

JM ProcessWise Webinar

Carbon formation issues in steam methane reformers

May 2020

Questions and Answers

- Q1. What is the effect of catalyst loading on the carbon formation? And what is the optimum free space inside the top of reformer tubes?
- A1. Alkalised catalyst can help to increase the rate of carbon gasification and hence move the boundary of the carbon deposition zone. For the set of operating condition, the catalyst vendor will normally assess the potential for carbon formation and advise the best catalyst solution.
Thermal transients can lead to crushing of the catalyst and level of the catalyst can fall during operation. Hence, it is generally recommended to load at least 300mm above the heated length. Care should also be taken not too load too close to the pigtails, as the gas velocities can lead to milling of the catalyst.
- Q2. Carbon laydown, specifically at 1-3 meters top of reformer tubes (top fired Reformer); what could be the possible causes?
- A2. For a top fired reformer, typically 20-40% from the inlet of tube is where carbon is most likely to form due to high enough temperatures to drive the hydrocarbon cracking rations at a fast rate but low levels of hydrogen to methane. Carbon can form at this location due to several issues such as catalyst deactivation, catalyst poisoning and low S:C operation.
- Q3. What's was the maximum allowed temperature, the mixed feed could be heated up in mixed feed coil to keep it away from methane cracking?
- A3. The maximum allowable temperature is dependent on the full gas composition, the hydrogen content, the S:C ratio and the catalyst.
- Q4. What is the effect of increasing skin temperature of the reformer tube on carbon formation?
- A4. A higher outer TWTs typically means hotter process gas temperatures and hotter inner TWTs. Consequently, this would normally increase the potential for carbon formation.
- Q5. How does heat flux and fuel composition impact hot bands formation, specifically at 1-3 meters length along the tubes from the top (top fired reformer)?
- A5. Normally, 20-40% from the inlet of tube is where carbon is most likely to form due to high enough temperatures to drive the hydrocarbon cracking rations at a fast rate but low levels of hydrogen to methane. Higher heat fluxes normally mean hotter process gas temperatures and hotter inner TWTs. Consequently, this would normally increase the potential for carbon formation.
- Q6. Having higher conc. of CO₂ at reformer inlet with stream coming from pre-reformer outlet and a reformer inlet temp of 650deg C; will the high CO₂ will contribute C Laydown?
- A6. As stated in the webinar, CO₂ can assist with the gasification of carbon, but he conditions with CO₂ increase the potential for Boudouard carbon ($2CO \rightleftharpoons CO_2 + C$). Concentrations of other components (including hydrogen), the S:C ratio, the catalyst type, temperature profile of the tube and the reformer geometry also influence the potential for carbon formation. Consequently, we would please consult your catalyst vendor for more details.

- Q7. For direct injection of BFW upstream of reformer inlet, how it will contribute to the carbon laydown specifically on top side? Will it be reversible impact?
- A7. The addition of BFW should help increase the S:C ratio and thereby help reduce the potential for carbon formation. BFW chemicals however can lead to deposition of poisons/foulants on the catalyst, which could then result in carbon formation. The possibility to reverse the effects would be dependent on the type of poison/foulant.
- Q8. What is the typical dP increment observed of a JM Catalyst subject to carbon formation?
- A8. The effect of carbon formation can significantly vary with any catalyst. A mild deposition of carbon may result in hot spots/patches but may not be evident in the pressure drop. Alternatively, a severe deposition of carbon can severely restrict the flow through the tube. The effect on the pressure drop would be dependent on the degree of carbon deposition and the number of tubes affected.
- Q9. which is the typical max allowed delta T among different tubes in reformer in order to avoid carbon formation or tubes damages?
- A9. Normally a TWT spread of less than 100°C is considered reasonable, however we would expect most plants to be able to achieve a spread in temperature of less than 75°C.
- Q10. With potash promoted catalyst, the K is mobile, therefore, does it lose its activity as the catalyst ages? And how long typically can this catalyst be used?
- A10. All catalysts lose their activity with age. There are examples of potash promoted catalyst having lives of over 10 years. However, operating conditions and catalyst types can significantly vary and hence there is no general rule of thumb. We would advise consulting your catalyst vendor for an appropriate changeout strategy.
- Q11. What are the negative traits of using alkalized catalyst?
- A11. If alkalised catalysts are mal-operated, then it is possible to accelerate the rate of potash migration which can lead to fouling of downstream units.
- Q12. Which is the typical arrangement or chemistry (of course not the exact formula) of an alkalised catalyst?
- A12. Alkalised reforming catalyst are catalyst that have been promoted with alkali or alkaline earth metals (e.g. potassium), to increase the rate of carbon gasification and thereby reduce the potential for carbon deposition issues. Most alkalised catalysts use potash or lanthanum promotion. Lanthanum keeps catalyst carbon free. Potassium can also keep the initial carbon formation area of the inner tube wall carbon free.
- Q13. Alkalised Catalyst - is the alkaline property a once off (meaning it will disappear after a few startups) or across the useful life of the catalyst?
- A13. The properties of the alkalised catalyst provide benefits against carbon formation over the whole life of the catalyst.
- Q14. What steam to carbon ratio protection would you advise for a top fired reformer with outlet of 740C?
- A14. 740°C is typical for a primary reformer on an ammonia plant, most hydrogen and methanol plants would operate with steam reformers with hotter outlet temperatures. However, the potential for carbon formation cannot be stated with the information provided alone. Concentrations of other components, the S:C ratio, the catalyst type, temperature profile of the tube and the reformer geometry also influence the potential for carbon formation. We would recommend consulting your catalyst vendor. Problems can also occur if operating at minimum turndown rates, for guidance on this operating mode, please consult your equipment and burner designers.

