KERNFORSCHUNGSANLAGE JÜLICH GmbH

Institut für Reaktorbauelemente

Methanation - Pilot Plant
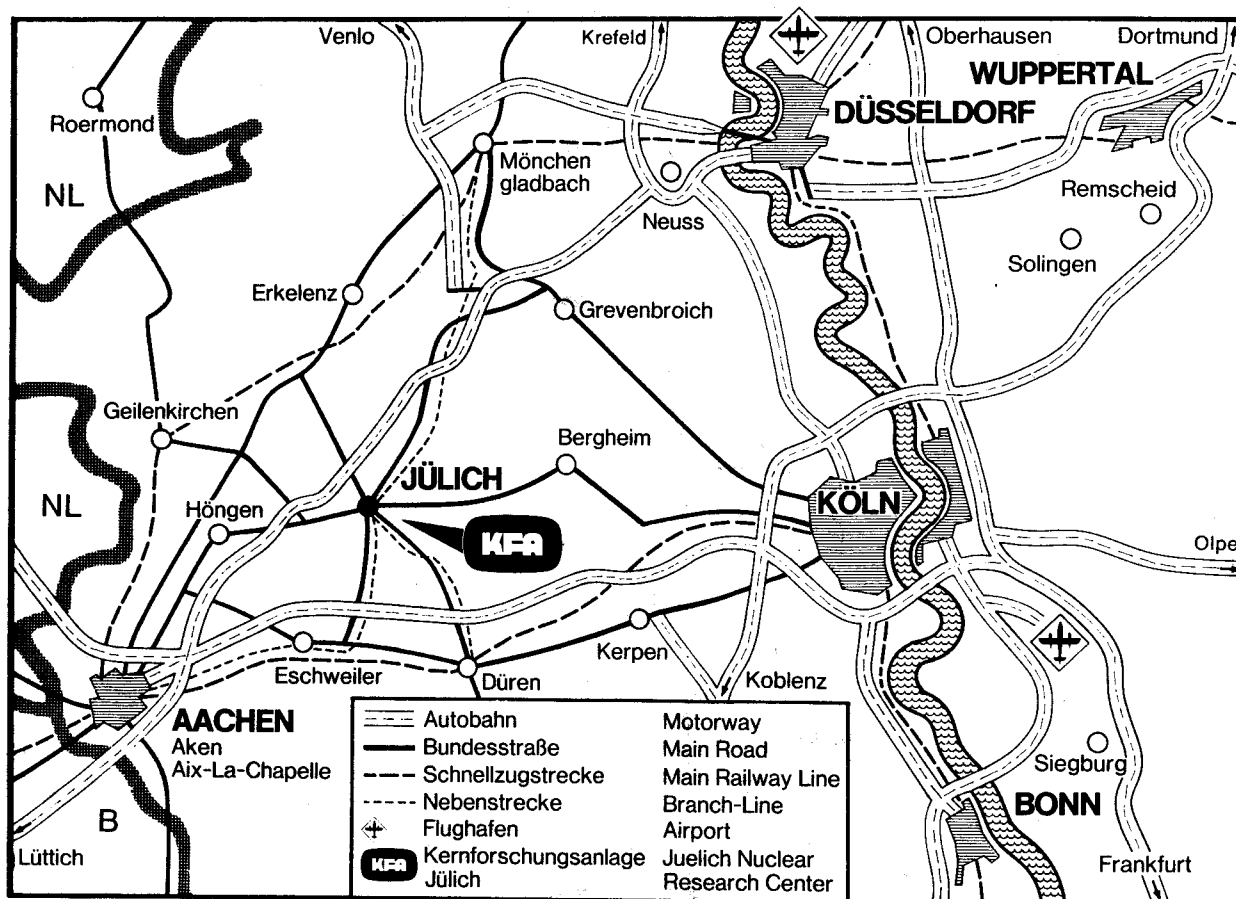
ADAM I (NFE Project)

and other Methanation Pilot Plants

by

B. Höhlein

≡≡≡	Autobahn	Motorway	
▬▬	Bundesstraße	Main Road	
─ ─ ─	Schnellzugstrecke	Main Railway Line	
-----	Nebenstrecke	Branch-Line	
✈	Flughafen	Airport	
KFA	Kernforschungsanlage Jülich	Juelich Nuclear Research Center	

Methanation - Pilot Plant
ADAM I (NFE Project)
and other Methanation Pilot Plants

by

B. Höhlein

This joint project is designed to develop a heat transportation process on the basis of chemical energy of a methane-steam-reforming / methanation system.

CONTENTS

A B S T R A C T

According to today's energy forecasts, the energy market requires a
considerable percentage of low temperature energy, and NUCLEAR
LONG-DISTANCE ENERGY represents a promising alternative source
for this energy.

In connection with nuclear coal gasification, the NUCLEAR LONG-
DISTANCE ENERGY SYSTEM provides an open gas circuit system for
both the transportation of chemical energy and the supply of raw gas for
various purposes. In this context, it appears to be reasonable to consider
a cyclic system with a high temperature nuclear reactor as heat source
for the methane steam reforming process at one side and the methanation
process with heat utilization at the other.

Together with the Rheinische Braunkohlenwerke AG, Köln, the Kernfor-
schungsanlage Jülich GmbH is building a pilot plant, ADAM I, in order
to study the heterogeneously catalysed methanation reaction, to develop
a flexible, consumer-oriented heat utilization, and to test the cyclic
system with the helium-heated steam reforming plant EVA I.

This report describes the pilot plant ADAM I, points out the fundamental
problems involved in the methanation process, and indicates possible
solutions. The experimental results achieved with the pilot plant ADAM I
and the results of catalyst tests will contribute considerably to the
optimization of the methanation process within the NUCLEAR LONG-
DISTANCE ENERGY SYSTEM.

In addition, the report indicates that many of the experiences achieved
so far with other methanation pilot plants as part of SNG production
processes will be helpful to the research work carried out within the
framework of the NUCLEAR LONG-DISTANCE ENERGY PROJECT.

1. INTRODUCTION: ENERGY SITUATION

Today's energy forecasts and the situation on the energy market call for an alternative source of energy. This is particularly true for that part of the energy market in which energy is consumed at low temperature levels /1/. These energy requirements which amount to more than 70 % of the total energy consumption in the Federal Republic of Germany, are largely met by natural gas and oil /2/. Both sources of energy, however, are liable to future shortage and increasing prices. In view of this situation, two developments would be desirable:

- the increase in energy consumption should be slowed down, and
- the impending energy shortage and the price increases to be expected for natural gas and oil should be overcome by technical innovations.

While the first argument has to undergo careful political and social analyses, the second idea will be the starting point of this paper.

2. HIGH TEMPERATURE REACTOR (HTR)
and
NUCLEAR LONG-DISTANCE ENERGY SYSTEM (NFE)

The High Temperature Reactor with its heat production at high temperature levels (see: Special Issue of "Nuclear Engineering and Design /3/) and an appropriate gas system for the transportation of chemical energy /4/ would constitute an important alternative for the supply of heat energy. Among the possible methods of heat transportation using a chemical circuit in which an endothermic reaction occurs at the HTR side and an exothermic reaction at the heat consumption side, a gas system involving a combination of the endothermic methane steam reforming process with the exothermic methanation process appears to be a preferable solution /5/. This so-called

NUCLEAR LONG-DISTANCE ENERGY SYSTEM (NFE System), described in many papers /1/, /2/, /6/, /7/, /8/, /9/, meets the requirements with regard to stable supply conditions, profitability, and environmental aspects.

This report will not include details as to when, under which conditions, and at which price this new application potential for the heating market might be available in the near future, since such a discussion is the subject of economic research. Rather, the following description will explain the NFE System from the engineering point of view, discuss some fundamental problems involved in the methanation process, and indicate possible solutions in connection with the pilot plant ADAM I.

2.1 NFE System

The NUCLEAR LONG-DISTANCE ENERGY CIRCUIT is mainly determined by the following reaction:

- the endothermic steam reforming of methane, which requires a large amount of energy at a high temperature level (HTR level):

$$CH_4 + H_2O \xrightarrow{800\ ^{\circ}C} CO + 3\ H_2$$
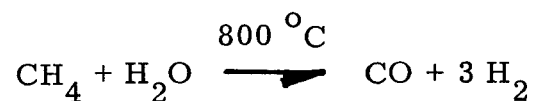
$$\Delta H_{298\ K} = +\ 205\ KJ/mol$$

- and the reverse exothermic methanation reaction where heat is set free over a wide range of temperature:

$$CO + 3\ H_2 \xrightarrow{300\ ^{\circ}C} CH_4 + H_2O$$
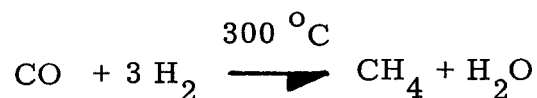
$$\Delta H_{298\ K} = -\ 205\ KJ/mol$$

This reaction is well-known; it takes place, together with the water-gas shift reaction, in heterogeneous catalytic systems.

For our process conditions, the BOUDOUARD reaction can be neglected because of its low reaction rate. While the endothermic steam reforming of methane at high temperatures leads to the formation of a synthesis gas with a favourably high CO/H_2 content, the exothermic methanation reaction taking place at low temperatures results in a product gas with a high methane content.

The NUCLEAR LONG-DISTANCE ENERGY CIRCUIT thus consists of three parts (Fig. 1):

-   the High Temperature Reactor (HTR) as heat source,
-   the methane steam reforming plant,
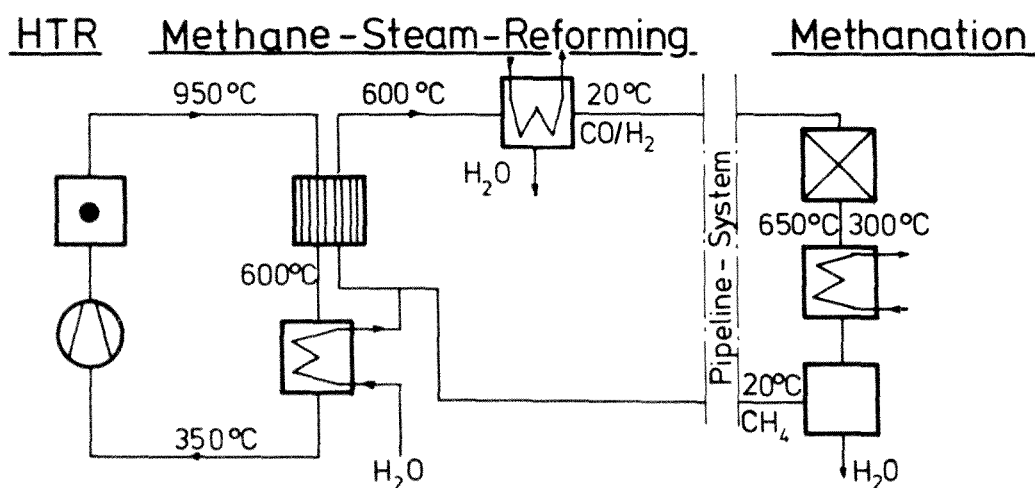   and
-   the methanation plant.

