

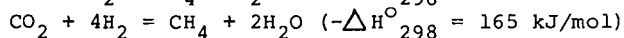
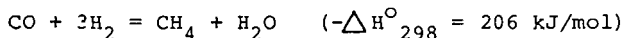
CATALYTIC ASPECTS OF HIGH TEMPERATURE METHANATION

Karsten Pedersen, Allan Skov and J.R. Rostrup-Nielsen

Haldor Topsøe Research Laboratories
Nymøllevej 55, DK-2800 Lyngby, Denmark

INTRODUCTION

Methanation of synthesis gas mixtures is an essential step in the manufacture of substitute natural gas (SNG):



The reactions are catalyzed by various metals of which supported nickel is preferred.

Methanation for SNG production is complex because the high concentrations of CO and CO₂ involved result in large potential temperature increases. This may cause sintering of the catalyst or for some cases a potential for carbon formation.

One solution is to include a recycle stream of product gas as a diluent. It is evident that this solution involves a loss of energy in the recycle operation, and that an economic process should allow minimum recycle. For an adiabatic process, however, this is equivalent to a large temperature increase.

Another solution is to carry out the methanation in a cooled reactor in which the heat of reaction is transferred from the reaction zone into a cooling medium, e.g. boiling water. For a cooled reactor, it appears advantageous to design for high "hot zone" temperatures, because this gives a better heat transfer.

When decreasing the operating temperature, the need for higher catalyst activity increases. Below a certain temperature the reaction will not "ignite". This problem may be aggravated because the catalyst having been exposed to the high temperature, may have to operate at the low temperature after ageing or poisoning of the catalyst at the reactor inlet.

Moreover, the steep temperature profile means that the operation temperature of a catalyst pellet may change 50-100°C within seconds in case of variations in load, recycle ratio and preheat temperature. This requires high mechanical stability of the catalyst.

Thus for adiabatic and for cooled reactors as well, in order to meet these process requirements, the catalyst should be active and stable both at high and low temperatures. This is a key problem to be solved when optimizing the methanation process for coal-based SNG.

The paper summarizes catalyst studies of important phenomena to be controlled in the development and use of an industrial catalyst meeting these requirements.

EXPERIMENTAL

The catalysts were studied in various test units. Sintering studies were performed in a tubular reactor ($D_i=32$ mm) in which various catalyst samples were exposed simultaneously to sintering at given temperature, pressure and atmosphere. Low temperature deactivation phenomena were studied in differential flow reactors ($D_i=0.8$ mm). The catalyst was used as 0.3 - 0.5 mm particles diluted with inert material. Standard activity tests, and determination of nickel surface areas were described earlier (1). The main part of the development work took place in a pilot plant with a 5 litre adiabatic reactor. The reactor had a full bed length (up to 2m) and operated at industrial mass velocities, leaving the reactor diameter as the only scale-up parameter. Catalyst samples from pilot tests were used for physical and catalytical examination.

RESULTS

Sintering

The methanation reaction on nickel requires a large ensemble of nickel atoms (2), and the specific activity is influenced by nickel crystallite size (3), by the composition of the support (4,5,6), and by non-linear poisoning effects (1). Therefore, the reaction appears sensitive to the structure of the catalyst and to its history of operation.

Sintering of the nickel crystals results in loss of surface area, and in principle recrystallization may change the nickel ensembles available, and hence cause a decrease of the specific activity. We showed previously (4,7) that heat treatment of nickel crystals on a stable low area ceramic support resulted in no sintering at 550°C over a period of 1000 hours, whereas the nickel surface area dropped to around 40 to 25% over the same period at 700°C and 850°C respectively, this result corresponds to the rule of Tammann, according to which sintering is expected above 0.5 times the melting point ($^{\circ}\text{K}$) (8) of the metal. The growth mechanism of supported metal crystals appears very complex (9,10). The growth rate might be influenced by the wetting properties of the metal to the support, and by the micropores of the support material. It was illustrated that the diffusion of a metal crystallite is impeded, when the size of the metal crystallite is of the order magnitude of the diameter of the pore (11,12). In general, the metal particles may hardly grow to a size larger than the pore diameter of the support. This means that a stabilized micropore system of the support effectively prevents sintering of the nickel crystals.

