Defining Reformer Performance

At present, performance evaluations of steam-hydrocarbon reformers are subjective and arbitrary. The procedure described here will enable a precise definition of what is happening in this equipment.

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The overheating of steam-hydrocarbon reformer tubes and their resultant shorter lives has been the topic of much discussion and study over the past several years. Such problems are not new, however, the advent of the high pressure fired tube reformer has magnified the problem due to its more significant effect on 'production economics. Various approaches have been used by-industry to predict and extend tube life in order to avoid premature tube replacement or unanticipated production interruptions. Industry agrees that a tube must be operated at the lowest possible temperature to accomplish maximum life. This requires precise definition of reformer performance in order to adjust operations to optimum conditions.
The definition of steam-hydrocarl

The definition of steam-hydrocarbon reformer performance in large ammonia and hydrogen plants today is generally much too arbitrary. What is the actual furnace condition when it is described as looking "good" or "bad?" Such descriptions may be meaningful to the plant operator, but they do not lend themselves to improving reformer performance through comparisons with other furnances or with other established performance criteria.

In a large furnace, under normal operating circumstances, a rather wide range of tubeskin temperature can be experienced, as well as the occurence of hot tubes, hot spots, or hot bands. We shall propose the use of a method that we have used to define furnace performance and discuss how major variables affect performance in a typical ammonia and hydrogen plant. Utilization of this procedure will eliminate subjectivity in the defining process and thus permit the operator to make more meaningful comparisons and corrective adjustments.

The procedure used to fully describe the performance of a fired tube reformer first requires the accurate definition of rates, temperatures, pressures, and gas compositions around the reformer, as well as a complete scan of the maximum tubeskin temperatures being experienced in various sections of the furnace. The maximum tubeskin temperatures are totaled, and an average of these hottest measurements calculated.

The range on the maximum tubewall temperatures in a large fired tube reformer can vary as much as 200°F at the same level in the tubes. The range in temperature from the

coolest tube to the hottest tube can be even greater than this. The individual tube temperature readings should serve as the basis for trimming the furnace.

The» question will immediately arise as to how to measure tubewall temperatures. How much error is introduced into the procedure with pyrometer readings? Which type optical pyrometer is most accurate and least prone to operator error? Is infrared better than optical? It is not intended to discuss this here. The tubewall temperatures measured by CCI in both pilot plant and commercially have all been with its Pyro optical pyrometer. Those measured by the plants are with Pyro and Leeds & Northrup optical pyrometer and infrared pyrometers. They have varied and each plant has its own preference. The subject of surface temperature measurements in fired tube furnaces has been discussed in detail by J.M. Lenoir *(1).* Whatever instrument is used, it should be kept in a good state of repair and calibration, and the operators all given the same instructions for use to minimize differences in the readings due to operator interpretation.

A full discussion of the measurements to be made around the reformer is given in Appendix A. It will not be discussed here as it is routine to most operators, however, it should be reviewed to assure that all measurements are being made.

To adequately describe the procedure to be used for characterizing reformers, it is necessary to discuss major operating variables and the effect of each on tubewall temperatures. It is a well recognized fact that there is ä high degree of interaction between the variables in steam-methane reforming and we shall attempt to distinguish the effect of each. The comments to be made apply to an operating reformer. We will not discuss those variables such as pressure, level of operation, etc., that relate to the initial design of the furnace.

Major Operating Variables

Methane leakage from furnace - The methane leakage controlled out of a fired tube reformer has a very significant effect on the tubewall temperatures experienced. In general, a reduction of 1% methane leakage from a fired tube reformer will result in an increase of about 25^oF on tubewall temperatures measured. To accomplish this 1% reduction in methane, the outlet temperature of the furnace must be increased about 18°F.

Feed rate to reformer — A less significant effect on reformer performance is due to total feed rate. In general, an increase of 1% in the feed rate will result in about a 2°F increase in the tubewall temperatures measured in the furnace — that is controlling to the same outlet temperature from the reformer. It should be noted the rate can be increased about 12% to increase tubewall temperatures comparable to a 1% reduction in methane leakage from the furnace.

Steam to gas ratio - An increase in the steam to gas ratio controlled at the inlet to the reformer of 3.5 to 1 to 4.0 to 1 will reduce tubewall temperatures about $25^{O}F$ if the furnace is operated to the same methane leakage. The outlet temperature will be about 33°F lower. The normal sequence of events when the steam to gas ratio is increased is to hold the same outlet temperature as was maintained at the lower steam to gas ratio. Under these circumstances, the tubewall temperatures will be increased as the result of increased flow through the furnace and the methane leakage will be reduced. If the magnitude of the increase in steam to gas ratio is from 3.5 to 4.0 to 1 then, at the same outlet temperatures, the tubewall temperatures will be increased about 15^{0} and the methane leakage will . decrease about 1.6%.

