Primary Reforming of Liquid Hydrocarbon Process Field Streams

The shortage of natural gas may force many ammonia producers to find alternate feedstocks for primary reforming. Tubular reforming of liquid hydrocarbons alone or mixed with natural gas may become attractive.

J.R. Rostrup—Nielsen
Haldor Topsoe
Vedbaek, Denmark

In Western Europe and Japan naphtha has been a principal feedstock for production of hydrogen, towns gas, and synthesis gas for the petrochemical industry. The discovery of natural gas in Western Europe and the construction of a transmission network allowing import of natural gas from the Soviet Union may change this picture. Many European towns gas units previously based on naphtha have been closed or converted into using natural gas, and several ammonia plants are using natural gas as feedstock. In the United States naphtha has not in the past been an interesting feedstock for primary reforming, as cheap natural gas has been available as far as required. The opposite trend of that experienced in Europe may develop in the United States as a result of the increasing shortage of natural gas. Gasification of naphtha and LPG may soon be introduced in several plants which are now being planned(1) for production of substitute natural gas (SNG). The shortage of natural gas may force many industrial plants to look for alternative feedstocks at least for certain periods in order to keep their process units running at full capacity. In this situation, primary reforming of liquid hydrocarbons alone or mixed with natural gas may become attractive.

In principle,.the individual plants might install units for gasification of liquid hydrocarbons as designed for the SNG plants. The product gas may then be used as feed for the tubular reformer. However, it appears a more simple solution to introduce the naphtha or LPG directly into the tubular reformer, alone or mixed with natural gas. This article deals with some aspects of replacing natural gas by liquid hydrocarbons as feedstock for tubular reformers. In addition, some difference between tubular reforming of naphtha and low temperature gasification are outlined.

Tubular Reforming

Use of naphtha as feedstock instead of natural gas introduces only marginal changes in the performance of the reformer. In principle reforming of methane involves establishment of the following equilibria:

$$CH_4 + H_2O = CO + 3H_2 \qquad (1)$$
$$CO + H_2O = CO_2 + H_2 \qquad (2)$$
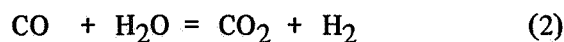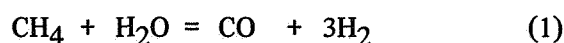
and the gas composition and the heat consumption are determined by the pressure and temperature exit the catalyst layer.

When using liquid hydrocarbons as feedstock, the mechanism becomes very complex, involving several consecutive and parallel reactions, some of which may result in formation of coke. However, the breakdown of liquid hydrocarbons instead of methane.

$$C_nH_m + nH_2O \longrightarrow nCO + (n + \tfrac{m}{2})H_2 \qquad (3)$$
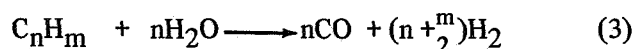
causes no significant changes of the absorbed duty of the reformer, as illustrated by an example in Figure 1.

Production of synthesis gas for the manufacture of 1,000 ton/day of ammonia has been considered using naphtha and natural gas as feed, respectively. On the basis of a simplified model for the kinetics of break down of the hydrocarbons(2), computer calculations of profiles of conversion, temperature, and absorbed duty have been performed. The results of the example show that, in order to produce equal amounts of synthesis gas, naphtha requires a smaller tube length than natural gas. Therefore, when switching feed from natural gas to naphtha in a given reformer, the tube wall temperatures can be reduced slightly. The result is not surprising considering the thermodynamics of the overall reaction.

Studies of the relative reactivities of various hydro-carbons show most of the hydrocarbons to be more reactive than methane, as indicated in Table 1. The have been estimated from rate constants at 500°C assuming first order kinetics with respect to the hydrocarbon.