Nickel catalysts designed for low temperature operation are normally based on high area supports such as gamma alumina, silica, chromia, etc. These supports suffer from significant sintering, which may be accompanied by weakening when exposed to temperatures above 500°C (4,13). The sintering may be accelerated by high steam partial pressure (14). Figure 1 shows results from sintering tests at conditions for accelerated sintering (i.e. $\text{H}_2\text{O}/\text{H}_2=10, 30$ atm). Three catalysts are compared: a low area steam reforming catalyst, a high area low

temperature methanation catalyst ($\text{Ni}/\gamma\text{-Al}_2\text{O}_3$), and the Topsøe methanation catalyst MCR-type. The MCR catalyst maintains a high total surface area and mechanical strength, whereas the $\gamma\text{-Al}_2\text{O}_3$ based catalyst deteriorates. All catalysts show significant loss in nickel surface area at 800°C .

Carbon Formation

Thermodynamics predict carbon formation for methanation above a certain temperature, depending on feed composition and pressure. This may influence the minimum recycle ratio allowed, as illustrated in Figure 2. However, the thermodynamic data are influenced by the catalyst, because it modifies the structure of the carbon. This allows operation at conditions more critical than those, which correspond to the limit predicted on the basis of ideal graphite. We have shown previously (4,15) that this effect is favored by small nickel crystals in the catalyst.

In practice, this means that the so-called principle of equilibrated gas (1,4), (i.e. carbon formation when the gas shows affinity for carbon, after the establishment of the methanation and shift equilibria) predicts no carbon formation for methanation. The validity of this principle is indicated by the results in Table 1, obtained from thermogravimetric studies (1). The conclusion has been further confirmed by the experience in the pilot tests.

Low Temperature Problems

Low operating temperatures favor the adsorption of poisons, e.g. sulfur on the catalyst. We have shown that the effect of sulfur is strongly non-linear (1) reflecting that the methanation reaction is structure sensitive. This, and other studies (16,17), show that a sulfur content in the feed stream of less than 10 ppb is required to obtain a reasonable methanation activity after equilibration of the sulfur adsorption. Therefore, the effect of sulfur poisoning should rather be analysed in terms of a dynamic model for fixed bed adsorption (18).

The operation at a low recycle ratio or the straight-through operation in a cooled reactor, implies high partial pressures of carbon monoxide at the reactor inlet. This results in two problems.

At temperatures below 230°C , there is a substantial risk that carbon monoxide reacts with nickel, forming nickel carbonyl. Operation in this temperature range, with a partial pressure of carbon monoxide of 2.5 atm resulted in transport of nickel in the catalyst bed. Moreover, the formation of nickel carbonyl resulted in a drastic growth of the nickel crystals, up to particles of 20,000Å, thus exceeding, by large, the pore size of the catalyst support. This growth resulted in break-down of the catalyst. The forces involved appear much stronger than observed in thermal sintering of the nickel crystals, as described above.

Another result from operating with high partial pressure of carbon monoxide, appears to be a deactivation phenomenon, called β -deactivation developing slowly in some pilot tests, and being reflected by

the appearance of an inflection point in the axial temperature profile. Figure 3 illustrates the movement of the temperature profile, and that the β -deactivation disappears above a certain inlet temperature. The activity could be restored by treatment in hydrogen, as explained below.

The low temperature deactivation phenomena were further demonstrated by laboratory tests on a Ni/ η Al₂O₃ catalyst in a differential reactor. As shown in Figure 4, no deactivation was observed if CO was replaced by CO₂. The deactivation rate increases significantly with the CO/H₂ ratio and by the presence of sulfur. The role of sulfur on other deactivation phenomena was indicated in our earlier studies (1).

The MCR-2X catalyst shows much less deactivation than the Ni/ η Al₂O₃ catalyst. Analysis of the spent catalysts indicated by the growth of nickel crystals showed that the Ni/ η Al₂O₃ catalyst had also been exposed to carbonyl formation in contrast to the MCR-2X catalyst. The large influence of catalyst composition on deactivation rate and carbonyl formation was also reported by Vannice and Garten (6).

The β -deactivation is probably due to the formation of a less reactive carbon state on the nickel surface, which might be the β -state identified by Wise et.al. (19,20).