Mixed-gas inlet temperature - An increase of 50°F on the mixed-gas inlet temperature to a reformer will result in about an 8°F reduction on the tubewall temperatures operating to the same reformer outlet temperature.

Catalyst activity level - We have found after checking numerous reformers in the manner described, and subsequently applying the corrections for variable differences, that a useful relationship exists which enables the operator to characterize the performance of his reformer. The effects of variables are algebraically additive, which means performance at any point in time can be compared with a base case or the design case to determine how much reformer operation has deteriorated. The algebraic expression used to relate the variables is as follows:

$$
\Delta TWT \cong \frac{C}{1\%} \frac{(-25^{\circ}) + R}{1\%} \frac{(2^{\circ}) + S}{0.5} \frac{(-25) + T}{50^{\circ}} \frac{(-8)}{(1)}
$$

 ΔTWT = change in tubewall temperature, ^OF

- $C =$ increase in CH_a leakage from base case, mole % CH₄
- *R =* increase in operating rate from base case, percent of design
- $S =$ increase in S/G ratio from base case
- $T =$ increase in mixed-gas inlet temperature from base $case$, $^{\rm OP}$

Note: If variables are decreased from base case, they should be entered into expression with appropriate minus sign.

Examples illustrating the application of this algebraic expression are given in Table 1. The first column is the base case used in the comparison. The second column shows that, as the operating rate *is* increased from 100% in the base case to 110% of design, the tubewall temperatures should increase 20°F. Columns three through five show the corrections for increase in steam to gas ratio, mixed-gas inlet temperature and methane leakage respectively. The last column is the normal instance when a number of variables have been changed from the base case used in the comparison.

In the comparison of any two sets of operating data on a reformer, a base case is selected from either the earliest data or the design case, and the comparative case adjusted for

the effect of the variables to give a calculated maximum tubewall temperature. The average of the maximum tubewall temperatures measured compared with this calculated value is a relative measure of the decline in catalyst activity, assuming other factors such as poisoning or catalyst breakage have not influenced operational results.

Effect of sulfur in feed gas - In the above discussion, the assumption has been made" that the process hydrocarbon feed to the reformer is sulfur "free." The effect of relatively small sulfur concentrations in the feed

	1 Base Operating Case	Increase Rate 10%	3 Increase S/G $3.5 \text{ to } 4.0$	4 Increase Mixed- Gas Inlet Temp 50 ^O F	5 Increase CH _A Leakage 1.0%	Increase Rate 10% Increase S/G Ratio 3.5 to 4.0 Hold M. G. Inlet Temp. Reduce CH ₄ Leakage 0.5%
Operating Rate,						
Mixed Gas Inlet						
$CH4$ Leakage from						
Estimated Tubewall Temperature, \circ F T _{Base} T _{Base} T _{Base} T _{Base} T _{Base} T _{Base}			$+200F - 250F - 80F$		-25° F	$+20 - 25 + 13 =$
						T_{Base} $+8$ ^O F

Table 1. Effects of variables on tubewall temperatures experienced in fired tube reformer.

* parts/million volume

gas is to dramatically increase the tubewall temperature and methane leakage by imposing a reduced activity on the catalyst. In Table 2, the effect of sulfur concentration in feed gas is tabulated with the change in the tubewall temperature and methane leakage *holding a constant heat input into a high pressure reformer.* Under normal circumstances, when sulfur is introduced into a furnace the plant operator either increases the furnace firing to hold the methane leakage, or reduces the firing to hold the tubewall temperatures with the methane leakage increasing. In severe sulfur poisoning instances, the plant rate may even be reduced.

In the normal range of sulfur concentrations experienced in high pressure reforming today (0.1- to 0.3 parts/million volume), it can be estimated that a 0.1 parts/million volume increase in the sulfur concentration of the feed gas will increase the tubewall temperatures about 3- to 4°F, and the methane leakage about 0.1 mole %. This effect of sulfur can also be algebraically added in the equation to calculate the change in tubewall temperature from a base case.

