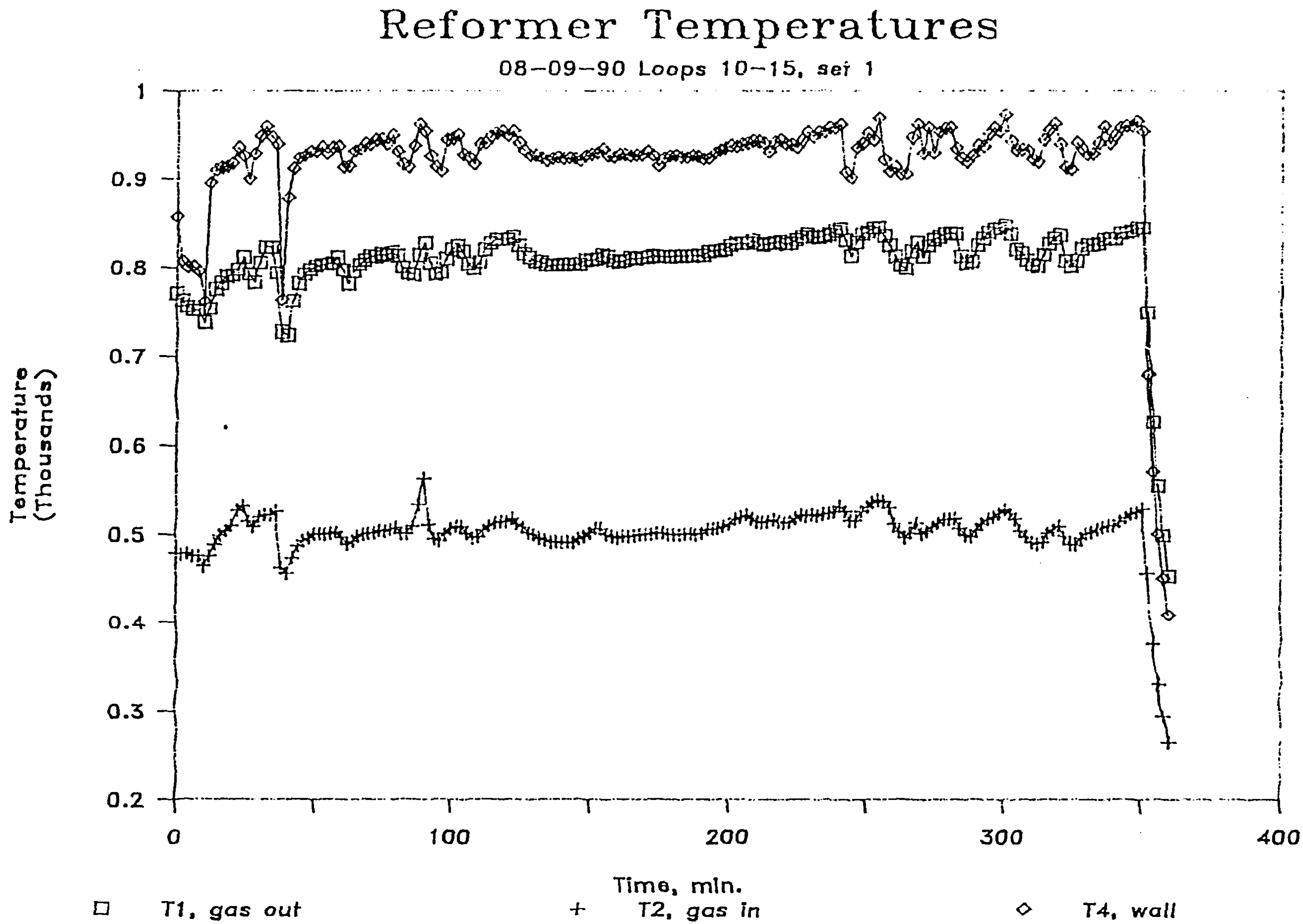


Figure 4

Reformer temperatures - feed, product and front wall, during a run of 6 hours (Set 1, loops 10-15).

