

Methanator Design and Operation

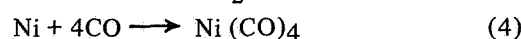
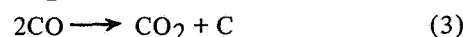
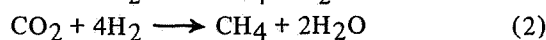
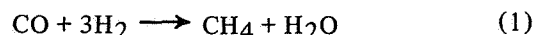
The environment in which methanator catalysts operate has changed so in the last 25 years that an entirely new set of criteria for the design and operation of methanators must now be used.

D. W. Allen and W. H. Yen, Chemetron Corp., Louisville, Ky.

Methanation as a means of removing final traces of carbon oxides from ammonia synthesis gas has come into commercial importance in the last 25 years. During this time, the environment in which methanation catalysts must operate has gradually changed. Pressure, CO₂ content, and water content have increased. The use of centrifugal compressors has made it necessary to reduce CO₂ concentrations to less than 5 parts/million. Thus, the many changes in plant design require the use of new criteria in sizing methanators. In addition, the production of synthetic natural gas from liquid hydrocarbons and coal impose an entirely new set of rules and design parameters on methanation steps used in these processes.

Methanator design

While there are a number of possible reactions that can occur in a methanator system, for design purposes we are primarily concerned with the following:



Reactions 1 and 2 are not equilibrium limited in H₂ and NH₃ plants, the equilibrium concentration of CO and CO₂ being on the order of 10⁻⁴ parts/million. Thus, rate equations tend to ignore the CO and CO₂ equilibrium values. On the other hand, the equilibrium concentration of carbon oxides must be considered when designing methanators for synthetic natural gas plants. Thermodynamically, it is possible for reaction 3 to occur in most methanators. For example, consider the following inlet conditions to an NH₃ plant methanator:

Inlet Temperature, 600°F
Pressure, 378 lb./sq. in. gauge

Composition	Mol%
N ₂	24.43
H ₂	74.23
CO	0.61
CO ₂	0.05
CH ₄	0.36
H ₂ O	0.32
	<u>100.00</u>

With this gas composition, it is possible for reaction 3 to take place at any temperature below about 1,300°F. This does not occur, however, since the reaction rate is negligible over the temperature ranges normally used. Under upset conditions carbon would probably be formed if the feed gas contacted catalyst at a temperature of 900°F.

Reaction 4 is the reaction representative of nickel carbonyl formation. For methanators operating at elevated pressures (above 300 lb./sq. in. gauge) this reaction will set the minimum operating temperature for

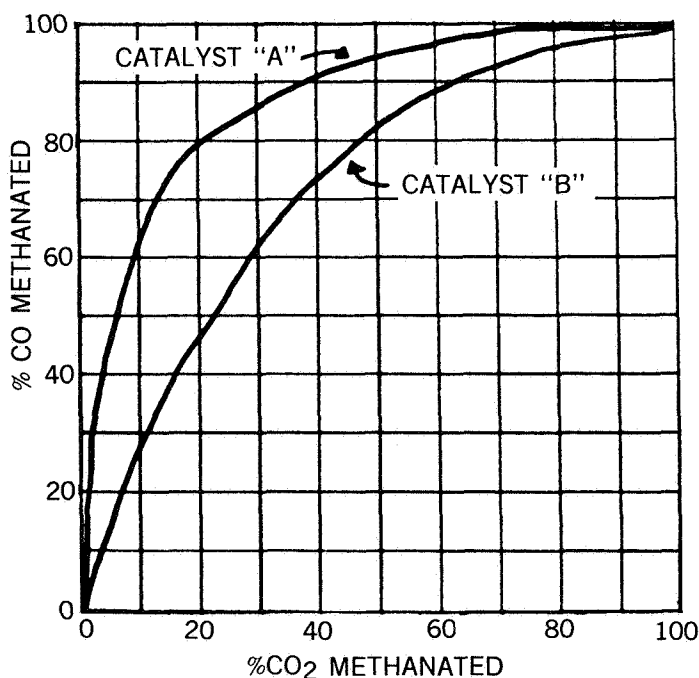


Figure 1. Effect of catalyst formulation on the methanation of CO vs. CO₂.