Fig. 1

NUCLEAR LONG-DISTANCE ENERGY CIRCUIT

The nuclear heat from the HTR is fed into the gas circuit via the endo-thermic chemical reaction of the methane steam reforming process. The chemical energy of the CO/H_2 gas-mixture can then be transported over

long distances before the energy is recovered in the vicinity of the consumer via the exothermic chemical reaction of the methanation process. The product gas with high methane content can then be fed back to the HTR via the natural gas pipe-line system. On the steam reforming side, steam is added, while on the methanation side, steam is condensed as a reaction product.

The closed NFE System can be operated without or with carbon consumption. In the former case, its only purpose is the transportation of energy, which on the methanation side of the circuit can be utilized for

- heating (household and industry),
- process steam (industrial purposes), and
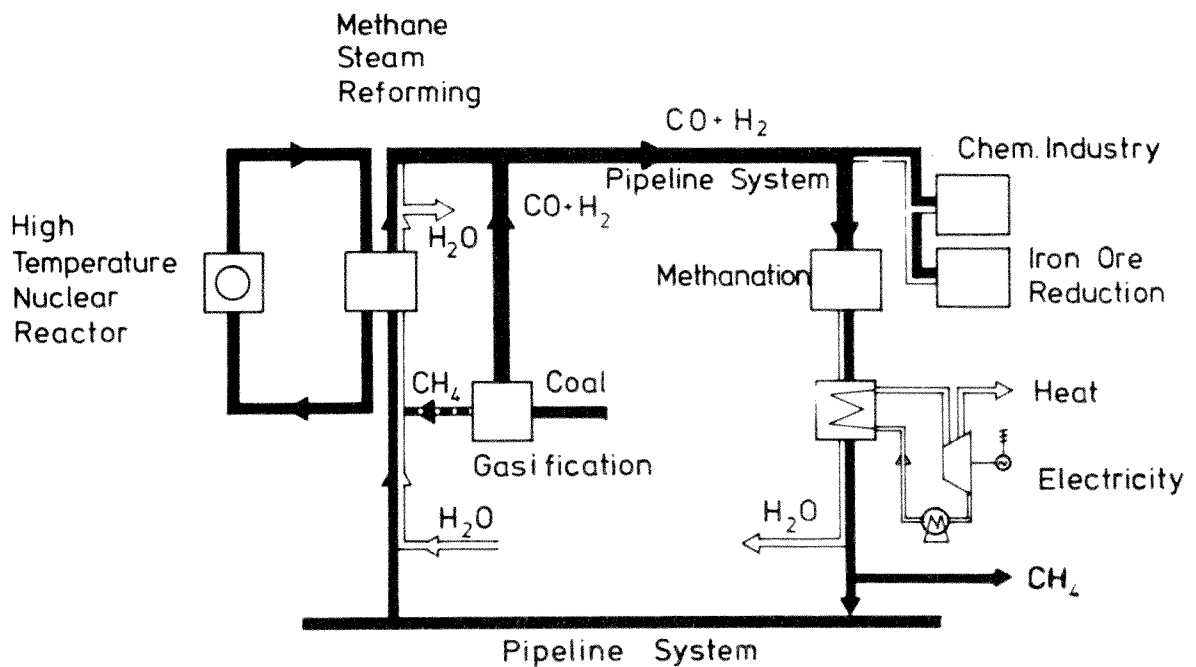- electricity production in the vicinity of the consumers.

Fig. 2

NFE Circuit with Gas Consumption /10/

On the other hand, an open system using nuclear coal gasification as a source of carbon is required if, in addition to the purposes mentioned above, the synthesis gas line is utilized for methanol synthesis, hydrogen production, oxosynthesis, and direct reduction of iron-ore, and/or, if the natural gas pipe-line is utilized for plants producing heat by combustion for periods of peak loads.

The process, modified to include coal gasification, is shown schematically in Fig. 2. The gasification can be carried out either by

- steam gasification, using nuclear heat,

or by

- hydrogasification, using hydrogen taken from the synthesis gas line.

2.2 NFE Methane Steam Reforming Process

The process shown in simplified form in Fig. 1 indicates that the conditions for the steam reforming of methane are largely determined by the temperature and pressure conditions prevailing in the HTR cooling-circuit. Thus, methane steam reforming takes place at a process pressure of 30 to 40 bar, and, with a maximum helium temperature of 950 $^{\circ}$C, it is possible to achieve a process gas outlet temperature of 800 $^{\circ}$C to 850 $^{\circ}$C. Under these conditions, the dry product gas of the methane steam reforming process contains more than 90 % of the products CO, CO_2, and H_2.

For the transportation of energy, a high percentage of products - i. e. a low percentage of methane - is preferable; with methane steam reforming, however, this result can only be achieved by means of a high H_2O/CH_4 ratio at the reformer inlet, and this would reduce the efficiency of the process. Before the synthesis gas is fed to the transportation system, it is pressurized to 60 - 70 bar.

Within the framework of the joint NFE project of the Kernforschungsanlage Jülich GmbH, and the Rheinische Braunkohlenwerke AG, Köln, several research activities are being carried out in connection with the steam reforming part of the energy system:

- single tube reformer pilot plant, EVA I (total heat: 1 MW) /11/, /12/
- test plants for catalyst experiments /12/
- mathematic models /13/, /14/
  and
- construction of a multitube reforming pilot plant, EVA II (30 reformer tubes, total heat: 10 MW).

2.3 NFE Methanation Process

The design of the methanation plant at the consumption end of the system is determined by the form of heat consumption required and by the parameters of the NUCLEAR LONG-DISTANCE ENERGY SYSTEM. The task of this methanation unit is to recover heat at different temperature levels, for the production of electricity and process steam and for heating purposes, as well as to produce a gas with a high methane content which can then be fed back to the HTR.

Only an adequate cost and consumption analysis will determine which form of heat consumption - electricity, steam, or heating - is to be preferred in the individual plant; it is the form of heat required by the consumer which will specify the design parameters of the methanation plant and determine the efficiency of the process and the energy price to be paid by the consumer.

Within the framework of the NFE project discussed above, two methanation plants are being built which serve for studying the NUCLEAR LONG-DISTANCE ENERGY SYSTEM in connection with methane steam reforming

plants. The larger of these two pilot plants is designed to recover methane for use in the helium-heated multitube steam reforming plant EVA II, whereas the smaller pilot plant will serve the special purpose of testing the methanation process. In the following section, this smaller pilot plant will be described in detail. Its name is "ADAM I" because it is connected with the helium-heated steam reforming plant "EVA I" which has been in operation since 1971 in the "Institut für Reaktorbauelemente" (KFA Jülich). The pilot plant ADAM I will go into operation in the summer of 1978.

3. PILOT PLANT: EVA I - ADAM I (Fig. 3)

When started, the interconnecting system between the pilot plants EVA I and ADAM I will be fed with Dutch natural gas at a rate of 200 Nm^3/h. In the heat exchanger E 3, the natural gas / steam-mixture, with a ratio of 1 : 3, is preheated to the process gas inlet temperature of 450 ^{o}C. In the reformer D 1, the process gas is catalytically reformed so that, after condensation of the surplus water in the cooler E 6, there is a gas mixture at the reformer outlet with 10 % CH_4, 10 % CO, 10 % CO_2, and 65 % H_2 (rest N_2). The heat from the helium circuit is transferred to the catalyst bed inside the reformer tube via an annulus around the tube. 65 % of this heat is used for the reaction.

In this pilot plant, the function of the HTR is simulated by the electric helium heater E 5. The production of process steam in the gas-fired steam generator E 1, the preheating of natural gas in the heat exchanger E 2, and the cooling of the product gas in the heat exchanger E 6 serve only the purpose of determining reasonable parameters for the experiments; this plant is not meant to demonstrate the profitability of heat utilization.

The reaction tube, which is filled with a conventional reforming catalyst, is of industrial size and has a heated length of 10 m and an inside diameter of 100 to 200 mm /12/.