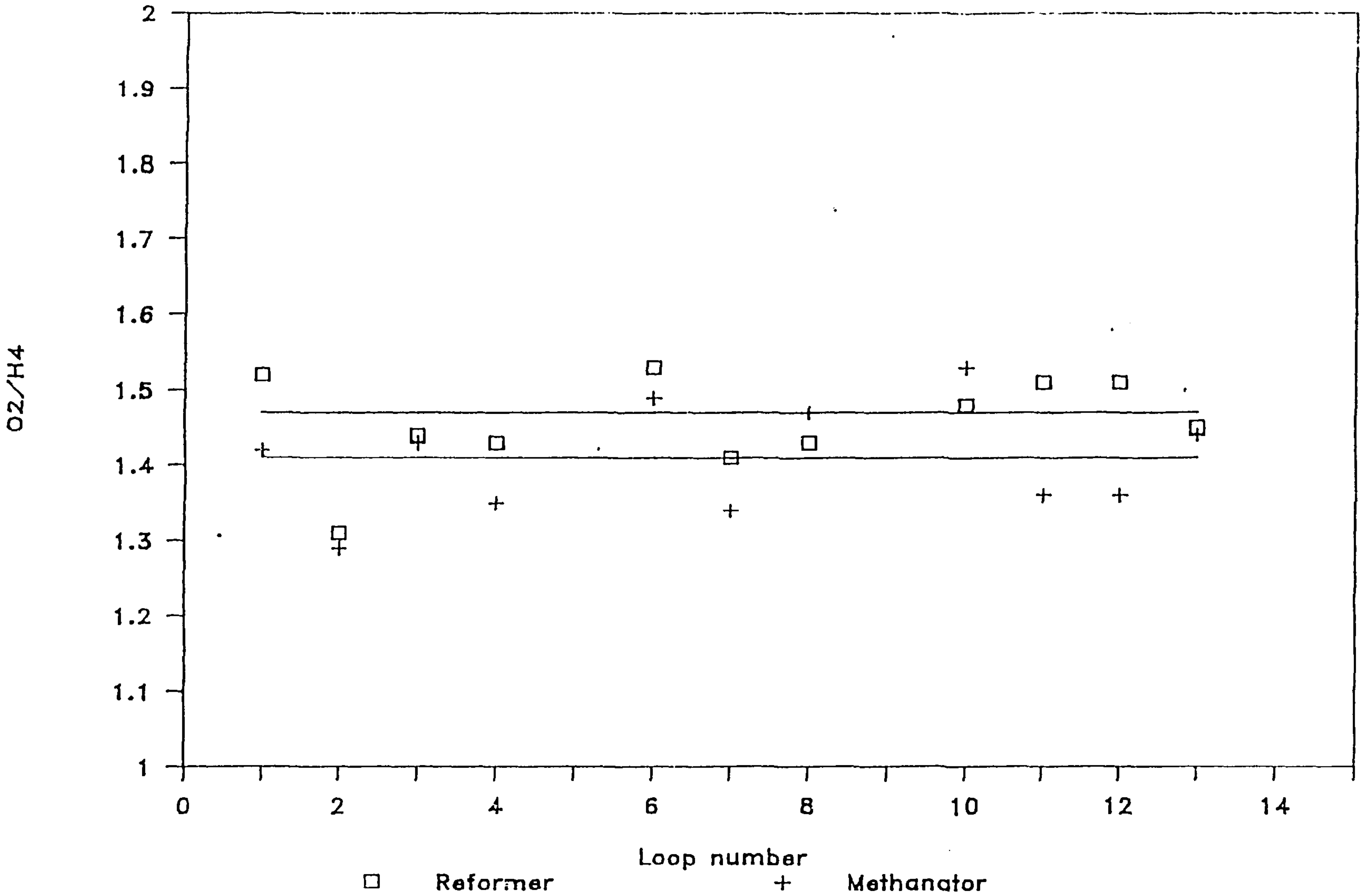


Figure 5

The O_2/H_4 ratio in the product gas along the loops, reformer and methanator (set 2, loops 1-13).