Sulfur has always been considered as a temporary poison for reforming catalysts. In the overall performance of a fired tube reformer, this may not be entirely the case. There is some commercial evidence that, when sulfur is removed from the feed gas and then eventually stripped off the catalyst, tubewall temperatures *in the maximum flux zone* do not return to their lower values, this despite the fact that methane leakage and methane approach to equilibrium may all return to normal. In the definition of a reformer as described here, the permanent effect of sulfur poisoning, if any, is more apt to be noticed.

Additional variables - The ammonia plant, with its fired tube reformer and secondary reformer, offers an additional degree of flexibility in the operation of the fired tube reformer. Normally, higher methane leakages from the fired tube reformer can be compensated for in the secondary reformer with very little penalty to the overall methane leakage from the secondary reformer.

In a typical high pressure ammonia plant, holding all other things constant, an increase in the primary reformer methane leakage of 1 mole % will increase the methane leakage from the secondary reformer by abeut 0.15 mole %. Under these circumstances, the secondary reformer outlet temperature will decrease about 35°F. To offset this 0.15 mole % increase in the secondary reformer methane leakage, the air addition rate to the secondary reformer can be increased about 5% to reduce the secondary methane leakage to its original level. The net effect will be to reduce the ratio of hydrogen to nitrogen at the secondary exits from about 2.6 to 1, to 2.5 to 1, which is relatively minor. As described earlier, the increase in primary reformer methane leakage of 1 mole % wiU reduce the tubewall temperatures in the fired tube reformer about 25^oF.

In the event that the secondary reformer is "sick," the fired tube reformer is usually overtired to compensate for the poorly operating secondary. This penalizes the tubeskin temperatures in the primary forcing a balance between tubewall temperatures and the secondary methane leakage. This will, in turn, force a balance between the plant production rate and process hydrocarbon efficiency experienced.

The effect of the 0.15 mole % increase in the secondary reformer methane leakage will be to reduce the plant production rate about 1.8 %. To compensate for this reduction in production, the process hydrocarbon feed rate can be increased about 1.8 % so that essentially no production is lost. Process efficiency will be lower, however, due to additional ammonia loop purge. To offset these negative factors, the tubewall temperatures in the fired tube reformer will have been reduced about 21^{OF} :

$$
(\Delta TWT \cong \frac{1\%}{1\%} (-25) + \frac{1.8\%}{1\%} (2) \cong -21^{O}F) \tag{2}
$$

The efficiency consideration in the operation of the ammonia plant will become an even more important one in view of the increasing costs of process hydrocarbon feeds. In the example above, the 0.15 mole % increase in the methane leakage from the secondary, if compensated for by increased feed rate to give the same production, will result in an increase in the total hydrocarbon usage of less than 0.5%/ton of ammonia produced. This effect has been further minimized as a result of industry using more active low temperature shift catalysts which dramatically reduce total inert introduction into the synthesis loop.

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Table 3. Maximum tubewall temperatures measured in a top fired tube reformer with 12 month old catalyst.

Operating'data

Production Rate $-1,083$ ton/day S/G Ratio $-4.0/1$ MG Inlet Temperature $- 880^{\circ}F$ Combined Outlet Temperature — ? Primary CH4 Leakage -10.8 mol $%$

Tubewall Temperature Surveys

The procedures outlined have been applied to numerous reformers to define performance at a point in time, and to compare performance after various periods of time. A typical survey is given in Table 3. Pyrometer readings taken by the plant operator and CCI at the same time are identified.

The maximum tubewall temperatures given in Table 3 were measured in a fired tube reformer after the catalyst had been in service for 12 months. Similar surveys in the same fired tube reformer were made after 17% months and 21 months operation. Between the 12 month and 17% month surveys, the activated carbon used to desulfurize the natural gas feed was replaced with fresh activated carbon as higher-than-normal sulfur introduction into the reformer was being experienced. The normal level of sulfur introduction into this furnace is less than 0.1 parts/million volume in the natural gas. Prior to replacement of the carbon, the sulfur level of the natural gas into the furnace was about 0.8 parts/million volume.

The maximum tubewall temperatures predicted by CCI's kinetic system for this plant, operating at a 100% of design rate with a "sulfur free" gas, is 1,635°F. In Table 3 the average hot spot temperature on catalyst tubes was 1,670°F.