Coking Problems in Tubular Reforming

The major difference introduced by naphtha is a higher potential risk of coking resulting in hot tubes and, eventually, blockage of the tubes. Special catalysts are required to solve this problem, This section summarizes some results from studies of coking mechanisms and
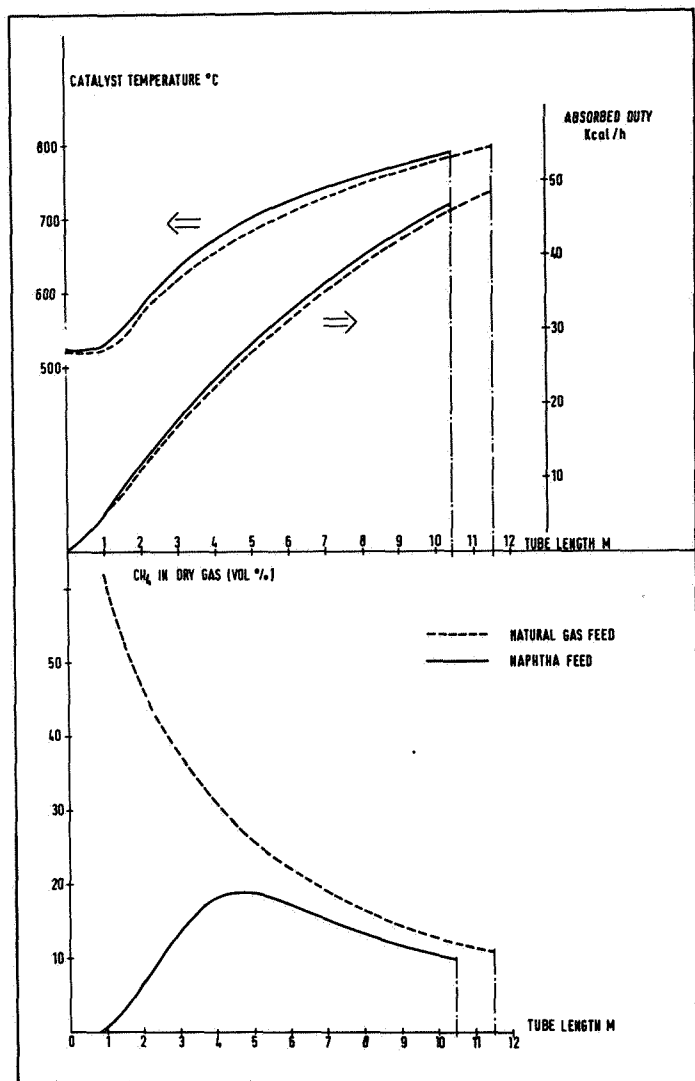
Figure 1. Reforming of natural gas and naphtha. Axial profiles of methane content, catalyst temperature, and absorbed duty. Catalyst A. (H_2O/C = 3.5, P = 35 atm., max. tube wall temp. 900°C).

Table 1. Relative reactivities of hydrocarbons

Catalyst: Topsoe RKN, 1-2 mm. particles
H_2O/C = 3.5-4.0 moles/atom
Pressure: 30 kg./cm²g.
Temperature: 500°C

The reactivities have been estimated from pseudo first order rate constants relative to the constant for methane.

Hydrocarbon	Reactivity per g.atom C
Methane	1.0
Ethane	8
Butane (17.8% Iso-Butane) (80.6% Normal Butane) (1.6% Propane)	11
Cyclohexane	17
Benzone	1
n-heptane	4
Trimethyl Butane	8
n-decane	4
Light Naphtha (FBP 110°C)	10
Full Range Naphtha (FB- 170°C)	4

catalyst activity obtained in the Topsoe laboratories. The details of these studies are to be submitted for publication in the near future.

Coking in naphtha reforming may, in principle, take place in the following ways:

A. Carbon may be formed on the nickel surface from carbon monoxide and methane when the equilibrium composition shows positive affinity for decomposition of these components:

$$2CO = C + CO_2 \tag{4}$$

$$CH_4 = C + 2H_2 \tag{5}$$

Deviations from graphite data should be included in the equilibrium calculations *(3)*. The deviations depend to some extent on the structure of the catalyst *(4)*. The decomposition reactions are eliminated at normal process conditions by use of excess of steam.

B. In a simple model, breakdown of the hydrocarbon may be considered as two competitive reactions on the nickel surface, one forming the gaseous products, the other resulting in formation of coke:

$$C_nH_m \xrightarrow{H_2O} \begin{array}{l} H_2, CO, CO_2, CH_4 \\ \\ "C" + H_2 \end{array} \tag{6}$$
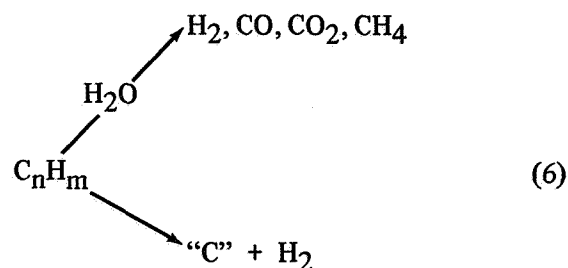
Coke may be formed due to poor activity and selectivity of the catalyst for conversion of hydrocarbons into gaseous products, and the carbonaceous deposits may be stable in a steady state even if the equilibrium predicts no formation of carbon. Examination of coked catalyst in an electron microscope revealed the coke to grow as whisker-like threads with a nickel crystallite at the top, as indicated in Figure 2.