STEAM REFORMING
PLANT
EVA I

G-He

E-4

E-5

D-1

E-6

E-3

E-2

E-1

H₂,CO

CH₄

H₂O

METHANATION PLANT ADAM I

K102

H102

H101

R101

R102

R103

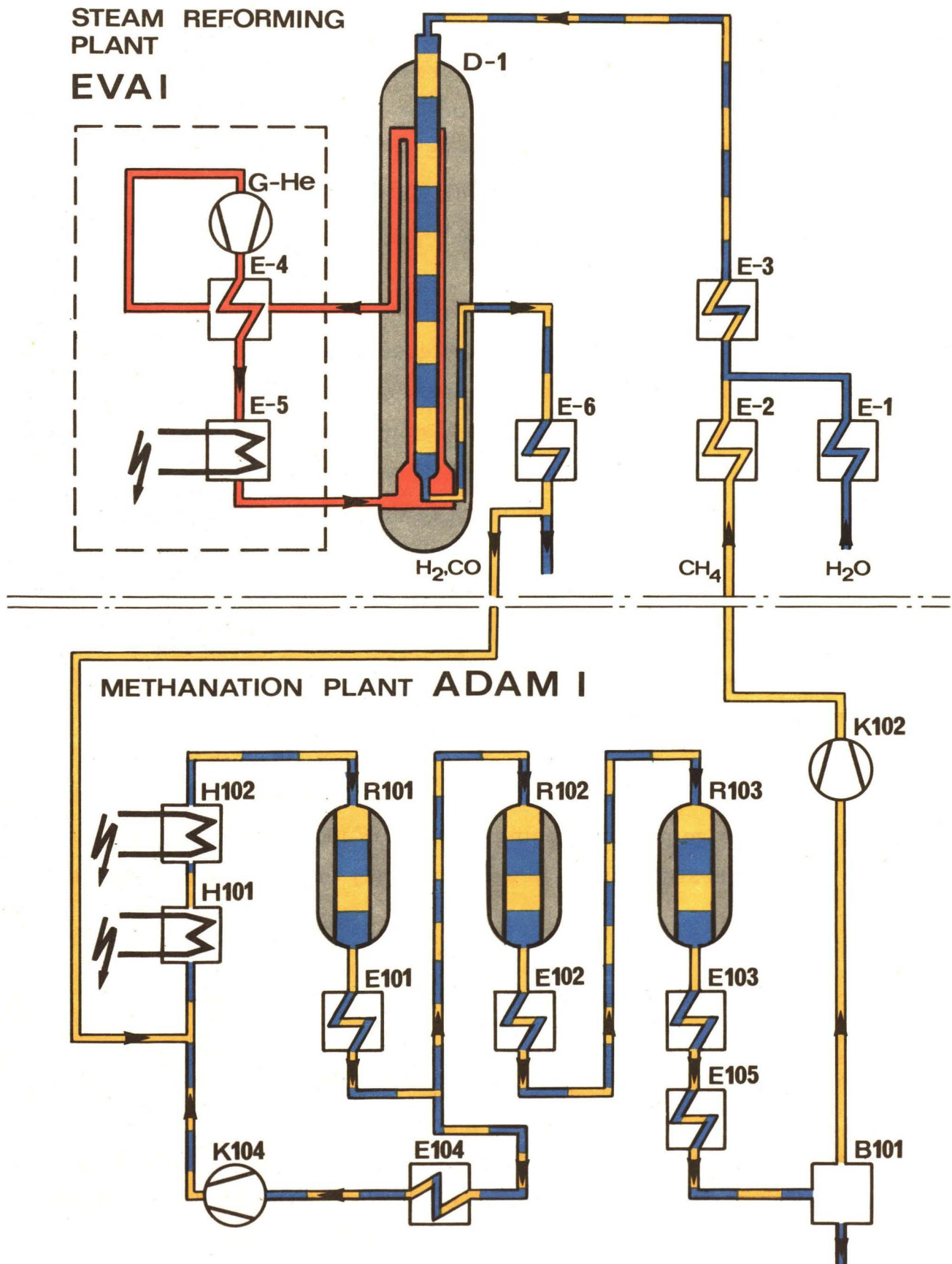E101

E102

E103

E105

K104

E104

B101

Bild 3 Versuchskreislauf: EVA I – ADAM I

Fig. 3

Pilot Plant Circuit: EVA I – ADAM I

If, as is planned within the NFE project, the steam reforming plant EVA I and the methanation plant ADAM I are interconnected, the cold, dry product gas (about 600 Nm^3/h) from the steam reforming plant flows into the methanation plant where it is preheated in the electric preheaters H 101 and H 102 to the starting temperature of the heterogeneous catalytic methanation reaction of about 300 ^oC. The plant is designed for a three-stage methanation procedure, each stage being equipped with heat exchangers for the heat removal.

The gas flows through the three reaction stages; after each stage, it is cooled to the starting temperature of the next stage. At the end of the procedure, the reaction water (about 40 % by mass) is removed from the product gas in the condensate separator B 101. The dry product gas with a methane content of 81 % can be fed back to EVA I by means of a compressor so that it is no longer necessary to supply additional natural gas. Thus, the circuit operates without gas consumption, apart from leakages and loss of gas dissolved in the condensate. Again, the heat exchanging units serve for determining the parameters of the experiment, not for demonstrating profitable heat utilization.

The three reaction stages are designed as adiabatic systems with catalytic fixed beds, the design pressure being 40 bar. An independent internal circuit with the compressor K 104 is used to supply the methanation stages with

- nitrogen for starting the plant,
  and with
- hydrogen for reducing the methanation catalysts.

After this rough description of the pilot plant, the two parts - especially the methanation part - will be examined more closely in order to point out some problems in connection with the NUCLEAR LONG-DISTANCE SYSTEM.

The methane steam reforming process has been practiced in industry since 1930. Accordingly, the problems occuring in this part of the pilot plant are largely limited to two areas:

- the heat transfer from the HTR-cooling-gas to the steam reforming system,

  and

- the optimization of the procedure for the inclusion of this system within the containment of a nuclear reactor.

The major problem occuring within the exothermic methanation process can best be illustrated by describing the dependence of the equilibrium methane formation on the equilibrium gas temperature (Fig. 4); the problem arises because of the difficulty of combining a highly exothermic methanation reaction with the low outlet temperature required for a high methane content in the product gas.
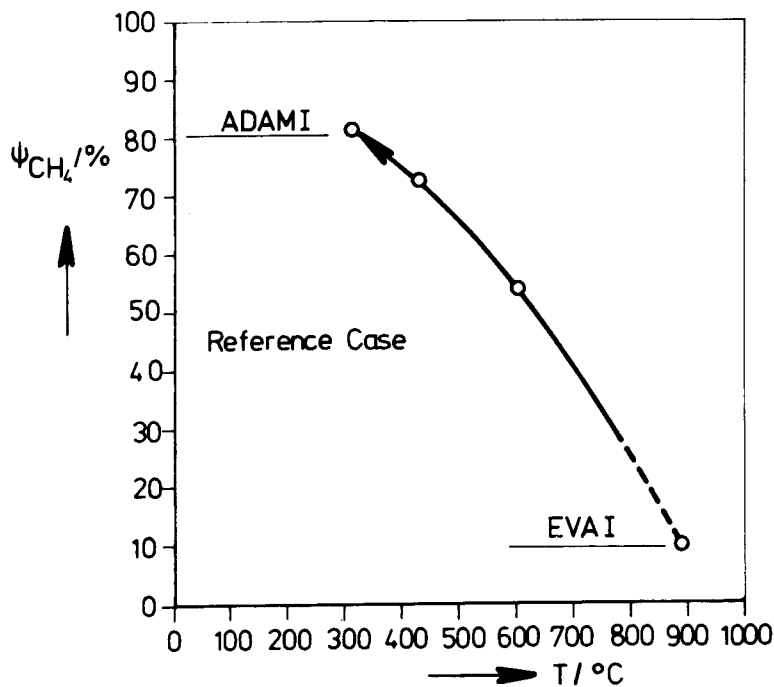

Fig. 4

Equilibrium Methane Formation

The data shown in Fig. 4 are based on a product gas resulting from the steam reforming of natural gas with a H_2O : CH_4 - ratio of 3 : 1, at a reformer outlet temperature of 800 $^{\circ}C$ and a pressure of 30 bar /15/. In the following discussion, these conditions are described as the reference case. The relatively high methane content of the gas (10 %) when leaving the reforming plant results from these parameters; it should also be recognized that the Dutch natural gas supplied to EVA I contains 14 % nitrogen.

3.1 Adiabatic Methanation Process

Since the formation of methane and the removal of heat takes place over a temperature range from about 800 $^{\circ}C$ to 300 $^{\circ}C$, it appears to be reasonable to start the methanation reaction in an adiabatic fixed bed at a temperature of about 300 $^{\circ}C$. A process gas inlet temperature of considerably less than 300 $^{\circ}C$ is not possible because of the carbonyl formation resulting from a reaction between the carbon monoxide of the process gas and the catalyst metal. The reaction heat liberated heats the gas up to 785 $^{\circ}C$; at this temperature, thermodynamic equilibrium conditions are achieved. This adiabatic temperature level can easily be increased up to 850 $^{\circ}C$ if the reforming conditions are changed. Even higher temperature levels are possible if the nitrogen content in the natural gas is reduced or if the inlet temperature in the methanation stage is raised.

The heat flow diagram (Fig. 5) - with the process gas temperature in $^{\circ}C$ on the ordinate and the heat flow in KJ/s on the abscissa - illustrates this case for the EVA I reference data mentioned above. This heat flow diagram is based on equilibrium conditions, depending on the process gas temperature /16/. If the gas is cooled from 785 $^{\circ}C$ to 300 $^{\circ}C$, it is· possible to recover heat at a rate of about 120 KJ/s. In a second adiabatic stage, a temperature of T = 659 $^{\circ}C$ is achieved and this, by means of a second heat exchanger, gives rise to a heat removal rate of 90 KJ/s. The
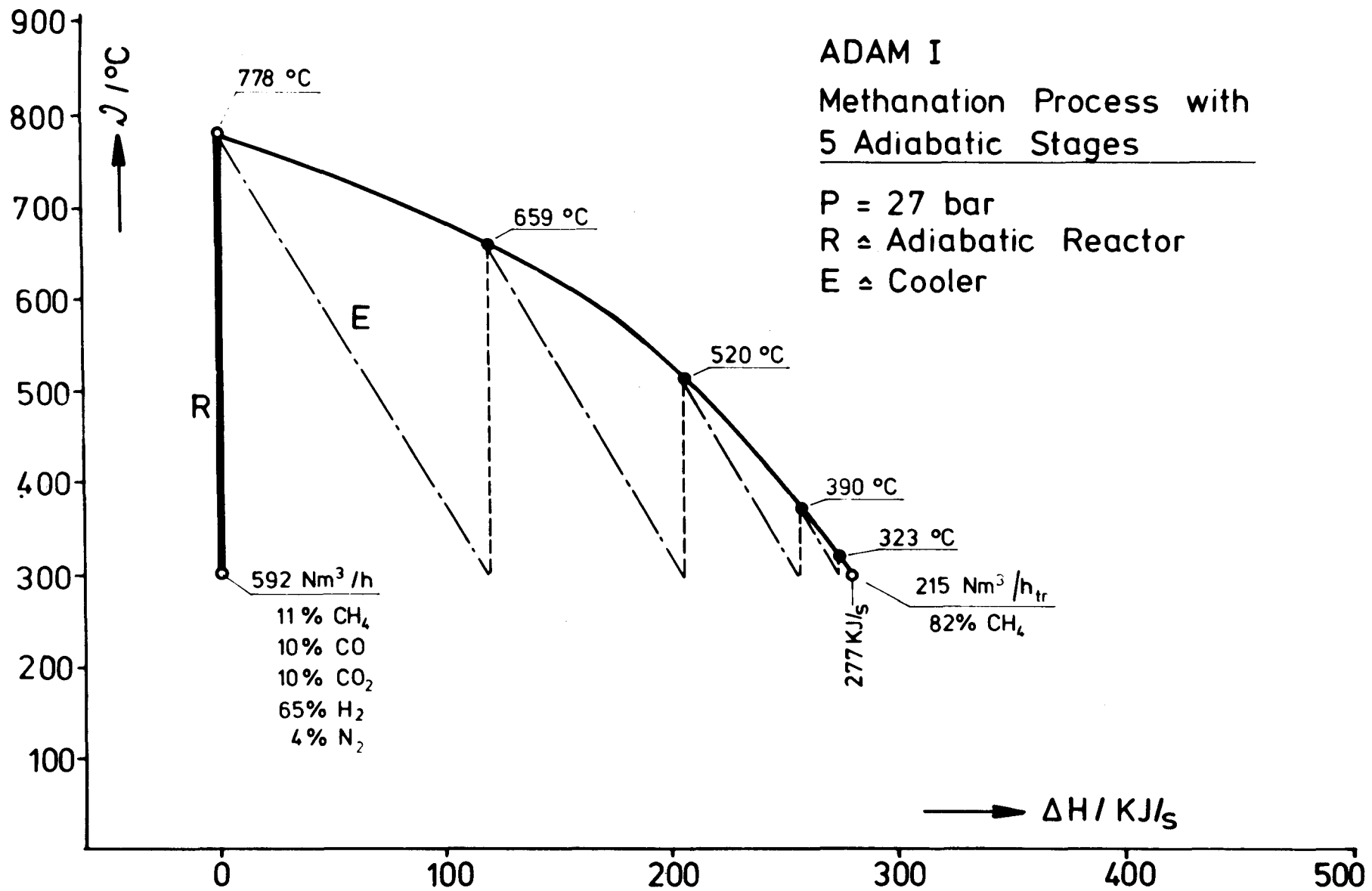
Fig. 5:   Heat Flow Diagram   -   ADAM I

Methanation Process with 5 Adiabatic Stages

continuation of this procedure results in a five-stage process with a total rate of heat removal of 277 KJ/s. Taking into account the amount of heat used for preheating the feed gas and an outlet temperature of no less than 70 $^{\circ}$C, 35 % of the recoverable heat can be removed after the first stage. The overall curve in Fig. 5 connects all the adiabatic stages at the highest adiabatic temperature level.