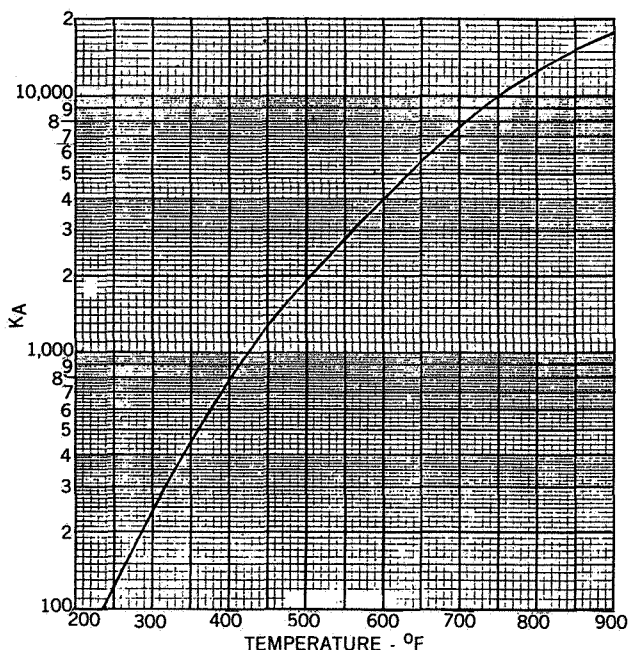


Figure 2. Activity of G-65 methanation catalyst vs. temperature at atmospheric pressure.

the methanator system. This is normally 400°F, although nickel methanation catalysts have fair activity at temperatures of 300°F.

Most of today's methanation catalysts are thermally stable and can operate at temperatures of 1,000°F or higher. Maximum temperatures, therefore, are normally determined by the economics of vessel design and heat recovery rather than catalyst limitations. Generally, methanators are designed to operate at maximum temperatures of 700- to 750°F.

At the conditions encountered in ammonia and hydrogen plants, reactions 1 and 2 are first order with regard to the carbon oxides. When both carbon monoxide and carbon dioxide are present, the reaction of CO is independent of the CO₂ reaction. The reverse is not true, however, and the methanation of CO₂ does not occur until the CO concentration is appreciably reduced. Catalyst formulation can affect the relative reaction rates. This can be important when producing SNG from coal gasification, for example, where it is desired to methanate CO in preference to CO₂ in a feed stream that does not contain enough H₂ to completely methanate all the carbon oxides. This effect is illustrated by the curves in Figure 1.

As shown, with catalyst "A", when about 80% of the CO has been reacted, only 20% of the CO₂ has been converted to methane. At 94% conversion of CO, the CO₂ conversion is 50%. With catalyst "B", when 80% of the CO has been converted, about 46% of the CO₂ has been converted. At 94% conversion of CO, 70% of the CO₂ has been methanated. Obviously, catalyst "B" would be preferred in NH₃ and H₂ plant methanators, whereas, catalyst "A" would be preferred in certain SNG applications. Reaction rates for CO methanation are about the same for both catalysts.

In sizing methanators some type of pseudo first order rate equation is used. One equation is:

$$K_A = SV \cdot \log \left(\frac{[CO_{in} - CO_{eq}] + 2[CO_{2in} - CO_{2eq}]}{[CO_{out} - CO_{eq}] + [CO_{2out} - CO_{2eq}]} \right) \quad (5)$$

where:

K_A = A rate constant that varies with the type catalyst and the temperature.

SV = Space velocity, volumes of inlet gas per hour per volume of catalyst. Gas volume is corrected to 60°F and 1 atm.

CO_{in}, CO_{2in} = Inlet CO, CO₂ concentration.

CO_{out}, CO_{2out} = Outlet CO, CO₂ concentration.

CO_{eq}, CO_{2eq} = Equilibrium CO, CO₂ concentrations at outlet temperature.

For ammonia and hydrogen plants the equilibrium CO and CO₂ values can be ignored and equation 5 can be simplified to:

$$K_A = SV \cdot \log \left(\frac{CO_{in} + 2CO_{2in}}{CO_{out} + CO_{2out}} \right) \quad (6)$$

In equations 5 and 6, the slower reaction rate for CO₂ methanation is compensated for by doubling the actual concentration of CO₂ in the feed. This approach works very well for ammonia and hydrogen plant methanators, but is not satisfactory for SNG methanators when the feed gas is low in CO and has a high CO₂ level. As an alternative to using either equation 5 or 6, the volumes of catalyst required to methanate the CO only and the CO₂ only can be determined by separate rate equations to arrive at the total catalyst volume required.