- Q15. How do tubes look 1) if there is carbon formation and 2) if there is sulphur poisoning, is there any difference between the two observations?
- A15. The appearance of the hot spots/patches can be very similar for both issues with sulphur poisoning and hydrocarbon cracking issues. This is because both effects reduce the endothermic steam-reforming reaction which result in the hot spots/patches. For any signs of hot spots, it is important to go through a troubleshooting process to identify the root cause.
- Q16. How can remove carbon deposition from internal surface of tubes after we unload the catalyst and before loading new catalyst?
- A16. It is not normal practice to clean the reformer tubes between catalyst changeouts. This is because it is rare to get deposition of carbon on the inner surface of the tubes after the reformer has been shutdown and steamed in that process, unless the carbon formation was severe. Small levels of carbon deposition would normally be removed as the catalyst is vacuumed out. If required a soft stainless-steel brush can be used. Other more aggressive techniques are also available but are not normally required unless there are issues with scale, which isn't likely to be an issue with carbon formation alone.
- Q17. My question was on maximum temperature allowed in a mixed feed of methane rich stream where there was no pre-reformer to prevent methane cracking?
- A17. As per Q3, the maximum operating temperature cannot be stated with the information provided alone. Concentrations of other components, the S:C ratio, the catalyst type, temperature profile of the tube and the reformer geometry also influence the potential for carbon formation. We would recommend consulting your catalyst vendor.
- Q18. Having Carbon Activity >1 at reformer inlet couple with high inlet temp 650°C and low S/C ratio <1.9 will contribute the laydown with no C2+ present?
- A18. As per Q17, an answer cannot be provided with the information provided alone. Concentrations of other components, the S:C ratio, the catalyst type, the heat flux and the reformer geometry may also influence the potential for carbon formation. We would recommend consulting your catalyst vendor.
- Q19. At what temperatures the mixed feed - NG+steam would tend to prior to coming in contact with the reforming catalyst in tubes?
- A19. The typical inlet temperature for a reformer operating with a NG feed is 450-650°C.
- Q20. How can you optimize steam:carbon ratio (mol/mol) after a pre-reformer without carbon formation? There is a recommended sensor which delivers S:C accurately?
- A20. There are feedback loops that help a plant calculate the steam:carbon ratio but the optimization is generally still manual. Unfortunately, there is no instrument that can assist with S:C optimisation. Your catalyst vendor should be able to advise based on their experience and analytical studies.
- Q21. Q: For Online Monitoring of carbon lay down potential / gap from carbon formation, have there been any implementation at DCS level to provide safe op. margins?
- A21. Many plants will calculate the S:C ratio on their DCS system, this can be used to provide an alarm. However, the emphasis is safe operation rather than production optimization.
- Q22. At what depth down the reformer tube does coking starts, or does it starts at top.
- A22. Generally, the initial signs of carbon deposition issues occur at 20-40% of the way down the tube from the inlet, as discussed in A2.
- Q23. For Silica contamination, how much reversibility is expected in catalyst after steaming activity.
- A23. Silica cannot normally be removed by steaming.