In the light of existing technology, however, this "straight-through methanation" has to be viewed rather critically. In particular, there is no appropriate catalyst available on the market which shows sufficient activity at low temperatures (about 300 $^{\circ}$C) and which, at the same time, is sufficiently economical with regard to loss of activity and strength, so that it can be used for the whole temperature range from 300 $^{\circ}$C to 800 $^{\circ}$C.

3.2 Adiabatic Methanation Process with Product Gas Recycling

The concept of utilizing the NUCLEAR LONG-DISTANCE ENERGY SYSTEM under certain circumstances involves the minimum requirement that steam for electricity production is supplied at a temperature of T = 540 $^{\circ}$C and at a pressure of P = 110 bar. Considering the heat transfer for the steam generation process, this means a minimum process gas temperature of 600 $^{\circ}$C. Thus, a procedure has to be found which allows temperature control up to this level.

There seems to be sufficient evidence that a temperature range for the methanation stage between 300 $^{\circ}$C and 600 $^{\circ}$C is technically feasible, using appropriate catalysts with economic performance.

These arguments led to a methanation system which is based only in part on the five-stage "straight-through methanation" process described above. In this new system, the first stage is characterised by a maximum temperature of 600 $^{\circ}$C which could be obtained by using one of the following four procedures:

- a kinetic procedure,
- an internal cooling system,
- steam addition,
- product gas recycling.

Certain problems will have to be taken into account in connection with these:

The kinetic procedure, in which the reaction does not lead to equilibrium conditions at the end of the catalytic reaction bed, will give rise to difficulties when the system is to be regulated or when the catalyst is ageing.

The internal cooling system is likely to be difficult to control because of changeable heat transfer conditions brought about by the migrating reaction zones caused by catalyst ageing. This means that the regulation of the system and the control of the temperature peaks in the catalyst bed are likely to be rather difficult.

Steam addition requires considerable investments since, for example, the adiabatic maximum gas temperature of 785 ^{o}C can be reduced to 650 ^{o}C only if at least 300 kg/h of steam are added to 300 kg/h of ADAM I feed gas. In addition, the steam sensitivity of the catalysts needed might also be a problem.

Product gas recycling is a possible procedure for controlling the temperature in the first stage, although such a system requires the additional installation of a compressor.

Such a methanation system with product gas recycling from the first stage and two subsequent adiabatic stages, each with intermediate cooling, is intended as a first design for ADAM I. Later, there will also be a possibility to test one of the other procedures or combinations of these.

In the heat flow diagram (Fig. 6), this methanation system (Fig. 7) shows the following characteristics:

About 600 Nm^3/h of dry feed gas are mixed with about 1 000 Nm^3/h of the product gas from the first stage so that the heat production is restricted to an increase in temperature from 300 $^{\circ}C$ to 600 $^{\circ}C$ in the first adiabatic reactor (R 101). With subsequent heat removal, it is already possible to set free more than 50 % of the recoverable heat. Thus, the next two adiabatic reaction stages without recycling (R 102, R 103) are essentially designed for final methanation. In the second and third stage, the maximum temperature levels are 436 $^{\circ}C$ and 302 $^{\circ}C$ respectively.

Typical data are shown in the following table for the reference case, both for the steam reforming side and for the methanation side with recirculation from the first stage.

Tab. 1 EVA I - ADAM I /16/

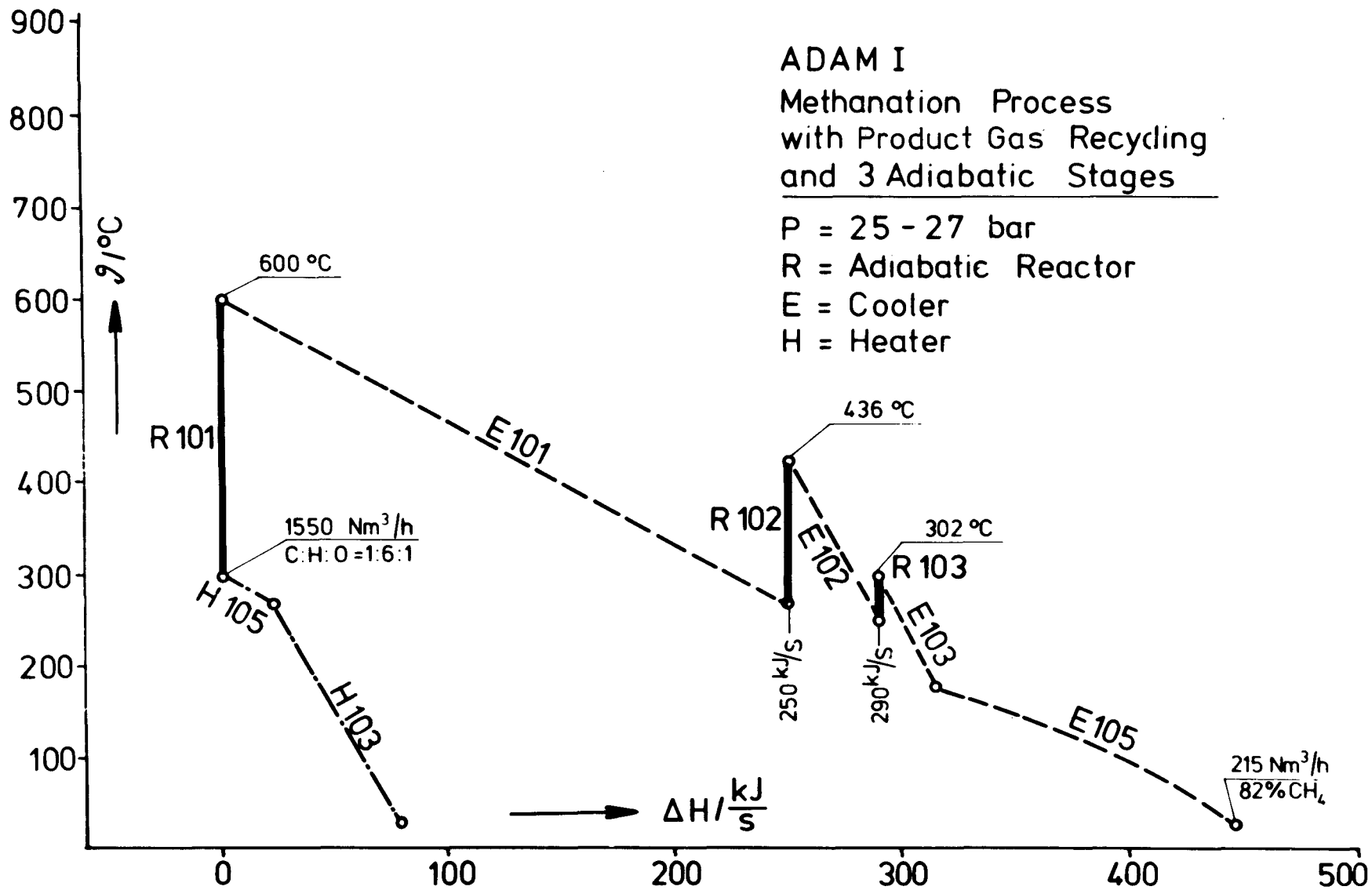|	E V A I			A D A M I				
	D 1 in	D 1 out	Product	R 101 in	R 101 out	R 102 out	R 103 out	Product
Gas/Nm^3/h	688	915	592	1550	1369	382	373	215
Press./bar	31	30	29	27.5	27	26	25	25
Temp./$^{\circ}C$	450	800	30	300	600/ 270	436/ 250	302/ 190	30
H_2O/Mol %	69.83	35.25	-	18.63	30.18	39.12	42.61	-
CH_4/Mol %	25.51	7.16	11.06	27.59	37.82	44.68	47.09	82.05
CO /Mol %	-	6.67	10.31	4.67	1.18	.05	-	-
CO_2/Mol %	0.60	5.92	9.14	6.51	4.88	2.57	1.42	2.47
H_2 /Mol %	-	41.91	64.73	36.55	19.10	6.19	1.32	2.29
N_2 /Mol %	4.07	3.09	4.76	6.05	6.84	7.38	7.57	13.18
Heat/KJ/s	-	-	-	-	250	40	20	133