Neither equation 5 or 6 will stand up under rigorous mathematical analysis. It should be remembered, however, that these equations are empirically derived, and are valid only when applied to conditions within the limits of the experimental data used to derive the equation. For example, these equations should not be used to design a methanator to methanate CO in the presence of CO₂ when methanation of CO₂ is zero, or where the total carbon oxides in the effluent is high.

Application of either equation 5 or 6 to size a

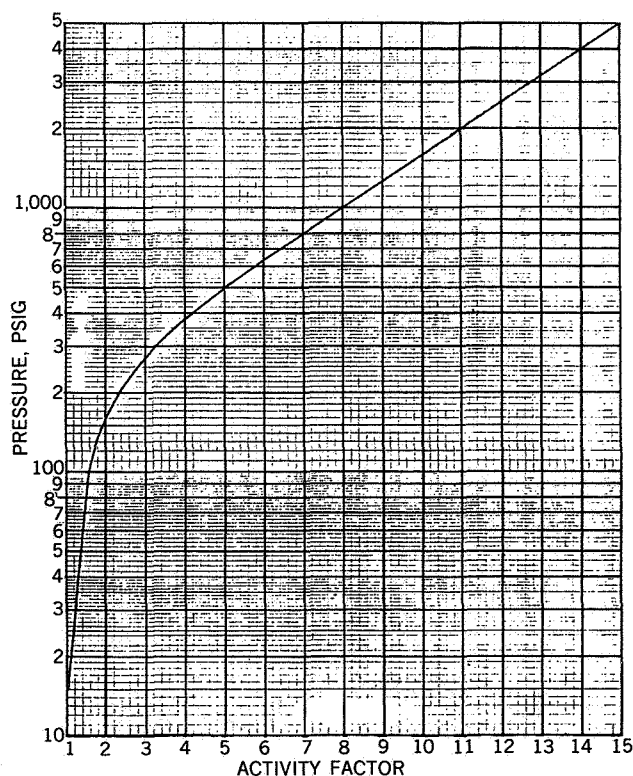


Figure 3. Pressure vs. activity factor of G-65 methanation catalyst.

Table 1. Temperature vs. equilibrium nickel carbonyl.

Temp., °F	Mol Fraction Ni (CO) ₄ @ Equilibrium			
	Pressure, atm.			
	1	5	10	20
125	0.92	0.98	0.995	1.0
170	0.78	0.93	0.97	0.99
215	0.48	0.82	0.89	0.94
260	0.12	0.63	0.77	0.85

methanator involves the following steps:

1. Calculate the temperature rise for the design conditions. In a stream that is primarily H₂ and N₂, the ΔT for each 1% CO methanated will be about 130°F, and for each 1% CO₂ methanated, it will be about 107°F.

2. Using the average of the inlet and outlet temperatures, select the appropriate value for the activity constant K_A. A plot of K_A vs. temperature is given in Figure 2. The K_A values given are based on expected end of run conditions. Using the average of the inlet and outlet temperatures introduces a certain degree of conservatism in the design since a large portion of the catalyst bed will be at or near the maximum temperature. This approach more than compensates for heat losses that normally occur from commercial systems.

3. Calculate the space velocity using either equation 5 or 6. The space velocity calculated is that suitable for atmospheric pressure operation.

4. From a plot of pressure appreciation vs. pressure, Figure 3, select the value for the pressure appreciation at the design pressure. The design space velocity is then the product of the space velocity calculated in step 3 above, times the pressure appreciation factor.

In general, when using the above design procedure, we would expect the catalyst life to be in excess of five years. It would be possible to use higher space velocities and lower catalyst volumes and accept a much shorter catalyst life. This would result in a smaller vessel, but would result in more frequent catalyst changeouts and an increased consumption of catalyst. A smaller catalyst volume would also reduce the safety factor and narrow the limits over which the catalyst could be operated.