The situation corresponds to the deactivation observed in steam naphtha reforming at low temperatures (21), and to a general model for carbon formation on nickel (22). The adsorbed intermediate (α' -carbon) may either be gasified to methane (2,19) or be dissolved in nickel as carbon and form carbon whiskers (1), or be transferred into encapsulating carbon (β -carbon). For the present case, apparently the conversion of α' into β is too slow at very low temperatures, e.g. 250°C, whereas at high temperatures the rate of hydrogenation of β -carbon exceeds the transformation rate of α' into β -carbon (20). These effects are overlapped by the influence of the surface concentration of α' -carbon such as the hydrogenation rate of α' -carbon and the parameters governing the chemisorption of carbon monoxide. The CO chemisorption depends on the partial pressure of CO and the temperature at a given position in the reactor, and it is also affected by the composition of the catalyst (5).

MCR-2X Catalyst

The development program for methanation catalysts at Topsøe's laboratories aimed specifically at solving the problem of operating over a wide temperature range. The work resulted in the MCR-2X catalyst. The support has a stabilized micropore system that effectively prevents sintering of the nickel crystals. The resulting high nickel surface area and the absence of alkali (sometimes added to prevent carbon formation) led to the desired high methanation activity. The catalyst is mechanically stable at high as well as low temperatures. The stability was proven in pilot tests with a total run-time amounting to 15,000 hours. This included 8,000 hours operation at the same catalyst filling at a maximum temperature of 600°C. Data in Table 2 demonstrates the thermo-stability of MCR-2X reflected by an almost unchanged mechanical strength and total surface area. The activity stabilized after 1,000-2,000 hours.

The mechanical and chemical properties of MCR-2X also offer flexibility in providing the capability for regeneration of spent catalysts. Table 3 shows results from regeneration tests performed on samples taken after 4700 hours operation in the pilot plant. The carbonaceous film responsible for the β -deactivation can be removed simply by treatment in hydrogen, whereas sulfur is more difficult to remove. However, the catalyst easily withstands a high temperature oxidation and re-reduction, which will not only remove sulfur, but also result in redistribution of any sintered nickel crystals. As shown in Table 3, more than 50% of the original activity of a new catalyst can be regained by this method.

The properties of MCR-2X can be utilized in different process schemes optimized for the feedgas in question. The critical step is the first methanation stage, where the full potential of MCR-2X is utilized, MCR-2X allowing maximum practicable temperature increase from ca. 300°C to 700°C.

The mechanical sintering problem could be solved by using steam reforming catalysts, which will, of course, be active also for methanation. However, the nickel surface areas in most steam reforming catalysts are too small to provide adequate low temperature activity, thus dictating operating at higher reactor inlet temperatures. This will not necessarily influence the overall conversion in the reactor, which is fixed by the exit temperature. However, for adiabatic operation, the reduced temperature rise means a higher recycle energy consumption. In principle this can be overcome by increasing also the exit temperature, but this means a greater number of reactors because of the smaller conversion per reactor. This situation is illustrated in Figure 5, in which the operation, based on MCR-2X, is shown (solid line) in a simplified example involving three adiabatic reactors, corresponding to an overall conversion of 95%.

The process path, TREMP (Topsøe Recycle Methanation Process) is compared with alternative routes of high temperature methanation (dashed lines) based on a reforming type catalyst. A temperature of 450°C is assumed as the minimum inlet temperature for the reforming type catalyst. To achieve the same conversion of the first reactor as obtained in TREMP, a recycle ratio 2 times higher as in TREMP is required. This means higher energy consumption. If recycle is excluded, four reactor stages are necessary with reforming catalysts to obtain a conversion equivalent to that of the first TREMP reactor. Moreover, this solution is doubtful because of the excessively high exit temperature of the first reactor.

By the use of a combined bed of a non-nickel catalyst with MCR-2X, the inlet temperature can be decreased to 200°C, thus allowing a temperature increase of 500°C at a reduced recycle rate. The wide operating range of MCR-2X may be utilized in the design of boiling water reactors for methanation. With MCR-2X, design for "hot zone" temperatures of 700°C is realistic, since this leaves a good safety margin. An explorative test was made in the pilot plant in which MCR-2X was exposed to 780°C in the "hot zone". For simplicity the test was made in an air-cooled reactor. The inlet temperature was

300°C and after the hot zone, the reaction temperature was decreased to about 250°C. The tube wall temperature in the hot zone was between 300 and 400°C, which is close to the expected value in an industrial boiling water reactor. Measured and calculated temperature profiles are shown in Figure 6. No significant deactivation of the catalyst was observed at the test, which supports the possibility for designing for high hot spot temperatures, being important for optimum reaction and heat transfer conditions.