Some studies in a thermogravimetric system showed the coking rate on a given catalyst to depend on steam to carbon ratio, temperature, and type of hydrocarbon. Figure 3 shows plots of percent carbon deposits on catalyst vs. run time obtained in experiments with various hydrocarbons. The results show that the rate of carbon lay-down depends strongly on the unsaturated character of the hydrocarbon.

No carbon was observed when using the carrier without nickel, which indicates that the coking reactions take place at the nickel surface. This is in accordance with the observation of no coking by this route on a sulfur poisoned catalyst. Other studies *(5)* have confirmed the role of the nickel surface in coking by naptha reforming.

C. At higher temperatures coking may result from pyrolysis of the hydrocarbons or from catalytic cracking on acidic sites on the carrier. The rate of these reactions was found to depend on hydrocarbon type, steam to carbon ratio, partial pressure of the hydrocarbon, temperature, and acidity of the carrier.

In reformers operating at extremely high heat fluxes there may exist increased risks of coking by route C and
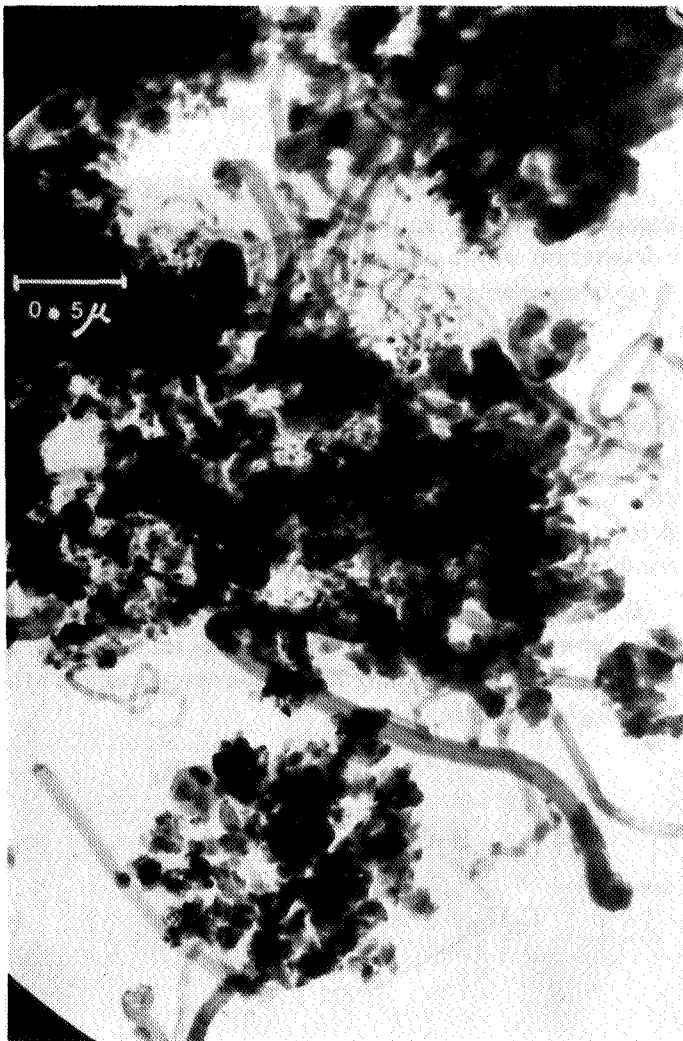
Figure 2. Electron micrograph of whiskerline coke formed by naphtha reforming at 500°C.

operation on mixed naphtha and natural gas may be preferred instead of alternating between the two feedstocks. Even methane may form coke by this mechanism which could contribute to "hot bands" as experienced in many natural gas reformers operating at very high heat flux.

Coking by route A is a matter of thermodynamics and may hardly be affected by a catalyst. Catalysts for naphtha reforming should, therefore, be able to retard coking by the two remaining routes. Coking by route B can be eliminated by using a catalyst with high activity and selectivity for the gasification reactions. This shall be discussed in more detail below. Coking by route C can be eliminated by using a non-acidic carrier and by high activity of the top layer. A non-acidic carrier will have poor activity for catalytic cracking of hydrocarbons which may result in coking. High activity for gasification reactions will allow only small amounts of unconverted naphtha to pass on to the hotter part of the tube where thermal cracking might occur. Figure 4.