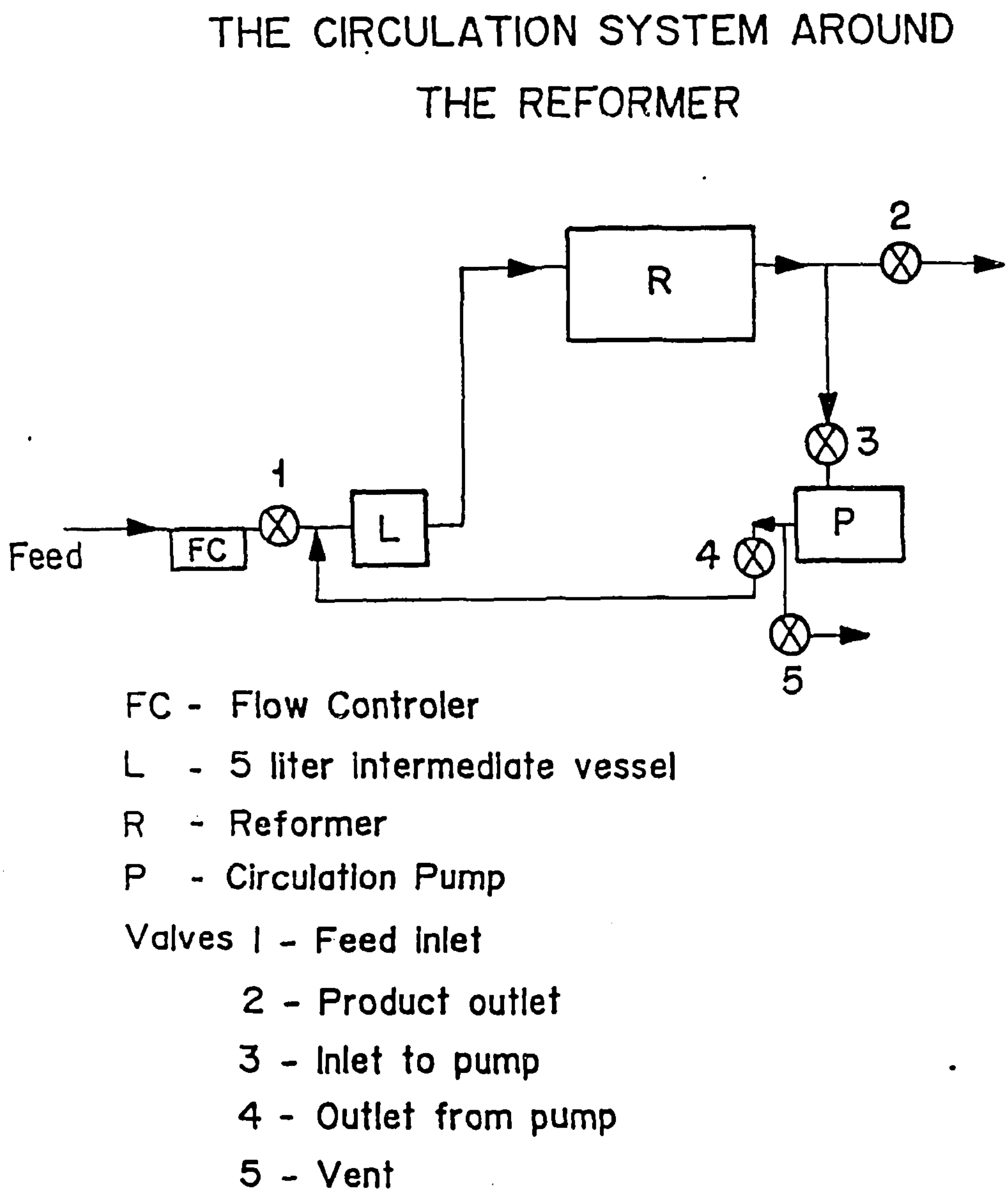


Figure 6

The circulation system around the reformer
(for operation - see text).