Startup

Once the methanator has been designed, the plant operator must then be concerned about the following before placing the catalyst in operation:

Catalyst loading—Catalyst vendors will supply detailed loading instruction. The key points here are:

1. Inspect the catalyst support system, including screens, to insure that they are properly installed. Measure the vessel and mark the proper bed depth to give the required volume.

2. When the methanation catalyst arrives at the plant site, it should be relatively free of fines, and probably will not require rescreening unless it has been subjected to very severe handling during shipment. Any fines, if present, will be in the bottom of the drum and screening may be restricted to the bottom few inches of the catalyst in each drum.

3. Free fall of the catalyst should be limited to about 5 ft. during loading.

4. During loading it is necessary to level the catalyst bed as it is being loaded to insure uniform loading and packing.

5. The weight of the catalyst loaded should be recorded and checked. With the proper weight of catalyst

loaded, the vessel should be filled to the design volume.

6. Before closing the vessel, inspect to be sure that it has been loaded to the proper depth, the top of the bed is level, and there are no foreign objects or material in the reactor.

Purging the methanator system—Part of the procedure followed in preparing a new plant for startup is purging the methanator system free of oxygen. This is normally done using nitrogen.

Reduction of the methanation catalyst—When new catalyst is placed in service, it is normally in the oxidized state, and it is possible to heat the catalyst to the operating temperature using the methanator feed gas. If the catalyst has been reduced, however, this is not advisable because of the possibility of forming nickel carbonyl. The process gas should not be used for heat-up if it contains appreciable quantities of steam.

Plant design and operating conditions vary widely, and it is suggested that startup procedures be reviewed with the catalyst supplier. It would be well to make note of the following points, however:

1. With a new plant be sure that adequate thermocouples have been installed and are working properly. In addition to inlet and outlet couples we recommend that at least three couples be located in the bed: one at about one-fourth of the bed depth, one at half bed depth, and one at three-quarters bed depth. In larger systems, or one where catalyst poisoning may occur, we suggest additional couples be installed.

2. The thermocouples at one-quarter and one-half bed depth should be tied into a high temperature alarm system to insure that the design temperature for the vessel is not exceeded. Under upset conditions such as high CO₂ or CO feed, the vessel should be bypassed and the feed line blocked off. Under extreme conditions, it may be necessary to depressure and purge the methanator with cold nitrogen or steam. The possibility of an upset in the CO₂ removal system is probably higher during the initial startup than at any future time.

3. Do not use process gas for heat-up and reduction if it contains more than 3 mol % H₂O. We have found that methanation catalyst activity is appreciably diminished if it is reduced with a wet gas, even though it is later operated on a dry gas. Conversely, we have found that when a methanation catalyst is reduced with a dry gas, it will give good performance on a feed gas containing 8% H₂O.

4. If the normal feed gas is high in moisture, it is possible to use a prereduced and stabilized methanation catalyst. In this case, the methanation catalyst should be heated to about 400°F with CO, CO₂-free nitrogen before introducing the process feed.

5. Some methanators are designed for inlet temperatures of 400- to 500°F, and it is very difficult and time consuming to reduce the catalyst at these temperatures. In this case, using pre-reduced and stabilized methanation catalyst in the top 10% of the bed, appreciably reduces the time required for reduction. This is also a time saver for methanators that use an inlet-outlet heat exchanger to attain the desired inlet temperature.

6. Before introducing feed gas to any methanator, it must be analyzed to insure that the CO, CO₂, and O₂ levels are within acceptable limits.

Operation

Once the catalyst has been reduced and the methanator placed on line, the operation is relatively simple and requires very little attention. The plant operator should maintain a history of the temperature profile. A gradual change in the ΔT pattern will occur.

As the ΔT moves down in the bed, a prediction can be made regarding catalyst changeout. A sudden change in the ΔT pattern could indicate catalyst poisoning.

Most of today's methanation catalysts can withstand upsets that result in high temperatures. Upsets that result in carryover of liquid from the CO₂ removal system can cause physical damage to the catalyst. In addition to possible liquid carryover, the type of CO₂ removal system used can have some effect on methanation catalyst life. The general type CO₂ removal systems and their effect on methanation catalyst performance can be summarized as follows:

1. Amine and methanol systems—No adverse effect.
2. Carbonate Systems—Some carryover and deposition of salts that can reduce catalyst life. In addition, promoters, such as arsenic, are poisons for nickel catalysts.