To ensure high activity of the top layer, poisoning should be avoided, which implies that the sulfur content of the feed should be less than 0.2 parts/million S on total feed basis. This requires pretreatment of the naphtha in a
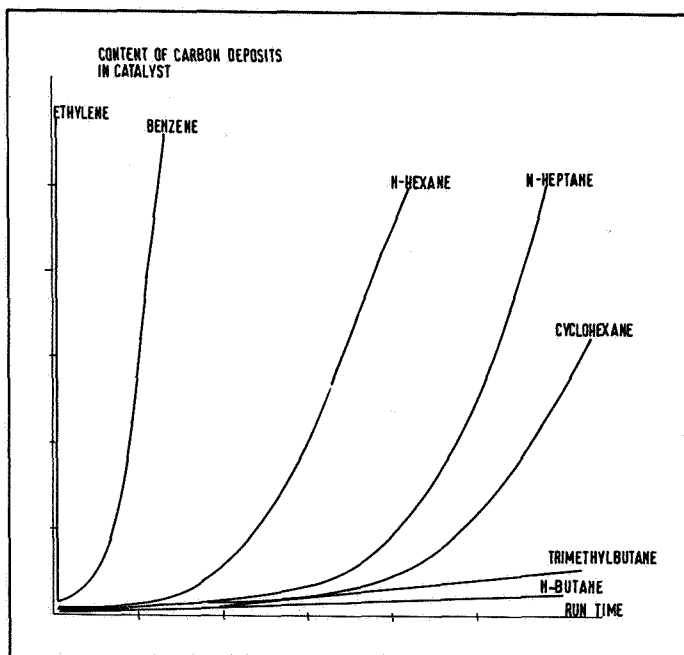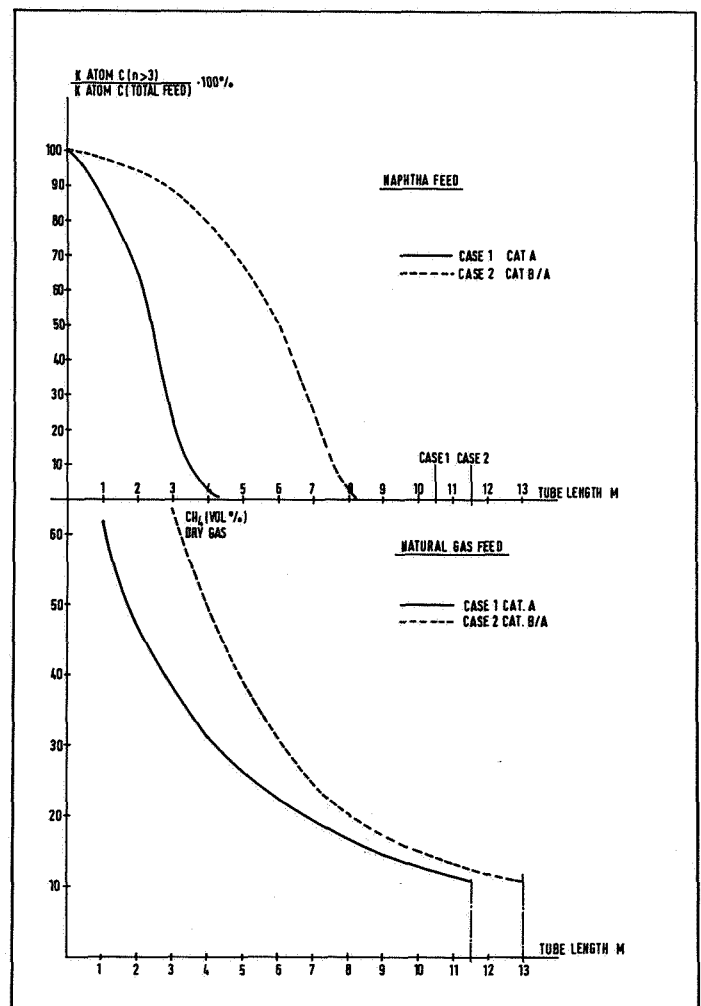

Figure 4. Influence of catalyst activity on conversion profiles. (H_2O/C = 3.5, P = 35 atm., max. tube wall temp. 900°C) Activity of A is ten times that of catalyst B. Case 1: Catalyst A. Case 2: 50% catalyst A, 50% catalyst B.

Figure 3. Relative coking rates of various hydrocarbons at 500°C. Thermogravimetric measurements.

Table 2. Result from monotube pilot runs on naphtha reforming

Catalyst: Topsoe RKN (some experiments, including standard natural gas reforming catalyst RKS, in lower part of the tube).

Total bed length: 6 m.