Fig. 6   Heat Flow Diagram - ADAM I

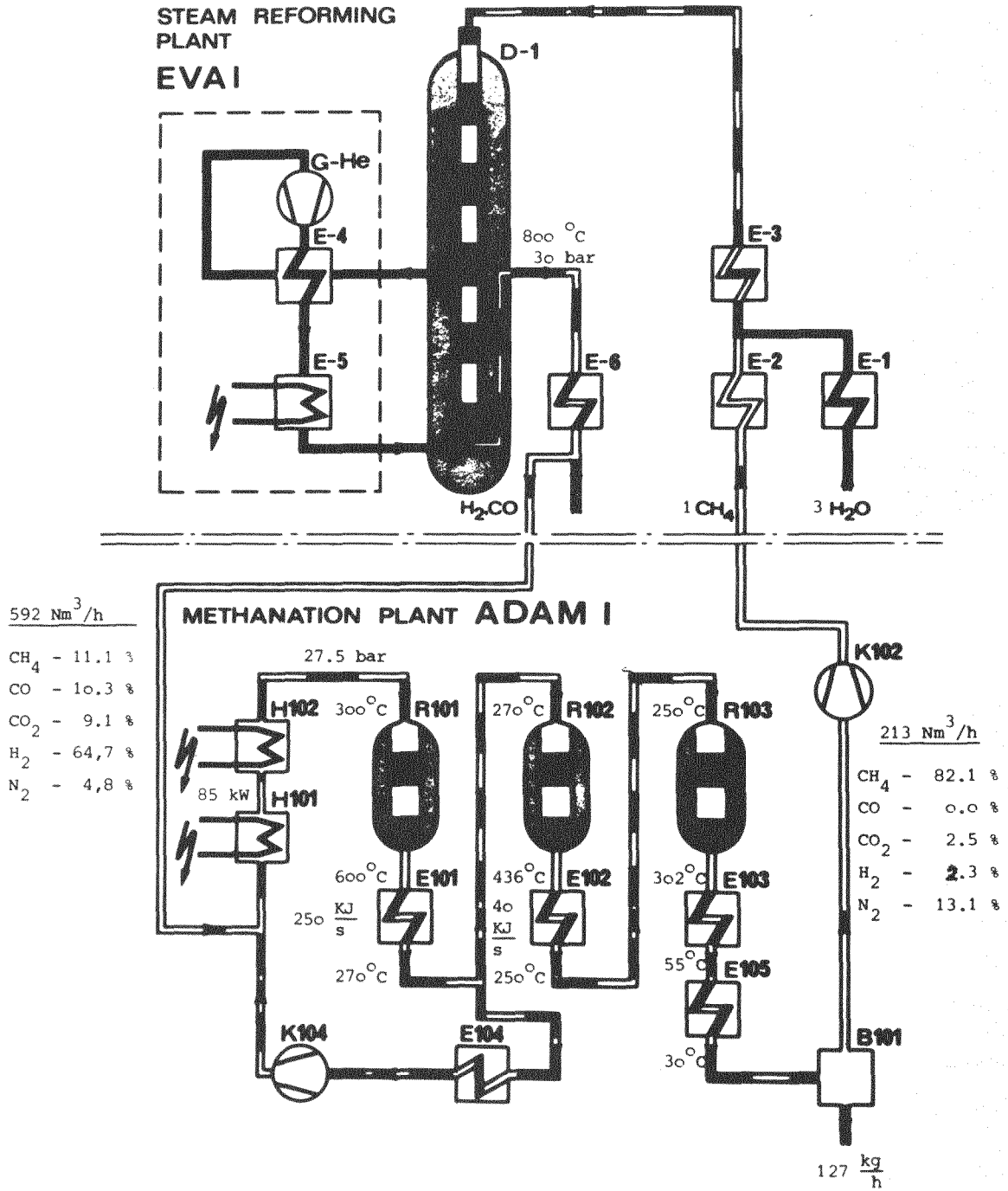Methanation Process with Product Gas Recycling and 3 Adiabatic Stages

Fig. 7

Pilot Plant Circuit: EVA I - ADAM I with Product Gas Recycling

The system is slightly different if the process gas is not recycled from the first stage but from the third stage. In this case, the mass ratio between recycling gas and feed gas is reduced to 1.4 : 1. This implies, however, that the heat removal after the first stage over a temperature range from 600 $^{\circ}$C to 280 $^{\circ}$C is also reduced.

The advantages and disadvantages of these two procedures - or of other procedures - for future industrial application will ultimately depend on how much heat is required and at what temperature level and for which form of energy consumption it is needed. The consumer situation has to be analyzed before an industrial application of a methanation plant can be optimized with regard to the number of stages, temperature control, and heat removal systems.

4. RESEARCH PROGRAM

The research program to be carried out in the pilot plant EVA I - ADAM I will be initiated in summer 1978 with the start of ADAM I. Initially, the pilot plant EVA I will supply the methanation plant ADAM I with synthesis gas in order to test the different plant units and the whole methanation process with 3 stages. In 1979, the EVA I - ADAM I circuit will be closed in order to test its dynamics under typical NFE conditions. Within the framework of this research program, it seems to be possible to provide an answer to the following basic problems:

- catalytic fixed bed stability as a function of catalyst activity, gas flow, space velocity, and regulation;
- catalyst performance;
- heat control;
- starting conditions;
- operational breakdown;

- dynamics of the methanation process as a function of the make up gas quality, inlet temperature, and process pressure;
- dynamics of the NFE system as a function of different methane steam reforming conditions and decreased total gas flow.

5. METHANATION CATALYSTS

Methanation catalysts have been in use for more than 25 years in connection with ammonia synthesis. At present, attempts are being made to develop these catalysts for use in the production of Substitute Natural Gas (SNG) based on rich gas and coal gasification as well as for use in the NFE system.

In case of hydrogen production for ammonia synthesis on a steam reforming basis, the dry steam reforming product gas still contains about 0.5 % carbon monoxide. The removal of this rest of carbon monoxide before the ammonia synthesis requires a catalytic methanation at temperatures of less than 300 $^{\circ}$C with subsequent gas purification. In this case, the resulting heat production is very low. There are available many catalysts which are appropriate for the process characterised by low CO content in the feed gas and low temperature levels. However, the situation is slightly different if a gas with high methane content is produced on the basis of

- rich gas (CRG - SNG),
- gas from coal gasification (C - SNG), or
- gas from synthesis gas (NFE)

via a methanation process. In these cases, the CO/CO_2 content in the feed gas is higher than 10 Vol %, and this means both more heat production in . the catalytic reaction system and higher temperature levels.

Considering this new field of catalyst development, many projects have recently been initiated to develop catalysts with the following characteristics:

- carbon and sulphur stability;
- high temperature stability
  - SNG: $T \leqslant 500\ ^{\circ}C$
  - NFE: $T \geqslant 650\ ^{\circ}C$;
- stability in steam atmospheres;
- stability of mechanical strength.

Within the framework of these requirements, the following catalyst developments have been initiated or continued:

- metal on a support material (see patent literature);
- Raney Nickel (Bureau of Mines, USA);
- metal from Ni (CO_4)-decomposition /12/.

The results achieved so far are included in the literature on the pilot plants for SNG production on the basis of rich gas and coal gasification (see 6.).

Because of the higher temperature level required for the methanation process within the NFE system (in order to produce superheated steam), the catalyst development for the NFE project encounters particularly complex problems which - especially as far as the influence of temperature, steam or carbon formation on the ageing process of the catalysts is concerned - go far beyond the difficulties to be solved with regard to catalyst parameters for SNG production.

6. OTHER PILOT PLANTS FOR METHANATION PROCESSES

Throughout the world, there are various methanation pilot plants based on catalytic rich gas and coal gas which are either on stream or still under construction. Although the NFE project involves different parameters with regard to gas composition, heat removal, and temperature level, some of these plants will be compared with the NFE system (see Table 5).

6.1 SNG from Rich Gas

6.1.1 CRG Hydrogasification /18/

A recent development in the production of substitute natural gas is the CRG process, which the Gas Council is now offering for commercial use /17/. In this process, the CRG reactor is followed either by a hydrogasifier and one methanator or by two methanators with subsequent CO_2 removal. Fig. 8 shows the CRG double methanation process (on Naphtha basis) with a temperature increase of 88 $^\circ$C in the first methanator (300 $^\circ$C - 388 $^\circ$C) and 40 $^\circ$C in the second methanator (300 - 340 $^\circ$C). The catalyst used in the methanation stages is identical with the CRG catalyst used in the CRG reactor (450 $^\circ$C - 505 $^\circ$C). Table 2 shows some typical methanation data:

Table 2:   CRG Process - Pilot Plant - Methanation data /19/

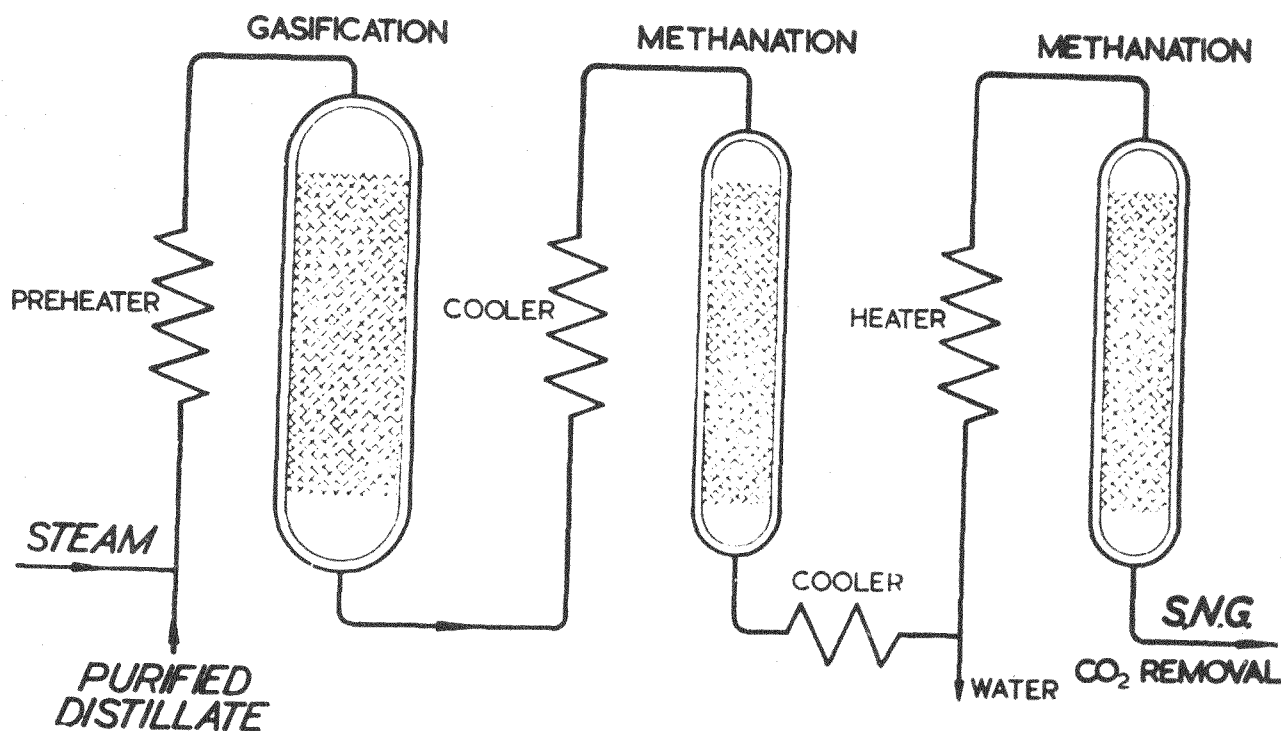|	Make up Gas	1. Stage in	out	2. Stage in	out	Product dry	CO_2-out
Temperature/$^\circ$C		300	388	252	292	30	30
Pressure/bar	25						
CH_4 / Mol %	37.25	37.25	41.3	68.7	72.5	77.75	98.3
CO / Mol %	0.9	0.9	0.15	0.25	-	-	-
CO_2 / Mol %	13.1	13.1	12.2	20.35	20.25	21.70	1.0
H_2 / Mol %	10.05	10.05	2.65	4.45	0.5	0.55	0.7
N_2 / Mol %	-	-	-	-	-	-	-
H_2O / Mol %	38.70	38.70	43.70	6.25	6.75	-	-

Fig. 8

CRG - Double Methanation Process

(Pilot Plant - Gas Council /19/)