3. Sulfinol—Some carryover of sulfur gradually poisons the nickel methanation catalyst. With improved designs, methanator catalyst life is in excess of three years. It is possible to minimize catalyst usage by only replacing the top 1/3 or 1/2 of the bed.

Higher than design CO concentrations can usually be handled without difficulty since the increase in operating temperature results in an increase in catalyst activity that more than compensates for the additional duty imposed. Increases in CO₂ cannot always be handled, however, and may result in an increased leakage of both CO and CO₂. It is possible to handle higher CO₂ levels by increasing the inlet temperature.

In some instances, a decrease in the CO level below design can result in an increase in CO and CO₂ leakage. This occurs because the loss in activity resulting from the decreased average operating temperature is greater than the reduction in catalyst duty resulting from the lower carbon oxide content of the feed gas.

During normal operation, it is unlikely that C₂ and heavier hydrocarbons will come into contact with the methanation catalyst. Methanators used in ethylene plants will, however, occasionally process feeds containing ethane and ethylene. Some hydrogen plants processing refinery off-gases may occasionally be exposed to hydrogen containing heavier hydrocarbons. C₂ and heavier hydrocarbons will be hydrocracked to CH₄. This reaction is exothermic and will add to the ΔT across the methanator. The following reactions are typical:



Hydrocracking of C₂H₆ starts at about 500°F and C₃H₈ at about 450°F. C₂ and C₃ olefins may either hydrocrack or be hydrogenated, depending upon the temperature.

Shutdown

Temporary, short duration shutdown—If a short shutdown is expected, and the temperature in the methanator will not fall below 400°F, the methanator may be blocked in under an atmosphere of process gas. This procedure should not be followed if there is any possibility that the shutdown will be prolonged and the catalyst temperatures will drop below 400°F because of the possibility of nickel carbonyl formation.

Long term shutdown—If the methanator is to be out of service for a considerable period of time, the catalyst temperature may drop below 400°F. If the methanator is not going to be opened during the shutdown, we

Table 2. Parts/million of Ni(CO)₄ existing at various CO concentrations and temperatures (total pressure of system, 200 lb./sq. in. gauge).

Temp., °F	Mol % CO				
	0.2	0.5	1.0	2.0	3.2
150	0.3	12	190	3,000	20,000
200	0	0.2	3	49	320
250	0	0	0.1	1.6	11
300	0	0	0	0.1	0.5
350	0	0	0	0	0.03
400	0	0	0	0	0

recommend the following procedure be used:

1. Discontinue the flow of process gas and depressure the reactor.

2. Purge the methanator with N₂ that is free of CO, CO₂, and O₂ or with H₂ that is free of O₂, CO, CO₂, and hydrocarbons. Temperature should be above 500°F when the purge gas is admitted.

3. When analysis of the purge gas effluent indicates no CO or CO₂ is present, the reactor may be blocked in under an atmosphere of the purge gas. Provisions should be made to maintain a positive pressure of purge gas in the system to prevent a vacuum forming as the reactor cools.

4. The methanator should be blocked in using a double block and bleed valve system or blinds to insure that CO containing gas cannot enter the methanator.

5. The blanketing gas or purge gas should be constantly maintained free of CO and O₂. There have been cases where N₂ containing a high O₂ level has inadvertently been admitted to the system resulting in temperatures exceeding 1,500°F and damage to the catalyst.

Shutdown for removal of the catalyst—If the catalyst is to be removed and discarded, the following procedure can be used:

1. Discontinue the flow of process gas and depressurize the system while purging with steam. The steam purge should be started before the catalyst temperature drops below 500°F.

2. Cool the reactor with steam to the minimum temperature possible with the available steam supply.

3. Establish and maintain a N₂ purge and cool to 300°F or lower.

4. If it is desired to inspect the top of the bed before dumping, the top manway may be opened. After inspection, the top manway must be closed before opening the bottom manway for catalyst unloading. This will prevent a chimney effect and help insure that air will not enter the reactor.

5. Open the bottom manway and unload the catalyst into steel drums or a steel bodied dump truck. A water hose with a spray head should be available to spray the catalyst as it is discharged.