	Run Number				
	1	2	3	4	5
Number of Measurements	53	31	6	21	3
Naphtha Feed FBP ($^\circ$C)	106	162	227	90	227
H_2O/C (moles/atom)	7	4.5	4	1.8	1.8
Pressure (atm. abs.)	31	26	30	31	31
Temp. Exit Catalyst ($^\circ$C)	848	820	786	680	680
Catalyst Type	RKN/ RKS	RKN/ RKS	RKN/ RKS	RKN	RKN
Total Feed, $\dfrac{\text{kg steam + naphtha}}{\text{(liter catalyst) . h}}$	4.62	3.60	4.36	7.78	7.62
CH_4 in Dry Exit Gas (vol. %)	0.52	2.34	4.74	32.1	33.0
$t_{exit}-t_{equil.}$ ($^\circ$C)	16.5	−9.6	−16.5	1-3.3	−9.0

Note: t_{exit} was measured in the center of the exit layer of the catalyst bed. The presence of radial temperature gradients implies that this temperature is below the mean temperature of the gas. This will bias the results making the reported difference $t_{exit}-t_{equil.}$ closer to zero.
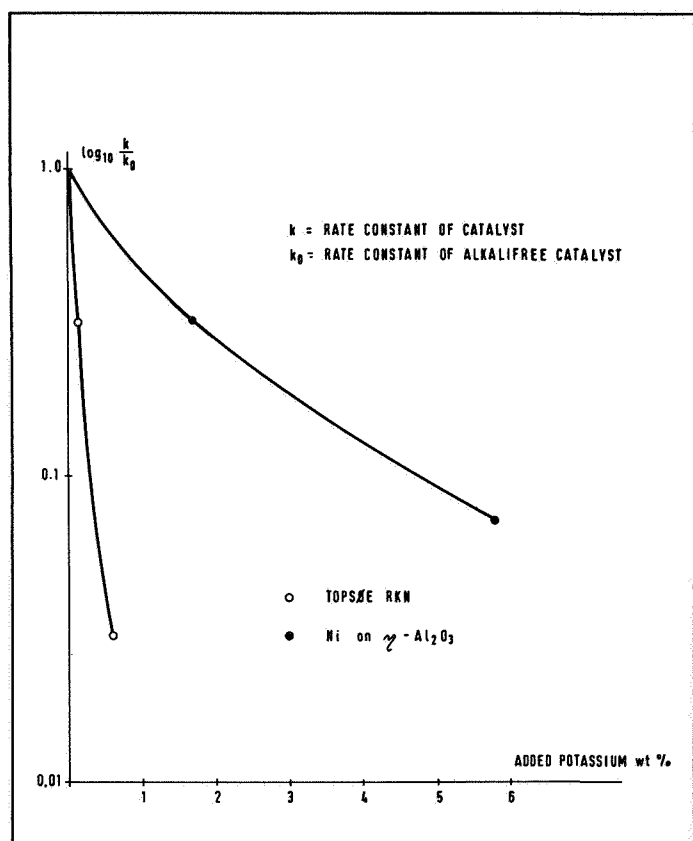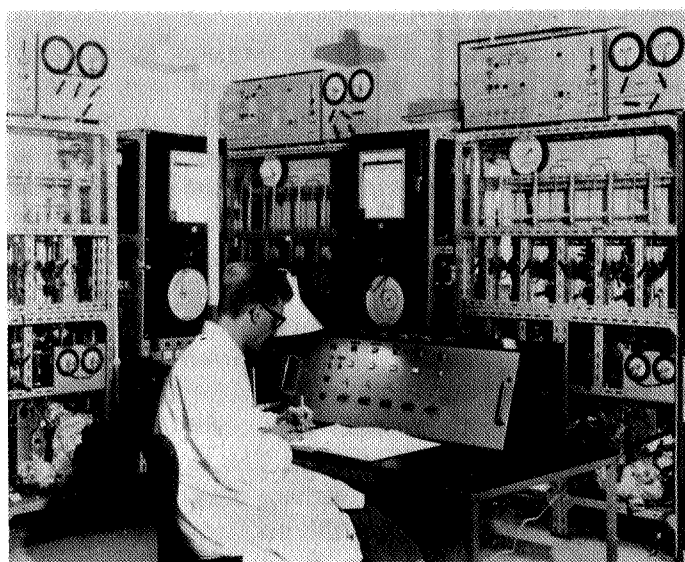

Figure 5. Influence on catalyst activity of alkali. Intrinsic rate constants determined from experiments on steam reforming of ethane. Temperature: 500°C (932°F) Pressure: 1 atm. abs. Catalyst particle size 0.3-0.5 mm.