6.1.2 Gassynthan (BASF/Lurgi) /20/

The Gassynthan process provides a possibility to produce SNG. A SNG plant involves naphtha desulfurization, naphtha catalytic reforming with steam to rich gas, the methanation of rich gas (H_2 and CO_2) and the removal of CO_2 in order to achieve the desired gas quality. The rich gas from the rich gas stage contains H_2 (~ 15 % dry) and CO_2 (~ 22 % dry). The wet methanation in the adiabatic methanator increases the temperature by 50 $^{\circ}$C at a temperature level of about T = 300 $^{\circ}$C. The reaction takes place on a catalyst similar to, or identical with, the rich gas catalyst which establishes equilibrium during methanation.
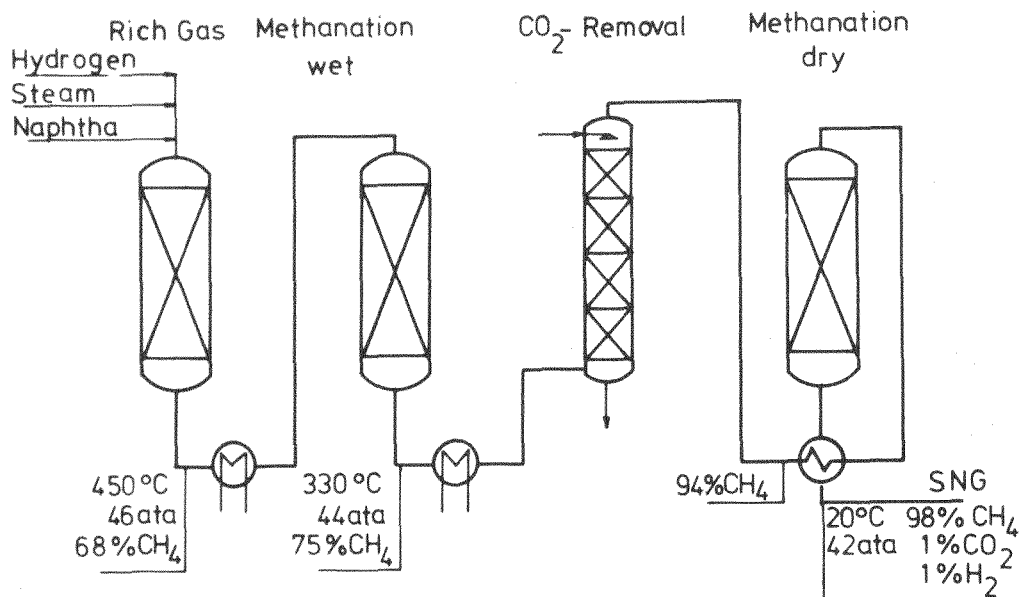
Fig. 9:

Gassynthan Process /27/

6.2 SNG from Coal Gas

6.2.1 Hygas Process /21/, /22/

In 1973, the first large-scale conversion of coal (3 t/h) to substitute natural gas was accomplished with the Hygas process pilot plant.

This process involves coal preparation, coal feeding, hydrogasification by steam and oxygen (at about 1 000 ^{O}C), gas purification and methanation. The methanation process with two catalytic fixed beds and the IGT splitting coldgas recycle method for control of heat release (see Fig. 10), /22/, was started in April 1973. The packed bed downflow reactors were loaded with 1/4 x 1/4 in pellets of a Harshaw Chemical Company catalyst (Ni 0104 T, nickel-on-Kieselguhr).

Table 3 shows some typical methanation data for the Hygas process. In all pilot plant tests, the temperature in the first and second stage reactors has been kept within the necessary temperature limits (290 ^{O}C - 485 ^{O}C).

With the total space velocity of SV ≤ 5 000 1/h, the temperature profile was fully developed in the first stage within 75 cm of the top of the catalyst bed.

Table 3   Hygas - Pilot Plant - Methanation data /22/

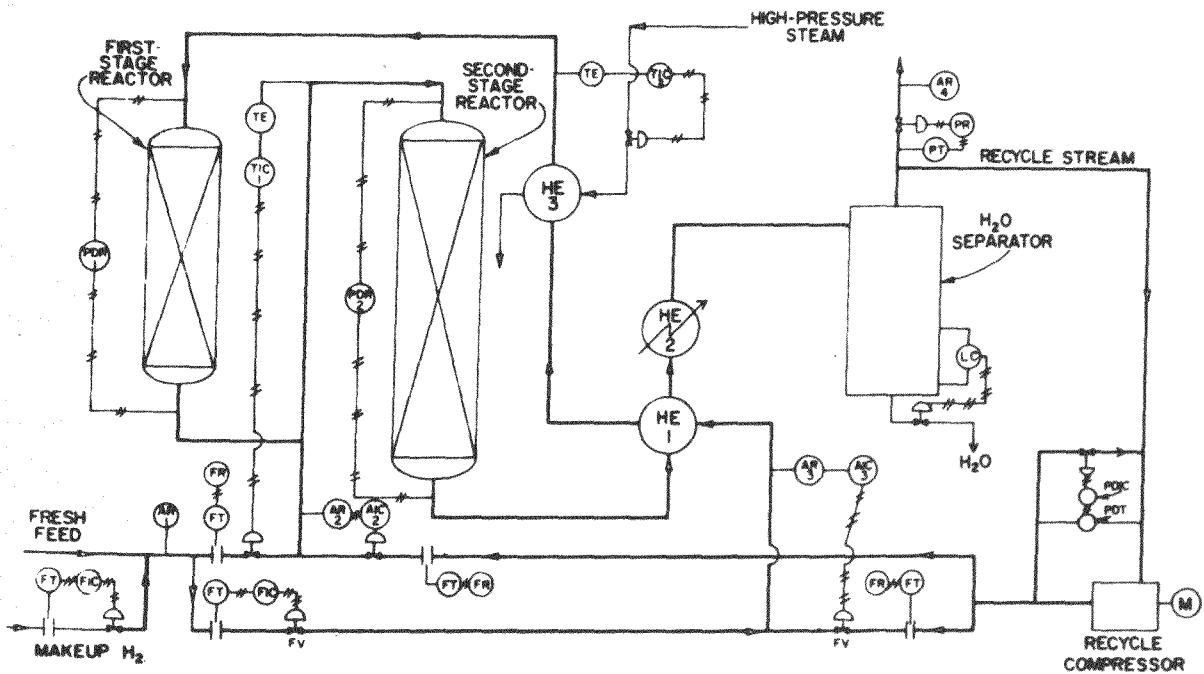|	Make up Gas	1. Stage in	1. Stage out	2. Stage in	2. Stage out	Product
Flow/Nm^3/h	430					
Temperature/^{o}C		285	430	280	380	30
Pressure bar	70					
CH_4 / Mol %	30.72					61.56
CO / Mol %	11.90					-
H_2 / Mol %	34.57					7.68
N_2 / Mol %	22.66					30.56
Ar / Mol %	0.15					0.23

Fig. 10

Hygas - Methanation Process (Pilot Plant /22/)

6.2.2 Lurgi Process /23/

Lurgi and South African Coal, Oil and Gas Corporation designed and erected a plant to demonstrate the overall process for the production of SNG by the methanation of gas from coal pressure gasification.

Fig. 11 shows the methanation pilot plant with two methanators, cold gas recycling from the first stage, and steam addition to both methanators. The temperature in the first and second stage reactors has been kept within the temperature limits of 300 - 450 $^{\circ}$C for the first 1 500 operating hours and of 260 - 450 $^{\circ}$C for the second operating period up to 4 000 hours. For this process, a special methanation catalyst was developed by BASF. Table 4 shows some typical methanation data.

Table 4   Lurgi - Pilot Plant - Methanation data /23/

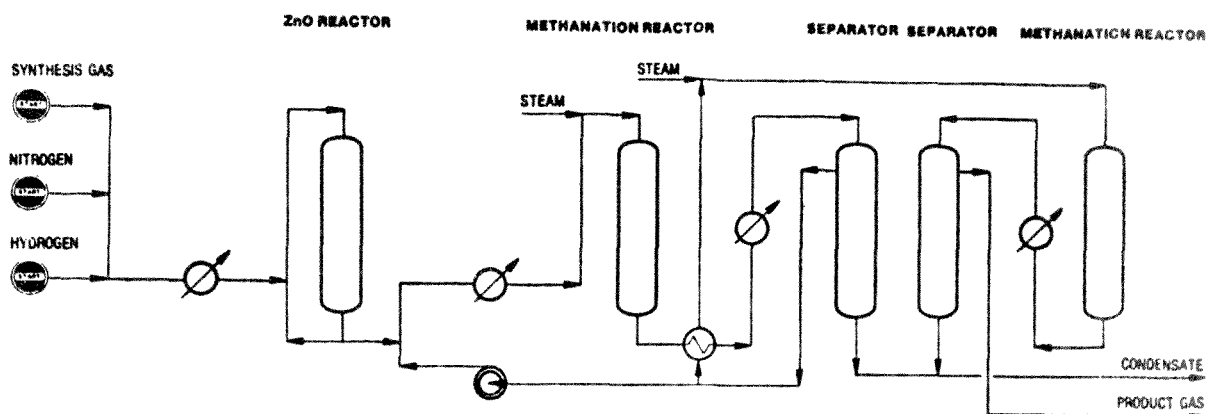|	Make up Gas	1. Stage in	1. Stage out	2. Stage in	2. Stage out	Product
Flow/Nm^3/h	20	105.4	99.2	8.6	8.5	7.8
Temperature/$^{\circ}$C	270	300	450	300	365	30
Pressure / bar	18					
CH_4 / Mol %	9.8	51.6	66.8	66.8	75.1	75.1
CO / Mol %	10.7	3.2	0.4	0.4	0.05	0.05
CO_2 / Mol %	15.9	19.8	21.2	21.2	21.2	21.2
H_2 / Mol %	62.5	23.6	9.6	9.6	1.7	1.7
N_2 / Mol %	0.9	1.7	2.0	2.0	2.0	2.0
H_2O $\frac{Vol}{Vol\ dry\ gas}$	-	0.42	0.58	0.04	0.08	-

Fig. 11

Lurgi - Methanation process (Pilot plant /23/)

6.2.3 Bi-Gas Process /24/

The Bi-Gas process is designed for the production of substitute natural gas by coal gasification and final methanation. The total process will be tested in Homer City by the gasification of 5 t coal/h. Among its several unit operations, one of the major steps is tested in a separate pilot plant - the fluidized-bed reactor for catalytic methanation - by Bituminous Coal Research (BCR). The objective of the BCR methanation program is to find the right combination of catalyst and operating conditions to effect a high conversion of carbon monoxide to methane in a single pass through methanation reactor. **Fig.** 12 shows the methanation pilot plant (PEDU) with one fluidized-bed reactor and an internal cooling system.