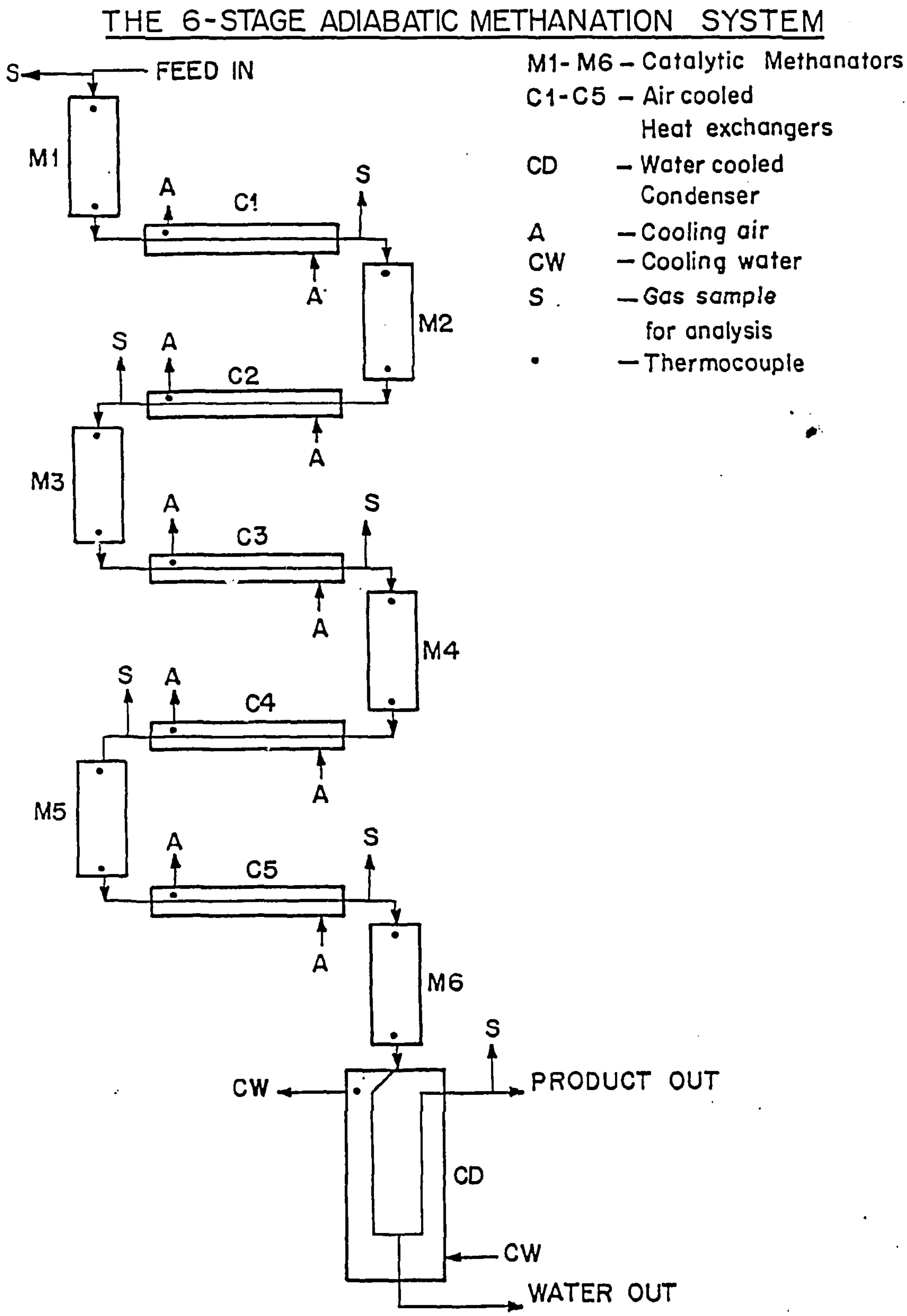


Figure 7

The 6-stage adiabatic methanation system