Apparatus used for experiments noted in Table 1.

conventional hydro-desulfurization unit (i.e., NiMo- or CoMo-catalysts, and ZnO). In principle, catalysts for reforming of natural gas are also poisoned by higher contents of sulfur as sulfur poisoning is a simple matter of a chemisorption equilibrium(6), but normally coking by route C is not so critical when using natural gas.

Our studies have indicated that the selectivity for supressing coking reactions by route B is related to the ability of the catalyst for adsorption of steam. One method

to achieve high selectivity for the gasification reactions is to add alkali to the catalyst which at the same time may neutralize acidic sites(5). A number of this type of catalyst have been in commercial operation for several years (7, 8, 9). However, the presence of alkali involves potential problems since the volatility of alkali in steam may cause fouling of catalysts and equipment following the reformer as well as corrosion (10).

Moreover, addition of alkali to an alkali-free nickel catalyst results in a drastic drop in the activity of the nickel surface. As indicated on Figure 5, this could amount to a change of more than one order of magnitude of the intrinsic rate constant. This may result in a methane content of the reformer effluent corresponding to an equilibrium temperature deviating significantly from the reformer exit temperature (11). In addition, the operation of the catalysts at low temperature as used in production of towns gas may cause breakthrough of higher hydrocarbons (9, 12).

Another means of suppressing coking has been the use of

85

Final Product:	1 H_2	2 H_2	3 NH_3	4 Towns Gas
Pressure Exit Reformer, kg./cm.^{2}g. (lb./sq. in. gauge)	40 (570)	26 (370)	34 (484)	24 (342)
H_2O/C moles/atom	6.5	4.5	3.5	2.4
Space Velocity, vol. C_1/vol./h.	700	970	1170	1950
Temperature Exit Reformer, ^oC (^oF)	850(1,560)	800(1,470)	795(1,460)	675(1,245)

a catalyst based on a neutral carrier and showing selectivity and high activity for the gasification reactions. The selectivity has been obtained by some features in the preparation of the catalyst improving its ability for adsorption of steam. The high activity is achieved by the absence of alkali and by a large nickel surface area. These factors are more important than the nickel content of a reforming catalyst (13).

The high activity is reflected by very close approaches to equilibrium attained at various conditions. This is illustrated in Table 2 showing data from a monotube pilot plant. The data show very small values of temperature approach, being of same order of size as the uncertainties of analyses and measurements. Furthermore, the high activity has allowed industrial operation at reformer exit temperature as low as 650°C (1,200°F) with no breakthrough of higher hydrocarbons. Some examples of experienced industrial conditions are shown in Table 3.

The high activity of a naphtha reforming catalyst is particularly important when operation is alternating between natural gas and naphtha. This is evident, as low activity for reforming of methane may result in poor approach to equilibrium, and this may require use of higher tube wall temperature. As an illustration, conversion profiles for some cases have been shown in Figure 4. These include operation on catalysts showing high and low activity, respectively. The calculations, which should be considered as arbitrary examples, have been performed assuming identical maximum tube wall temperatures and a ratio of 10:1 of the effective activities of the two catalysts. It is apparent that with low catalyst activity, higher concentrations of methane are to be expected in the hotter part of the tube, thus presenting increased risk of cracking of methane contributing to "hot bands".
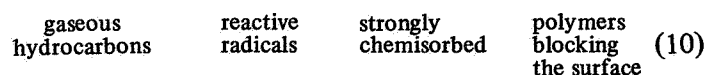
Low Temperature Gasification

As several plants for production of substitute natural gas will be installed in the next few years it appears worthwhile to elucidate the main differences between the gasification step in these units and tubular reforming of naphtha. Gasification in a SNG plant is normally performed by adiabatic steam reforming over a catalyst placed in a simple vessel. The overall reaction taking place at relatively low temperatures, 380- to 500°C (716- to 932°F) is slightly exothermic. Various processes have been developed using

slightly different process conditions (1, 14, 15). All catalysts are subject to deactivation, probably caused by formation of polymers blocking the active nickel surface. The reaction zone is moving through the bed resulting in breakthrough of unconverted naphtha. Thus, the catalysts are consumed with time. At fixed conditions, catalyst life depends strongly on the characteristics of the naphtha (16, 17) and the preferred feedstock is light straight run naphtha with low contents of aromatics.