Secondary CH4 Leakage -0.35 mol $%$

Furnace ΔP – 50 lb./sq. in. at approximately

450 lb./sq. in. gauge outlet pressure

Maximum Tubewall Temperature Average — 1,670°F Range of Maximum Tubewall Temperature $-1,600 =$

to 1,765°F

Using the data at the three points in catalyst life, corrections for differences in the variables were made to the design maximum tubewall temperature calculated. In Table 4 these calculated temperatures are compared with the actual average hot spot temperatures measured. As will be noted the average maximum tubewall temperatures experienced through 17% months agree very well with what would be predicted on the basis of differences in the variables from those used in the design. This means that the catalyst activity level is close to design. It would appear that in the 21st month the catalyst activity had significantly declined.

Similar determinations of catalyst activity levels for other fired tube reformers are given in Table 5. In all these plants, performance is compared with the design. When the difference between the measured and estimated maximum tubewall temperatures is negative, then catalyst activity level is better than design. Positive differences mean the catalyst activity level is less than design.

Plants A and B, Table 5, having been on stream only a short time when surveyed, reflect the very high activity of new catalyst. Plant C is exhibiting activity essentially at design level which is not as good as anticipated after only four months óf operation. Plant D is operating with an activity level considerably lower than design and will Table 4. Comparison of calculated maximum tubewall temperatures with actual hot spot temperatures in a top fired tube reformer.

Table 5. Comparisons of maximum tubewall temperatures measured and estimated in high pressure fired tube reformers

require replacement after a relatively short life. Plants F and K are in this same category with respect to activity level and will be replaced. In the case of Plant F, operation during the initial seven to eight months was with very high sulfur levels in the feed gas. After removal of the sulfur from the feed gas and other operations to ensure that sulfur was swept off all the catalyst, the activity never returned to a satisfactory level. All other plants appear to be demonstrating satisfactory performance.

The exact significance to be placed on the absolute values of the differences between the measured and predicted maximum tubewall temperatures and the rate of change of this difference with catalyst age or catalyst loading is not well defined at this time. More data are required to establish this. It appears now, however, that when tubewall temperatures are the same as or lower than estimated from the design, furnace performance is very satisfactory. Also, when tubewall temperatures are about 30°F higher than design, replacement of the catalyst is required. It is planned to continue the definition of fired tube reformers in the manner described and further reports will be available as more data are collected.

Figure 1. Variables to be determined and measured around a fired tube reformer.

In Figure 1, the necessary rates, temperatures, pressures, and gas compositions at the required points of measurement around a fired tube reformer are shown. The nomenclature that is used throughout this article is also given. The following paragraphs discuss the data to be measured.

Process feed rates - The rates of steam and hydrocarbon introduction to the reformer are normal operating measurements taken from the streams' respective flow meters. Corrections for temperatures and pressures and hydrocarbon feed analyses are required only if detailed heat balances and computer analyses are to be performed. For general day-to-day comparisons, corrections of meter readings and hydrocarbon feed analyses are not required. The ratio of the steam to hydrocarbon feed ratio or the steam to gas ratio is generally sufficient for use in these comparisons.

Inlet temperature - The mixed-gas inlet temperatures have been observed to vary within rather wide limits (as much as 100°F) on a furnace. As the degree of preheat of the feed to the reformer affects the quantity of heat input in the fired box, and thereby the tubewall temperatures, it is required to record and use this temperature in comparisons.

Pressure drop — A plot or comparison of reformer pressure drop vs. time on stream since catalyst charging gives an indication of the degree of carbon deposition, catalyst fouling, and catalyst breakage occurring if such values are corrected for variance in rate. Comparisons of the pressure drops at different rates can be made by correcting

Figure 2. Equilibrium constants for the water-gas shift reaction at temperatures from 1,000- to 2,000°F.

all pressure drops to the same rate using a factor of the ratio of the total mass flow rates in consistent units raised to the 1.8 power. This is shown in the equation below:

$$
\Delta P_2 = \Delta P_1 \quad \frac{\text{Total Mass Rate 2}}{\text{Total Mass Rate 1}} \quad \frac{1.8}{}
$$
 (3)

Outlet temperature - In fired tube reformers with multiple outlet headers, it is necessary to average all of the tube outlet temperatures measured to give the combined temperature out of the reformer. In some furnaces the reformed gas out of the catalyst tubes if further heated in risers within the firebox and then combined and the temperature of this combined gas measured. This temperature should also be noted.

Exist gas analyses - The dry gas analyses on the reformer exist are routine determinations of the concentrations of methane, carbon monoxide, carbon dioxide, hydrogen, and nitrogen. The accuracy of the analyses can be checked by determining equilibrium constants for the steam-methane reforming and water-gas shift reactions.