A special application of methanation is related to the Long Distance Energy Transport System NFE or ADAM/EVA system, which is being developed at the German Nuclear Research Center KFA-Jülich, in cooperation with Rheinische Braunkohlenwerke AG in Cologne. In this system (23,24), nuclear energy released in a helium-cooled high temperature reactor is transferred to steam reformer (EVA) with a hot helium as heating medium. The product is transported by pipeline to power plants in which the heat is recovered in a methanation plant (ADAM). The high exit temperature which can be accepted of MCR-2X makes it possible to raise superheated high pressure steam at the destination for electricity production as required in the NFE system. Topsøe has supplied the semi-commercial demonstration plant ADAM-1 to KFA - Jülich. The plant is based on three adiabatic methanation steps, and it is processing synthesis gas manufactured from up to 200 Nm³ per hour of natural gas (23). Figure 7 shows temperature profiles from an ADAM I run which was made by KFA in cooperation with Topsøe (25). MCR-2X was installed in the first two methanation steps, whereas the third methanator operated on MCR-4 which is a highly active low temperature catalyst.

CONCLUSIONS

The use of a nickel catalyst for methanation is limited to a minimum operating temperature because of the risk of carbonyl formation and deactivation, and to a maximum operating temperature because of sintering and in certain cases the risk of carbon formation. Between these temperature limits, the activity and stability of the catalyst determines the optimum layout of the methanation process. The Topsøe MCR-2X catalyst allows operation in the temperature range 250°C to well above 700°C. By combination with a non-nickel catalyst, the operation range can, for certain cases, be extended to 200 to 700°C. This capability of high temperature methanation offers the possibility of design for low recycle, or for optimum boiling water reactors.

REFERENCES

1. Rostrup-Nielsen, J.R., and Pedersen, K., J.Catal. (in press).
2. Araki, M., and Ponec, V., J.Catal. 44, 439 (1976).
3. Coenen, J.W.E., Schats, W.M.T.M., and van Meerten, R.Z.C. Bull.Sco.Chim.Belg. (1979) (in press).
4. Rostrup-Nielsen, J.R., "Steam Reforming Catalysts", Teknisk Forlag, Copenhagen 1975.

REFERENCES (Cont'd)

5. Schoubye, P., J.Catal. 14, 238 (1969).
6. Vannice, M.A., and Garten, R.L., J.Catal. 56, 236 (1979).
7. Rostrup-Nielsen, J.R., J.Catal. 21, 171 (1971)
8. Garner S.W., "Chemistry of the Solid State", Butterworths, London 1955, p 307.
9. Ruckenstein, E., and Pulvermacker, B., AIChE Journal 19, 356 (1973).
10. Wynblatt, P., and Tae-Moon, Ahn, "Sintering and Catalysis", Materials Science Research 10, 83 (1975).
11. Ruckenstein, E., and Pulvermacker, B., J.Catal. 37, 416 (1975).
12. Borisova, M.S., Fenelonov, V.B., Dzisko, V.A., Simonova, L.G., Kinet.Katal. 17, 653 (1976).
13. Williams, W., Butler, G.A., and Hammonds, J., J.Catal. 24, 352 (1972).
14. Levy, R.M., Bauer, D.J., Roth, J.F., Ind.Eng.Chem.Prod. Res. Develop. 7, 217 (1968).
15. Rostrup-Nielsen, J.R., J.Catal. 27, 343 (1972).
16. McCarty, J.G., Wentrcek, P.R., Wise, H. and Wood, B.J. DOE Contract 76-C-03-115, Annual Report Oct. 26, 1978.
17. Fitzharris, W.D., PhD Thesis, University of Delaware, 1978.
18. Christiansen, L.J., and Andersen, S., Proc. 6th Int. Symp. on "Chemical Reaction Engineering", Nice 1980 (in press).
19. McCarty, J.G., and Wise, H., J.Catal. 57, 406 (1979).
20. McCarty, J.G., Wentrcek, P.R., and Wise, H., in "Proc.Amer. Chem.Soc.Symposium", Chicago, Aug. 28-Sept. 2, 1977", p 1315.
21. Moseley, F., Stephens, R.W., Stewart, K.D., and Wood, J., J.Catal. 24, 18 (1972).
22. Rostrup-Nielsen, J.R., and Trimm, D.L., J.Catal. 48, 155 (1977).
23. Harms, H.G., Höhleln, B., and Skov, A., Chem.Ing.Tech.(in press).
24. Boltendahl, V., Niessen, H.F., Theis, K.A., GWF-Gas/Erdgas, 117, 517 (1976).
25. Harms, H.G., Höhleln, B., and Skov, A., Oil and Gas J. (sub-mitted).