The following model for the deactivation is supported by some studies of exchange reactions of hydrocarbons on nickel with deuterium (18):

At the conditions for low temperature reforming the adsorbed hydrocarbon radicals may become converted into strongly adsorbed species which are not intermediates in the gasification reaction. These radicals may react further to polymers blocking the nickel surface:

$$\text{gaseous hydrocarbons} \rightarrow \text{reactive radicals} \rightarrow \text{strongly chemisorbed} \rightarrow \text{polymers blocking the surface} \quad (10)$$

Tubular reforming differs from the adiabatic low temperature process in several aspects. Firstly, the process is endothermic. Secondly, in a tubular reformer, owing to the higher temperature, no deactivating polymers are formed as the hydrocarbon may crack directly to coke not poisoning the catalyst. As mentioned previously, the naphtha reforming catalyst should be designed to suppress this coking reaction.

Tubular reforming catalysts are less sensitive to the characteristics of the naphtha. The rates of gasification, Table 1, show relatively small differences between various hydrocarbons, and industrial operation has been performed on heavy naphtha with final boiling point of 220°C (428°F). With an active catalyst, the main hindrance for operating on even heavier feedstock appears to be problems in the desulfurization unit.

Conclusions

The shortage of natural gas may force many ammonia producers to look for alternate feedstocks for primary reforming. Provided naphtha will be available for use in petrochemical units, tubular reforming of liquid hydrocarbons alone or mixed with natural gas may become attractive. Introduction of naphtha implies only minor changes in the operation of the reformer.

It appears advantageous to use a catalyst with no

content of alkali, as alkali causes a drastic drop in activity which may be insufficient for conversion of natural gas, whereas the alkali-free catalyst operates equally well on natural gas and on liquid hydrocarbon.

Tubular reforming of naphtha is less sensitive to the characteristics of the naphtha than is the low temperature gasification process in SNG plants. This feature may be important as it has been emphasized *(19)* that the SNG-plants may create intense competition for naphtha supplies. SNG producers may be able to pay higher prices for light naphtha being the preferred feedstocks for SNG production. Heavy naphtha and cracked naphtha, being less valuable for SNG production and for ethylene processes, may be more easily available for ammonia producers.

Literature Cited

1. *Oil Gas J.*, 31 (December 6, 1971) (1971).
2. Topsoe, H.: *IGE Journal*, 6, 401 (1966).
3. Dent, F.J., et al.: *Trans. Inst. Gas Eng.*, p.602 (1945-46).
4. Rostrup-Nielsen, J.R.: *J. Catalysis* (to be published).
5. Andrew, S.P.S.: *Ind. Eng. Chem., Prod. Res. Develop.*, 8, 321 (1969).
6. Rostrup-Nielsen, J.R.: *J. Catalysis*, 21, 171 (1971).
7. Rooke, D.E.: *IGE Journal*, 7, 586 (1967).
8. de Winton, C.J.P.: *Gas Journal*, 331, 237 (1967).
9. Bridger, G.W., Wyrwas, W.: *Chem. Proc. Eng.*, 48, 101 (1967).
10. Vancini, C.A.: "Synthesis of Ammonia," London (1971).
11. Bridger, G.W.: *Chem. Proc. Eng.*, 53, 38 (1972).
12. Moakler, P.T.: *Gas Journal*, 343, 129 (1970).
13. Rostrup-Nielsen, J.R.: *Chem. Eng. Word*, 5, 550 (1970).
14. Jockel, H.: *Gas Wasserfach*, 110, 561 (1967).
15. Davies, H.S. et al.: *IGE Journal*, 7, 708 (1967).
16. Moseley, F. et al.: *J. Catalysis* 24, 18 (1972).
17. Thirkill, H.: *Chem. Proc. Eng.*, 53 44 (1972).
18. Frennet, A., Lienard, G.: *Surface Sci.*, 18, 80 (1969).
19. Spitz, P.H.: Chem. Eng., 79, 77 (1972).

ROSTRUP-NIELSEN, Jens

DISCUSSION

D.E. RIDLER, ICI, Ltd., Agricultural Div., Billingham, England: I would agree with a number of the concepts described in the paper, but would disagree on the solution to a number of problems that arise from these concepts. It is agreed that the analysis of the reactions occurring on top of the reforming catalyst, which form carbon, are very complicated and very difficult to ascertain and describe. And there are a number of theories on the formation of carbon. Basically, there are two ways of tackling the problem of formation of carbon.