1. Steam-methane reforming reaction $CH₄(g) + H₂O(g) \xrightarrow{\longrightarrow} CO(g) + 3H₂(g)$ 2. Water-gas shift reaction $CO(g) + H_2O(g) \xrightarrow{\longrightarrow} CO_2(g) + H_2(g)$

Figure 3. Equilibrium constants for the steam-methane reaction at temperatures of 1,000- to 2,000°F.

The water-gas shift reaction goes to equilibrium, and the equilibrium constant given in Figure 2 can be used to determine the actual temperature exit the reformer. This is then compared with the combined outlet temperature measured for the reformer. In many instances, the outlet temperature determined from the water-gas shift equilibrium will be higher than the measured outlet temperature.

The equilibrium constant for the steam-methane reforming reaction can be used in Figure 3 to give the equilibrium temperature for the steam-methane reforming reaction. The difference between the measured outlet temperature or the water-gas shift equilibrium temperature and the steam-methane equilibrium temperature is the approach to equilibrium for the steam-methane reforming reaction.

> Approach to equilibrium $=$ Measure outlet temperature minus equilibrium temperature for steammethane reforming reaction or

> Approach to equilibrium $=$ Equilibrium temperature for water-gas shift reaction minus equilibrium temperature for steam-methane reforming reaction.

The approaches to equilibrium must be positive, and in a good operating reformer are about 20- to 40°F. If the use of both the measured outlet temperature and the water-gas shift equilibrium temperature give negative approaches to equilibrium, then the gas analyses should be suspect to error and another analytical determination of the reformed gas composition made. If the approach to equilibrium using the measured outlet temperature is a negative value, whereas the approach using the water-gas shift equilibrium is positive, then most probably the measured outlet temperature on the reformer is in error and is reading low. The gas analyses in this latter case should be satisfactory for comparison. If both give positive values, then of course, the analyses are satisfactory for comparison.

Tubewatt temperature measurements - The final information to be gathered in the definition of the reformer's performance is the maximum tubewall temperature and the tubewall temperature profile. Each type of furnace, whether top fired, side fired, or bottom fired, has a section of the tube that exhibits the maximum temperature on that tube.

For comparative purposes, it is well to measure the maximum tubewall temperature on each end of the reformer row on each row in the reformer from the front side and then the back side of the row. In this manner, each row of tubes will have at least four measurements. More readings of the tubewall temperatures can be made if desired, however, the procedure specified above is the minimum that should be used for comparisons of maximum tubewall temperature and for furnace trimming.

To establish the average tube temperature profile over its entire length, the procedure above can be performed on at least three, and preferably more, different levels on the tubes. The values measured at each level can be averaged to give the temperature at that point on the tubes. The averages at the different levels then define a tube temperature profile. Alternately, temperatures on single tubes can be measured at different levels and then these values averaged to give an average tube temperature profile. The difference between these two methods will be negligible if a sufficient number of measurements are taken.

In Conclusion

The above information gathered and tabulated routinely should be the basis for fully defining the performance of a fired tube reformer. From this information changes in operating variables and the furnace firing pattern can be programmed and followed to ensure minimum tubewall temperatures necessary to do the job. It should serve as the basis for catalyst replacement in the tube, either in all the tubes, or in only a few of them. It can also be an aid in pinpointing those tubes in the furnace that have been operating with tubewall temperatures above a maximum limit and which should be replaced during a shutdown as a preventive measure.

It should be noted that the data can be used whether the fired tube reformer is operated with a sulfur-free hydrocarbon feed stream or with one containing sulfur. The effect of sulfur on performance has been described in this article.

Literature cited

1. Lenoir, J.M., *Hydrocarbon Process., 91* (October 1969).

DISCUSSION

ANON: I would like to know which type of catalysts were used in the plants.

LOMBARD: Well, I don't want to get into the type of catalyst that are installed, because the important thing that we're trying to do here is to put forth a procedure that we feel may be very helpful in defining the catalysts lives and rate of changes that will be experienced. But almost every supplier's catalyst are represented in the surveys that we've taken. It is not only CCI's catalysts, but other suppliers' catalysts. And I don't want to get into any commercialism right now.

ANON: So they are not all CCI catalysts?

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 \mathcal{L}

 ~ 100

LOMBARD: Not all of the plants included in this survey are CCI's catalysts.

 $\zeta=\zeta$

 \mathcal{L}

 \overline{f} $\mathcal{L}_{\rm{in}}$

 $\frac{1}{2}$

are CCI's catalysts. **J. F. LOMBARD R. A. CULBERSON**