Table - 1

Carbon Formation, Thermogravimetric Tests

Experimental conditions re ref (1)
Catalyst, 13wt% Ni, $D_{Ni} = 300 - 3500 \text{ \AA}$

Carbon limits calculated from "principle of equilibrated gas"

	1	2
CO/H ₂	0,33	0,7
PCO atm	0,2	0,33
Temp. °C	400-470	400
Calc. carbon limits		
Carbon for (Temp. °C):		
Graphite	$415 < T < 800$	$T < 1069$
Catalyst ($D_{Ni}=3500\text{\AA}$)	$600 < T < 350$	$T < 684$
Carbon Formation	No	Yes

Table - 2

High Temperature Stability of MCR2X

Results from Pilot Tests

O p e r a t i o n Time at Temp. h °C	BET Area m ² /g	H ₂ Area m ² /g	D _{Ni} Å
New MCR2X	52	7	220
8127 600	30	3	295
1895 600 followed by 860 700	35	3	345

Table - 3

Regeneration of MCR2X Catalyst

Samples from HTAS-run 5

Operating time at temp. h °C	Regeneration Conditions	Activation Conditions	Intrinsic Activity relative to unused cat.	
			Before	After
4800 290-385	H ₂ , 15h, 500°C	-	0.006	0.05
4800 290-385	H ₂ , 4h, 700°C	-	0.006	0.15
3900 280-300	H ₂ O, 16h, 700°C	800-850°C, 2h	0.025	0.42
3900 600	H ₂ O, 16h, 700°C	800-850°C, 2h	0.11	0.50

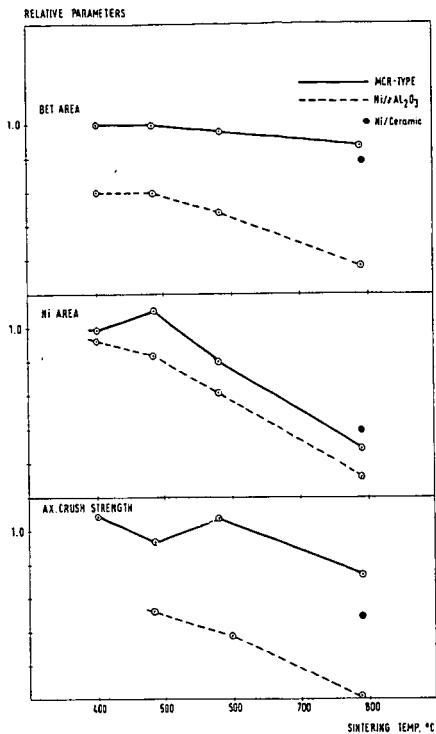


Figure 1

Sintering of Catalysts

30 kg/cm²g, H₂O/H₂=10, 140-170 hours

MCR-type. BET-area = 33 m²/g

Ni/γAl₂O₃. BET-area = 101 m²/g

Ni/Ceramic. BET-area = 1.2 m²/g

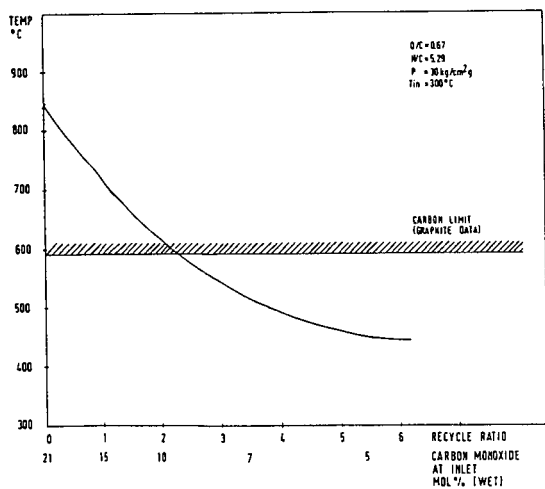


Figure 2

Carbon Limits

Recycle ratio and outlet temperature of adiabatic equilibration of gas. The example refers to a feed-gas containing 12 vol% CH₄. Correction for carbon-structure on catalyst moves carbon limits to 950-1050°C.