The first one is to, in the manner described by the speaker, prevent the formation of carbon in the first place. The other way of tackling the problem is to accept that carbon might well be in the chain reactions which occur on the catalyst, and to design the catalyst in a manner which will ensure that if carbon is formed, it will not stay in the catalyst; in other words, that the rate of removal of the carbon from the catalyst will be faster than the rate of deposition. ICI has considered both of these possibilities, and the first one we found relied very heavily upon a strict definition of the operating conditions of a reformer. We felt, in fact, that we would be walking something of a tightrope. We therefore decided to tackle the problem in the second way; that is, assume the carbon might be forming, and be sure that the rate of the removal of the carbon will be faster than the rate of deposition. It was the results of the researches into this side of the problem which led to the development of a potash-containing catalyst, and the successful operation of the 300 plants around the world in the last 7 or 8 years, I think, demonstrates the success of this particular way of tackling the problem.

We would also agree with the speaker that when reforming natural gas over an alkaline catalyst, the activity of the catalyst towards the natural gas is very low. Some two or three years ago, on our plants at Billingham, we had the need to reform either naphtha or gas on some of our older reformers. We therefore went back into some of our researches which are, in fact, continuing, to see whether any of the catalysts which we produced in our researches were suitable for installing in the lower part of a tube in a reformer, and we found that one of the formulations, now designated ICI 46-4, was suitable for installation in the bottom half of the tube, underneath the alkalised catalyst which would be at the top of the tube.

The 46-4, which goes in the bottom half, is an unalkalised catalyst, and is extremely active. The result is that the reformer in which we are now using this combination was able to reform either gas or naphtha, producing the same output, and in both cases producing a very small approach to the methane-steam equilibrium. This combination is now in operation in some four plants around the world, and we consider this combination eminently suitable for a plant which is required to reform either gas or naphtha or the two feedstocks together.

I would like to address a number of questions to the speaker. I'd first of all like to know, whether there is any large-scale commercial experience with this new catalyst and, if possible, to describe some of the conditions and for how long it has been in operation?

I would also like to know whether there are any problems associated with the start up and shut down of this catalyst; in particular, whether there are any problems associated with the hydration of the support?

I would also like to ask whether, if carbon is formed on this catalyst, can it be removed in some way? And as the speaker has indicated in the paper that a low heat flux is preferable, I would like to know, if possible, what sort of average heat flux the catalyst can stand?

ROSTRUP-NIELSEN: First I would like to say that I also agree in much of what you presented. At the International Congress on Catalysis in Palm Beach, Professor Kokes gave the first plenary lecture where he stated that catalysts are individuals, and that it is very dangerous to conclude from one catalyst system to another catalyst system. So I think what you are saying may be right for your system but I will stress that high activity in the top layer would be preferable when operating on mixed feed-stocks, and this would help you also.

First, the large-scale experience with this catalyst, Table 3 in the paper, shows conditions for the catalyst in various industrial plants covering production of hydrogen, ammonia, and towns gas. The catalyst is operating in about 20 units, and the first catalyst was installed in 1968. I would like to repeat that these industrial conditions include operation at high pressure (570 pounds per square inch, or 40 atmospheres) and at high steam partial pressure, where alkali escape would be more severe. They also include operation at low steam-carbon ratio as low as 2.4 moles per atom and at an exit temperature of 1245 degrees Fahrenheit. That is a town's gas unit, and no trace of higher hydrocarbons including naphtalene is observed.

The next question is whether there are problems in startup and shutdown. Yes, of course. You have problems with all catalysts. You have to develop procedures for all catalyst types and to take care not to expose the catalyst to steaming atmosphere in a critical temperature zone. Again, Professor Kokes' statement is true. Some catalysts will not withstand high-temperature steaming. Our catalyst will not withstand low-temperature steaming and should be heated up in an inert atmosphere, or in hydrogen, to 350°C. But having done so, you could easily go on stream as normally the catalyst is delivered in a pre-reduced form. By low-temperature steaming, that is steaming below 350°C, it is true that you will get hydration and, in fact, we have experienced such hydration in a few plants in the early days of catalyst.

Carbon removal. The catalyst can be regenerated by steaming, but the success of the regeneration depends very much on the ageing of the coke. We have experienced that a plant had no steam to the reformer but still naphtha, stagnant naphtha. An increasing pressure drop was observed. The operators added steam and hydrogen to the reformer and the pressure drop decreased to being normal. After this they could go on with operation and the unit operated satisfactorily for a long period of time. But, of course, in some instances this catalyst may break down due to coking, as all catalysts else will do. If the catalyst is coking slowly, it will be very difficult to remove the coke in a reducing atmosphere. Then you have to steam it. But this is possible. We have experienced mishaps in the industry, and we have brought our catalyst back on operation.

The maximum heat flux. We have just started up in Japan a hydrogen unit with this catalyst, operating at an average heat flux of 70,000 kcal per square meter per hour.