Oxidation prior to removal—Plant safety procedures may require oxidation of the catalyst prior to removal. Occasionally it may be necessary to remove catalyst and reuse it; a procedure that also requires oxidation before removal. To oxidize the catalyst the following procedure may be used:

1. Discontinue the flow of process gas and depressurize the system while purging with steam or CO, CO₂, and O₂ free nitrogen. Steam can be used if the catalyst is to be discarded. We would recommend using N₂ if the catalyst is to be reused. Purge gas should be admitted before the temperature drops below 500°F.

*Per % hydrocarbon H₂ steam.

2. Cool the reactor with steam or nitrogen to about 300°F.

3. Admit 1 mol % air to the purge gas. The oxygen will react with the reduced nickel. This reaction is exothermic and will result in a temperature rise across the bed.

4. Increase the air rate to 3 mol % while watching the bed temperature. If any temperature exceeds 750°F, the air flow should be discontinued.

5. When a temperature rise is no longer observed, the air flow may be increased to 5- and then 10%. If no temperature rise is observed, the catalyst can then be cooled with air and purge gas.

6. Even though it is assumed that the catalyst is oxidized, the top and bottom manways should never be opened at the same time. During unloading the top manway should be closed while the bottom manway is open. A small water hose should also be available for spraying the catalyst if it is necessary since it is always possible that small pockets of catalyst may not have been oxidized.

The above procedures are somewhat general in nature and are not intended in any way to supersede plant safety procedures. The primary purpose of these procedures is to minimize hazards resulting from the pyrophoric nature of reduced nickel catalysts. These procedures will also guard against the possibility of nickel carbonyl formation.

Nickel carbonyl

The possibility of nickel carbonyl formation is of great concern to many plant operators and well it should be. Ni(CO)₄ is a highly toxic material, and over the years there have been a number of industrial accidents that have resulted in deaths and serious illness. The toxic threshold of Ni(CO)₄ is 1 part/billion according to the *Hygienic Guide Series (1)*.

From the literature it appears that there is some difference of opinion concerning the temperature conditions under which nickel carbonyl will or will not form. It does appear that the following conditions are favorable for the formation of nickel carbonyl:

1. Reduced nickel—Generally, it is reported that carbonyls will not react with metal oxides. However, it has been reported that nickel and iron carbonyls have been found in cylinders of CO where it is presumed that reduced metal was not present.

2. High pressures and/or high partial pressures of CO.

3. Sulfur, selenium, and tellurium are listed as promoters for the formation of nickel carbonyl.

4. Low temperatures—There is some disagreement on how low is low. Safety dictates 400°F as the absolute minimum operating temperature. CO should be purged from methanators at temperatures above 500°F.

The data in Table 1 was developed by holding stoichiometric quantities of reduced nickel and CO at the various conditions until a constant Ni(CO)₄ concentration was obtained. Extrapolation of the data in this table indicates that it is possible, under proper conditions, to have nickel carbonyl present at rather high temperatures.

Equilibrium data published by Spice, Stanley and Harrow (2) was used by Catalysts and Chemicals, Inc. to calculate the equilibrium values given in Table 2. Extrapolation of this data also indicates that nickel carbonyl can be present at relatively high temperatures.

Some of the physical properties of Ni(CO)₄ are:

Density	— 1.310
Vapor Pressure	— 320.6 mm. @ 20°C
Freezing Point	— 25°C
Boiling Point	— 43°C at 751 mm.

Solubility — Slightly soluble in water, soluble in many organic liquids.

In contact with dry air, nickel carbonyl may burst into flame with a mild explosion.

Exposure to nickel carbonyl vapors can cause irritation, congestion, and edema of the lungs. Prolonged exposure to concentrations below the toxic limits can cause cancer of the lungs and nasal sinuses. In tests on rats, 36% of the administered Ni(CO)₄ was exhaled without metabolic alteration within 6 hr. after injection, indicating that the lung is a major route for excretion of nickel carbonyl.

The plant physician should be contacted for procedures to be followed in case of suspected nickel carbonyl poisoning. Certainly, the patient should be immobilized and rushed to the hospital so that proper treatment can be started as quickly as possible after exposure.