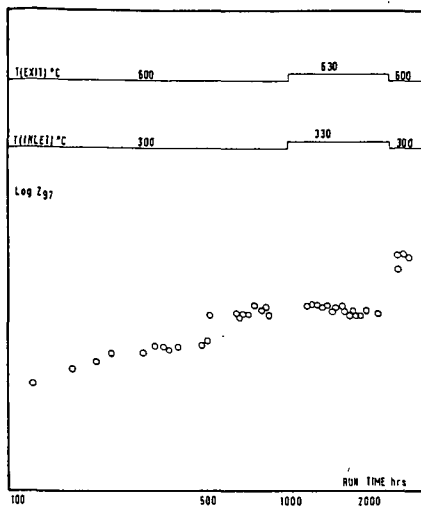


Figure 3

β -deactivation in Pilot Test

MCR-type catalyst.

O/C = 1., H/C = 6., P = 30 kg/cm²g,
PCO = 2 kg/cm²g.

Z₉₇ = axial distance from top of
catalyst bed for 97% conversion
of max. adiabatic ΔT obtained.

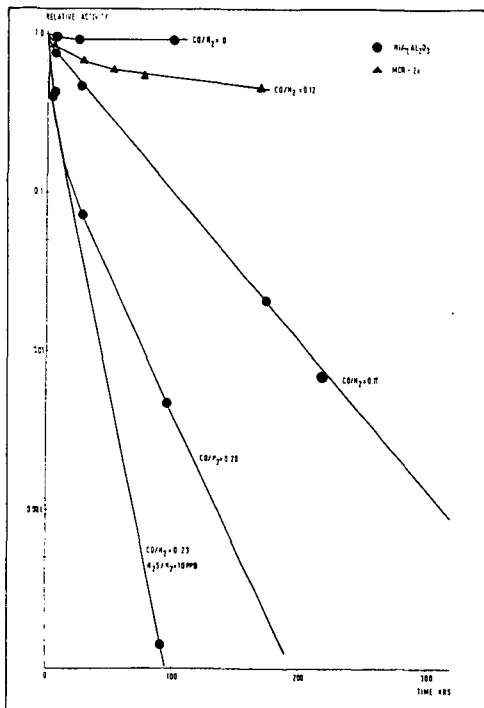


Figure 4

Low Temperature Deactivation

Laboratory Tests

300°C, 21.2 kg/cm²g, NHSV=10⁶h⁻¹

Feedgas (vol%):

H₂O (35)

CO (0-11)

CO₂ (5)

H₂ (rest)

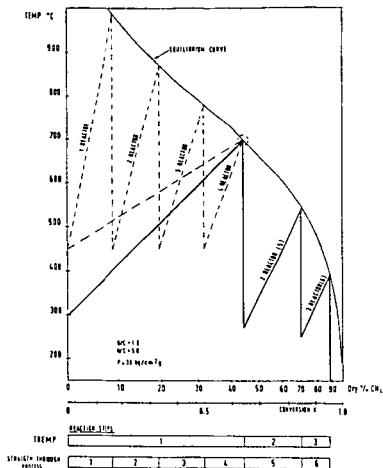


Figure 5

High Temperature Methanation Simplified Example

Comparison of TRESP reaction steps (solid line) with reaction routes based on a reforming type catalyst (dashed lines).

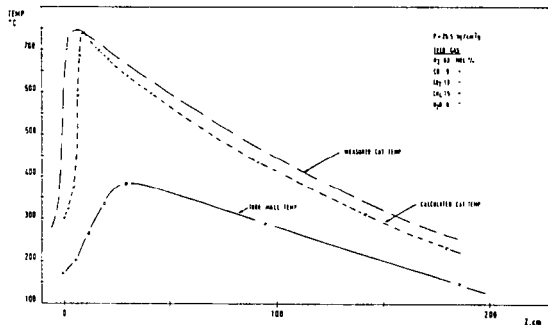


Figure 6

Explorative Pilot Test with Air-cooled Reactor

Measured and calculated temperature profiles. The calculation model did not consider axial radiation in the bed, which explains the difference of the two profiles.

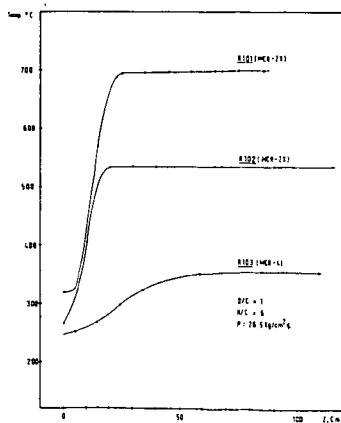


Figure 7

ADAM-1 Test Unit Temperature Profiles