The feed from the coal gasification to the methanation has the following approximate composition:

CH_4	-	20.0 Mol %
CO	-	19.3 Mol %
CO_2	-	0.2 Mol %
H_2	-	59.5 Mol %
N_2	-	0.9 Mol %
H_2O	-	0.1 Mol %

For this gas composition, the average temperature in the fluidized-bed reactor of the pilot plant (PEDU) is about T = 500 ^{o}C. The product gas contains for one of the test runs at

T	-	500	^{o}C
P	-	86	bar
V	-	67	Nm^3/h
CH_4	-	49.0	Mol %
CO	-	3.8	Mol %
CO_2	-	7.4	Mol %
H_2	-	37.2	Mol %
C_2H_6	-	2.5	Mol %
C_3H_8	-	0.1	Mol %

These results are achieved with a methanation catalyst from Harshaw Chemical Company at a space velocity of SV = 2240 h^{-1}.
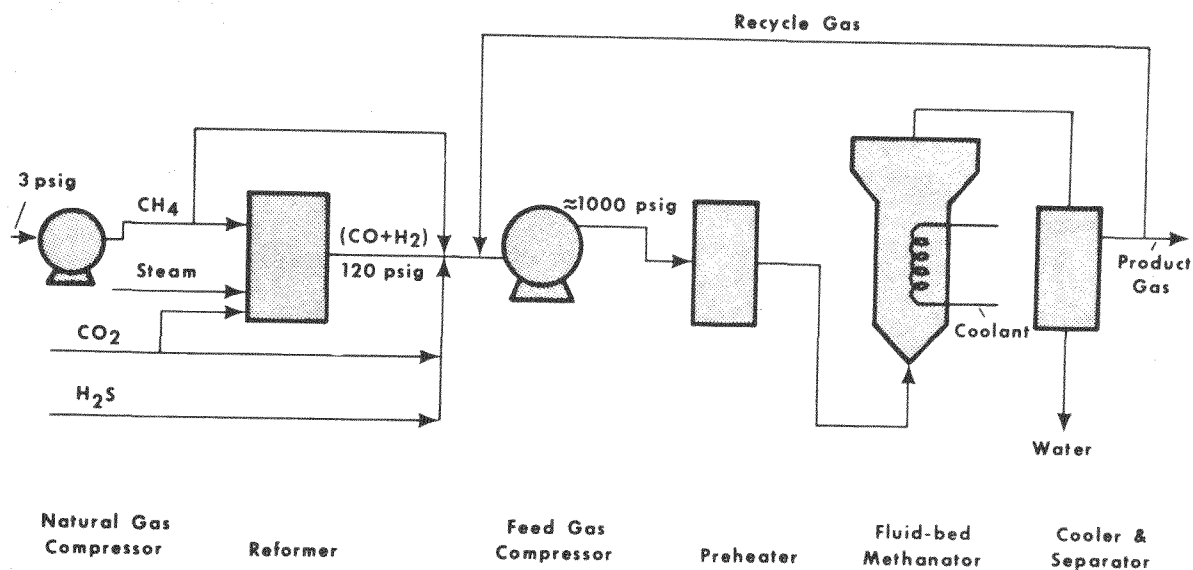
Fig. 12

Bi-Gas Process (Methanation Pilot Plant /24/)

6.2.4 One Stage Shift - Conversion and Partial Methanation Process /25/

Thyssengas designed and erected a pilot plant to demonstrate the one stage shift-conversion and partial methanation process as part of the SNG-production process on a coal gas basis. Influenced by the work of BCR, Thyssengas decided to test a fluidized-bed with an internal cooling system. Fig. 13 shows the flow diagram of this pilot plant. The pilot plant, which was started in 1977, has the following parameters:

Gas composition:

CH_4	-	0	-	5 Mol %
CO	-	25	-	50 Mol %
CO_2	-	0	-	6 Mol %
H_2	-	45	-	75 Mol %
N_2	-	0	-	2 Mol %

Process conditions:

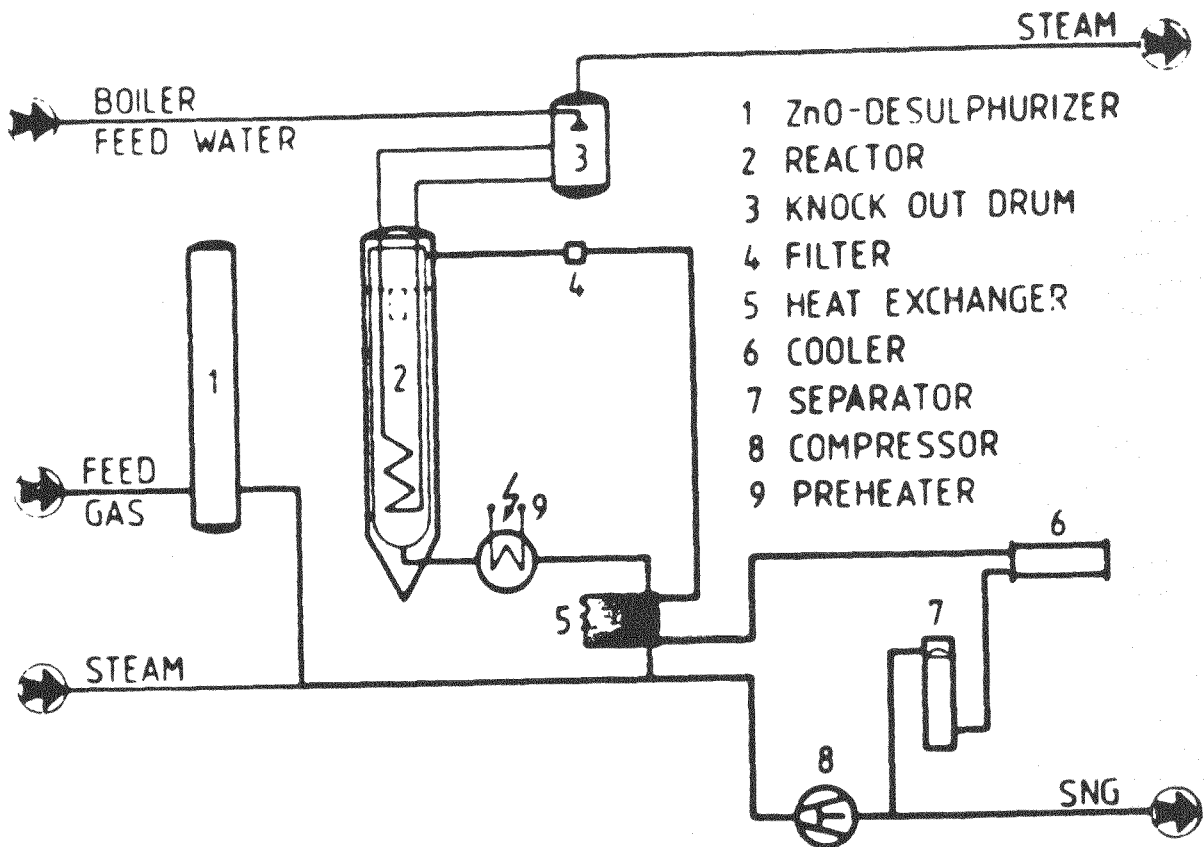|		
Temperature / °C	-	300 - 500
Pressure / bar	-	30 - 65
Steam / Feed Ratio	-	0 - 0.5
Recycle / Feed Ratio	-	0 - 2
Feed Gas / Nm^3/h	-	800

Fig. 13

Thyssengas Methanation Process (Pilot Plant /25/)

6.2.5 Haldor Topsoe Methanation Process - TREMP (26)

The Haldor Topsoe A/S methanation process, TREMP, has been developed for the manufacture of SNG from coal. It is a high pressure fixed-bed process with three adiabatic beds in series. The first bed operates at a maximum temperature of 600 to 650 $^{\circ}$C, whereas the hot and wet recycle stream and the fresh feed enter the reactor at 300 $^{\circ}$C. The high outlet temperature makes it possible to raise high pressure steam (up to 100 bar) and to use low recycle ratios. The effluent of the first bed is passed once through over two beds for final adjustment of the gas composition. The gas is cooled between the beds. After the final cooling of the gas for removal

of product water, it is withdrawn as product gas (see Fig. 14).

The process has been demonstrated in a pilot plant (one stage) using cracked methanol and hydrogen as feedstock. One run included a period of 7 000 hours' satisfactory operation.

6.2.6 Pilot Plants for Methanation

Table 5 shows some typical data from methanation pilot plants as far as substantial experimental results could be obtained.

In order to give a complete description of the methanation processes on a rich gas basis, it should be mentioned, however, that there is also the Methane Rich Gas process /28/ /29/   for SNG production which could not be discussed in detail.

With regard to processes for SNG production on the basis of coal gasi-fication in addition to table 5 the following two processes should be mentioned: RMP-process (Ralph M. Parsons Company) with 7 methanation stages and a steam / gas ratio of more than one /30/ and the Liquid Phase Methanation (LMP)-process (Chem. Systems Inc.) operating at low tem-peratures /31/.
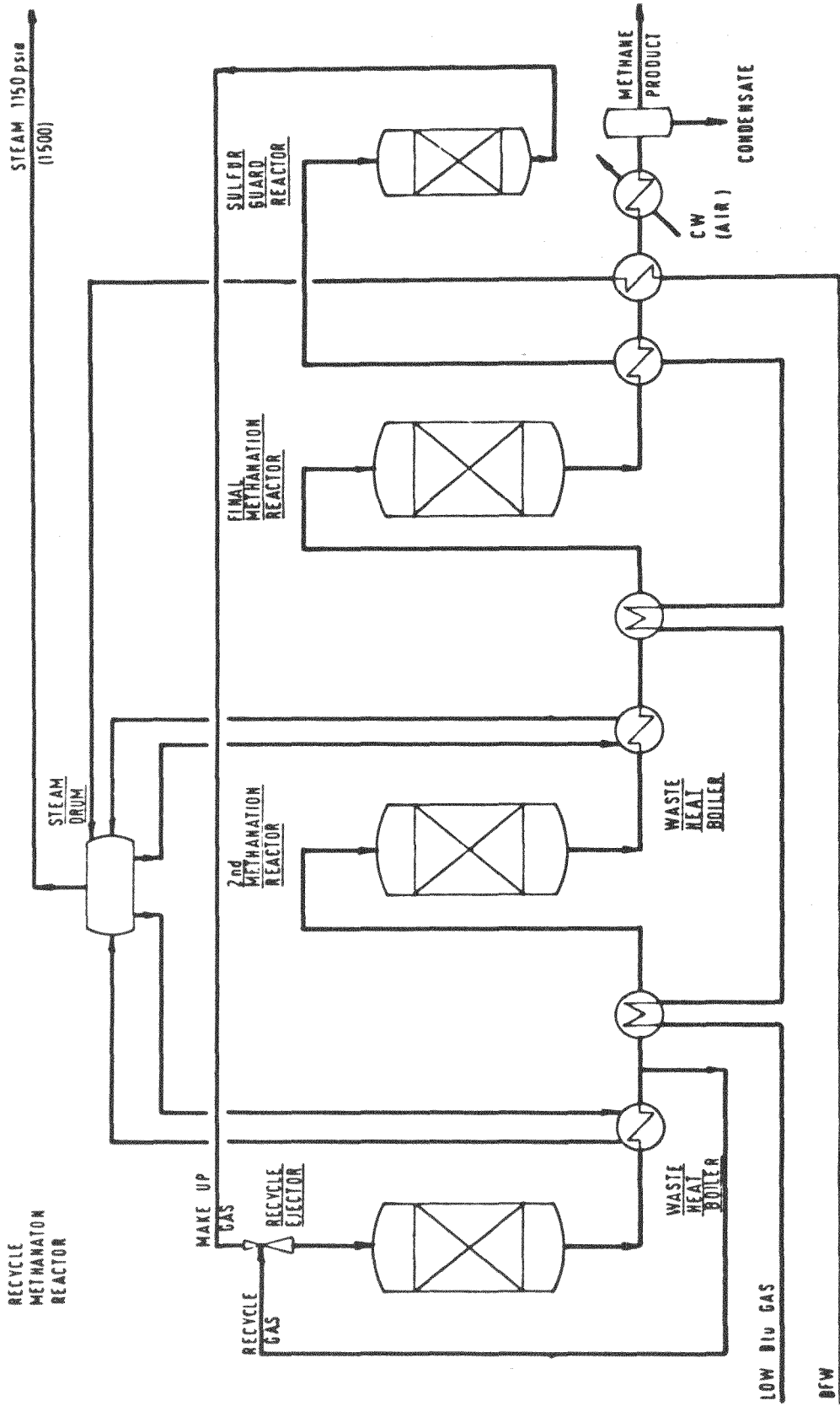
Fig. 14   Haldor Topsoe Tremp Process /26/