Symptoms of Ni(CO)₄ poisoning are: headache, dizziness, nausea, vomiting, fever, and difficult breathing. Later symptoms are coughing and cyanosis.

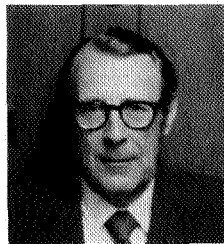
The Matheson Co. in New Jersey manufactures an instrument that is capable of determining nickel carbonyl at the 1 part/billion level. There may be others. Infrared spectrophotometry can also be used to detect both nickel and iron carbonyls in the range of 1- to 10 parts/billion.

If it is necessary for personnel to enter a reactor where the presence of nickel carbonyl is suspected, they should be equipped with self-contained air masks and skin protection. The properties of nickel carbonyl are such that it is possible for liquid carbonyl to be trapped in a catalytic reactor and not be detected by analysis of the reactor atmosphere.

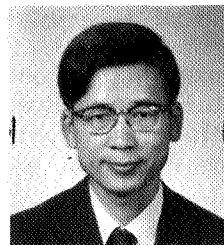
In closing, it would be well to put the nickel carbonyl problem in the proper perspective. It is a highly toxic compound that could be formed in a methanator. Proper precautions can be taken, however, to at least minimize, if not eliminate, the possibility of this compound being formed. Nickel carbonyl has been manufactured commercially for many years, and if one recognizes the potential hazards and takes the proper precautions, nickel carbonyl along with porcupines, wildcats, and grizzly bears can be coped with safely. #

Literature cited

1. *Hygienic Guide Series*, American Industrial Hygienic Association (May-June 1960).
2. Spice, Stanley, and Harrow, *J. Chem. Soc.*, (1955).



D. W. Allen received his B.S.Ch.E. from Speed Scientific School, University of Louisville. He holds the position of technical service director, with the Catalysts Div., Chemetron Corp.



W. H. Yen received his B.S. degree from National Taiwan University, and his M.S.Ch.E. from Speed Scientific School, University of Louisville. He holds the position of technical service engineer with the Catalysts Div., Chemetron Corp.

DISCUSSION

Q. What is the effect of water in the feed?

ALLEN: If the feed gas contains over 3% water and it is used to reduce the catalyst, it will have an adverse effect on activity, but you could still reduce and operate a methanation catalyst with a feed gas containing up to 8% water. If the catalyst is dry reduced, you could operate using a feed gas containing up to eight percent water with no adverse effect on performance. After all, some SNG systems have methanators that process feed streams having a one-to-one steam-to-dry gas ratio.

P. A. RUZISKA, Exxon Chemical: Regarding your comment about avoiding low temperature with gas containing CO, this is no problem on shutdown. We can easily purge out the process gas before the temperature gets to the point of carbonyl formation. But on startups, in the past, we've been advised to simply introduce process gas onto cold catalyst and heat up through the carbonyl formation range as rapidly as possible. Is this recommendation now out of date? And I wonder how many people do practice CO free startups and what their techniques are.

ALLEN: Well, I can't answer all your questions, but I am sure that most operators start-up with the feed gas and heat-up the methanator catalyst as rapidly as possible. The

adverse effect on activity is small as long as start-ups are infrequent. Even though you make some nickel carbonyl, it will decompose. You should realize there is a possibility of forming nickel carbonyl during start-up and make sure that you are not going to be venting gas in an area where it could be a toxic hazard. If you have a lot of start-ups using feed gas, you will remove a lot of nickel from the catalyst, and you will lose activity and this has happened. From a practical standpoint, and operating standpoint, yes, you use your process feed even though catalyst is in a reduced form, but you should be aware that you are going to form nickel carbonyl when you do this. The economic penalties are insignificant unless you have an accident.

JOHN S. CROMEANS: Catalyst Consulting Services, Inc.: We always caution - that when you are starting up a methanator with a gas containing CO in the event you have an interruption in your start-up, you should not allow maintenance men to work on the lines between the vessel and the vent system. One must recognize that the CO in the gas will react with the nickel in the methanation catalyst to form the toxic nickel carbonyl compound especially at temperatures below 300°F. Nickel carbonyl does not form and cannot exist in significant quantities at normal methanation conditions.