Table 5: Pilot Plants for Methanation Processes

Company	Process Make up from	Process Methanation Operation	Process Press. bar	Process Temp. Max. $^\circ$C	Plant Make up Nm^3/h	Inlet $\dfrac{H_2}{CO+CO_2}$	Plant Stages	Plant Operation	Object	Lit.
Gas Council	CRG (Naphta)	Wet, Dry	25	400		$\dfrac{10}{14}$	2	1968	SNG	19
Lurgi/BASF	Gassynthan (Naphta)	Wet, Dry	47	330		$\dfrac{15}{22}$	2		SNG	27
IGT (USA)	Hygas C-gasif.	Recycling	70	450	430	$\dfrac{35}{12}$	2	1973	SNG	21/22
Sasol/Lurgi	Lurgi C-gasif.	Recycling H_2O-Add.	18	450	20	$\dfrac{63}{27}$	2	1972	SNG	23
Topsoe	C-gasif.	Recycling	30	650	14	$\dfrac{66}{33}$	1	1974	SNG	26
BCR (USA)	Bi-Gas C-gasif.	Fluid.Bed.	86	530	80	$\dfrac{60}{20}$	1	1974	SNG	24
Thyssengas Didier Eng	C-gasif.	Fluid.Bed. H_2O-Add.	65	500	800	$\dfrac{75}{25}$	1	1977	SNG	25
KFA Jülich Topsoe	CH_4-Reforming	Recycling ADAM I	30	600(800)	600	$\dfrac{65}{20}$	3	1978	NFE	this report
KFA Jülich Lurgi	CH_4-Reforming	Recycling ADAM II	45	650	9000	$\dfrac{68}{20}$	3	1979	NFE	

7. CONCLUSION

In the foregoing report, the attempt has been made to give from an engineering point of view a description of the NUCLEAR LONG-DISTANCE ENERGY CIRCUIT for the example of a combined steam-reforming / methanation reaction system. The report describes the pilot plant ADAM I, at present under construction in Jülich, and points out the fundamental problems involved in the methanation process within the NFE system, as well as possible solutions. In addition, the report indicates that many of the experiences achieved so far with other methanation pilot plants as part of SNG production processes will be helpful to the research work carried out within the framework of the NUCLEAR LONG-DISTANCE ENERGY PROJECT.

BIBLIOGRAPHY

/1/   Bundesministerium für Forschung und Technologie

- Redaktion G. Dietrich, Kernforschungsanlage Jülich GmbH

Einsatzmöglichkeiten neuer Energiesysteme

Programmstudie "Sekundärenergiesysteme"

Teil IV: Fernenergie

Bonn 1975

/2/   Kernforschungsanlage Jülich GmbH - Programmgruppe:

Systemforschung und Technologische Entwicklung

Programmstudie "Sekundärenergiesysteme"

JÜL-1148-Se 1974, S. 9

/3/   High Temperature Reactor for Process Heat Applications

Nuclear Engineering and Design

Vol 34 (1975 No. 1, P. 1-49

North Holland Publishing Company

Amsterdam, The Netherlands

/4/   Nürnberg, H. W.; Wolf, G.: Dt. Pat. OS 160 1 001,

angem. 17.2.67; KFA-Jahresbericht 1967, S. 174;

US-Pat. 355 8 047; GB-Pat. 121 8 928; FR-Pat. 157 2 234;

IT-Pat. 836 485; Austral.-Pat. 33692;

angem. Febr. 1968; Nürnberg, H. W.: ACHEMA-Jahrbuch

1974/76, Bd. I, S. 259

/5/   Hilberath, F.; Teggers, H.

Dt. Pat. 129 8 233,

angemeldet am 16.1.68

/6/   **Harth, R.**

Das Projekt Nukleare Fernenergie

Jahresbericht 1975

Kernforschungsanlage Jülich GmbH 1976, S. 15 ff

/7/   Harth, R.; Nießen, H.F.; Theis, K.A.

Nukleare Fernenergie - ein Verfahren zum Transport von

Hochtemperatur-Kernreaktorwärme

Reaktortagung 1976, Düsseldorf

Deutsches Atomforum e.V. (DAtF)

Kerntechnische Gesellschaft im DAtF

/8/   Boltendahl, U.; Nießen, H.F.; Theis, K.A.

Transport von Kernwärme mit Hilfe chemisch gebundener

Energie

gwf-gas/erdgas 117 (1976), H. 12, S. 517 ff.

/9/   Nürnberg, H.W.; Wolff, G.

Nukleare Fernenergie

Die Naturwissenschaften 63 (1976), H. 4, S. 190

/10/   PNP-Prototypanlage Nukleare Prozeßwärme

Status-Bericht zum Ende der Konzeptphase

Bergbau-Forschung GmbH

Gesellschaft für Hochtemperatur-Technik mbH

Hochtemperatur-Reaktorbau GmbH

Kernforschungsanlage Jülich GmbH

Rheinische Braunkohlenwerke AG

1976, S. 81

/11/   Harth, R.; von der Decken, C.B.; Fehlhaber, K.

Large Scale Experimental Tests of the Heat Linkage between

HTR and Steam-Methane Reforming Process.

"The High Temperature Reactor and Process Applications"

British Nuclear Energy Society, Int. Conference, 1974, London

/12/   Fedders, H.; Harth, R.; Höhlein, B.

Experiments for Combining Nuclear Heat with the Methane

Steam Reforming Process

Nuclear Engineering and Design 34 (1976), No. 1, S. 119 ff.

/13/   Höhlein, B.; von der Decken, C. B.

        Basic Studies for the Reformer Calculation Model

        "The High Temperature Reactor Process Applications"

        British Nuclear Energy Society Int. Conference, 1974, London

/14/   Höhlein, B.

        Zweidimensionales, einphasiges Reformermodell

        Unveröffentlichtes Rechenprogramm

        Kernforschungsanlage Jülich GmbH

/15/   Neis, H.

        Gleichgewichtsprogramm für die Methanspaltung mit Wasser-
        dampf

        IRE-5-72, Februar 1971

        Kernforschungsanlage Jülich GmbH

/16/   Höhlein, B.; Bauer, A.; Kraut, G.; Scherbericht, F. D.

        Thermodynamische Berechnung eines Fernenergie-Kreislaufes

        JÜL-1232, August 1975

        Kernforschungsanlage Jülich GmbH

/17/   British Gas Corporation

        International Consultancy Service London, England

        Substitute Natural Gas

        Process Flow Sheets

/18/   Lacey, J. A.

        CRG-based SNG

        Principles and Process Routes

        Gas Council

        Midlands Research Station

/19/   Davies, H. S.; Lacey, J. A.; Thompson, B. H.

        Processes for the Manufacture of Natural-Gas Subsitutes

        Gas Council

        Midlands Research Station

        November 1968

/20/   Jockel, H.; Triebskorn, B.E.

Gassynthane process for SNG

Hydrocarbon processing

January 1973

/21/   Lee, B.S.

Hygas pilot yields operating data

The Oil and Gas Journal

February 11, 1974

/22/   Bair, W.G.; Leppin, D.; Lee, A.L.

Design and Operation of Catalytic Methanation in the Hygas

Pilot Plant

Institute of Gas Technology, Chicago, Illinois (1974)

Paper presented at the American Chemical Society Division

of Fuel Chemistry (1974)

/23/   Moeller, F.W.; Robert, H.; Britz, B.

Methanation of Coal Gas for SNG

Hydrocarbon Processing

April 1974

/24/   Diehl, E.K.; Stewart, D.L.; Streeter, R.C.

Progress in Fluidized-Bed Methanation

Bituminous Coal Research, Inc., Monroeville, Pennsylvania

Paper presented at the Sixth Synthetic Pipeline Gas Symposium

Chicago, Illinois (1974)

/25/   Flockenhaus, C.; Lommerzheim, W.

One Stage Shift-Conversion and Partial Methanation Process

for Upgrading Synthesis Gas to Pipeline Quality

Thyssengas GmbH

Paper presented at the Ninth Synthetic Pipeline Gas Symposium

Chicago, Illinois (1977)

/26/   Haldor Topsoe A/S

The Haldor Topsoe Methanation Process TREMP

H. Topsoe A/S, Kopenhagen (1978)

NFE-Communication

/27/   Müller, W. D.; Möller, F. W.; Jockel, H.

Synthetisches Erdgas aus Erdöl und Kohle

to be published in "Erdöl-Erdgas Zeitschrift"

/28/   Ullmanns

Enzyklopadie der technischen Chemie

4. nachbearbeitete und erweiterte Auflage

Band 14, Gaserzeugung aus Kohle und Kohlenwasserstoffen

Verlag Chemie, Weinheim, 1977, S. 416

/29/   Ishiguro, T.

Hydrocarbon Processing

47 (1968), Nr. 2, S. 87 - 91

/30/   White, G. A.; Roszkowski, T. R.; Stanbridge, D. W.

The RMP-Process

The Ralph M. Parsons Company

Pasadena, California (USA)

/31/   Frank, M. E.; Sherwin, M. B.; Blum, D. B.; Mednick, R. L.

Liquid Phase Methanation / Shift

PDU Results and Pilot Plant Status

8th Synthetic Pipeline Gas Symposium

Chicaco, Illinois, October 1976

Figures 8 to 14 and

Tables 2 to 4

are borrowed from the literature quoted