- Q24. At what temp does carbon formation occur?
A24. Carbon formation is dependent on many factors, such as the gas composition, S:C ratio, hydrogen content, catalyst type, catalyst age, etc.. Hence carbon formation can onset at different temperatures.
- Q25. In combined reforming process where the SMR bypass line mixes with the SMR outlet prior to ATR, is there a probability of carbon formation in this nozzle?
A25. It is possible to get carbon formation at the mixing nozzle due to the hotter temperature of the reformer effluent, however the partial pressure of hydrogen from the SMR should suppress carbon formation immediately after mixing.
- Q26. What is an alkalised catalyst?
A26. Alkalised reforming catalyst are catalyst that have been promoted with alkali or alkaline earth metals (e.g. potassium), to increase the rate of carbon gasification and thereby reduce the potential for carbon deposition issues. Please see A12.
- Q27. Should we do steaming every shut down?
A27. Steaming can also accelerate the rate of catalyst deactivation by sintering and lead to the oxidation of the catalyst. Hence it is recommended to only steam the reforming catalyst at temperature should there be a requirement and with advice from your catalyst vendor.
- Q28. I could not well receive the slide point which says, "nitrogen to facilitate monitoring", how please?
A28. When steaming to remove carbon, CO and CO₂ will be generated. Adding nitrogen into the steam, allows you to take a dry gas sample, hence allow you monitor how much CO and CO₂ are being evolved and thus monitor the effectiveness of steaming.
- Q29. How can high concentration of H₂ inhibit carbon formation?
A29. The carbon is form by hydrogen carbons cracking to for carbon and hydrogen. Hence increasing the partial pressure of hydrogen inhibits the reaction.
- Q30. Why does carbon formation occur only around 20-40% of tubes?
A30. Carbon can be formed at other positions in the tube under the right conditions, however this position is the closest to the carbon deposition zone for reasons explain in A5.
- Q31. How much increase of pressure drop can be expected if catalyst runs for 5 years?
A31. The reformer tube expands and contracts when the reformer goes through thermal cycles. The number of thermal cycles and the design of the catalyst impact the pressure drop rise that will be experienced. Typically, the increase in pressure drop over the catalyst is 2-6% per year.
- Q32. What percentage of catalyst recovery from carbon / sulphur poisoning is possible if the reformer has been operated with sulphur slippage for a few hours?
A32. Experience has shown that almost full recovery of the catalyst performance may be obtained, especially for instances where the level of carbon deposition/poisoning has been mild. This is not the case in all circumstances and some plants may not achieve the designed lifecycle of the reforming catalyst. Taking swift action to both solve the root cause and to steam the catalyst to remove any carbon laydown provide the best chance for minimising long-term impact for an incident of carbon formation.

- Q33. What is the maximum percentage of recovery from carbon deposition could achieved through gasification with steam?
- A33. Experience has shown that almost full recovery of the catalyst performance may be obtained, especially for instances where the level of carbon deposition has been mild and/or action has been taken swiftly but this may not be the case in all circumstances.
- Q34. What is the reduction rate of carbon formation tendency using structured as CATACEL SSR vs traditional catalyst pellet?
- A34. Structured reforming catalysts such as CATACEL SSR, can have a higher GSA per unit volume and better heat transfer properties, both of which aid in preventing carbon formation.
- Q35. Alkalized catalyst will give some margin from carbon lay down, but how much and till when (1 yr,2 yr) it can sustain at Ref Inlet 650°C and 1.8 S/C ratio?
- A35. For alkalised calcium aluminate catalyst, the steam ratio can be reduced by approximately 65% without forming carbon compared to an undoped alumina. The reason for this is due to both the acceleration of the carbon gasification reaction and the suppression of carbon formation reactions. The effect can last over the life of the catalyst. Please also see A10.
- Q36. Alkalized catalyst reliability to sustain performance without accelerated potash migration etc., while operating at harsh conditions (high heat flux, S/C 1.8, inlet T of 650C)?
- A36. Alkalised catalysts are presently used in the majority of reformers and typically achieve long lives without any issues. As with any type of catalyst, it is important to try and keep them in their designed operating window to avoid any issues or problems.
- Q37. What is the recommended lowest steam/carbon ratio?
- A37. The recommended minimum operating S:C ratio is dependent on the feed type, the catalyst and other operating parameters. We suggest discussing with your catalyst vendor for specific advice.
- Q38. What is the lowest outlet temperature as recommended?
- A38. A low operating temperature does not have any negative effect on the process or the catalyst, unless you are approaching condensation conditions (e.g. during a shutdown). Accordingly, the normal minimum operating temperature during normal operating is typically defined by the minimum turndown of the burners/fuel system and the desired conversion.
- Q39. Any recommended type of catalyst to minimize carbon laydown risk?
- A39. Alkalised catalysts, such as potash promoted catalysts, are normally used to manage operation with feeds and conditions that have a higher potential for carbon laydown.
- Q40. What is the problem in steaming the catalyst without feed for a very long period of time?
- A40. Steaming can also accelerate the rate of catalyst deactivation by sintering and lead to the oxidation of the catalyst. Hence it is recommended to only steam the reforming catalyst at temperature should there be a requirement and with advice from your catalyst vendor.
- Q41. Is there any planning for new types of JM reforming catalyst or a new schemes of loading?
- A41. Johnson Matthey continually invest in the research and development of reforming catalyst. We have recently launched our structured reforming catalyst, CATACEL SSR, and have several other projects on the horizon.

- Q42. Is there any recommend operational parameters to enhance the carbon removal reaction (gasification) during the startup?
- A42. Generally, a specific steaming procedure at more aggressive conditions would be required to resolve a known carbon laydown issue. Most carbon laydown issues tend to be near the tube inlet section, hence one of the challenges of an effective steaming is to target higher inlet temperatures to increase the potential for carbon gasification.
- Q43. Do you recommend tube skin thermocouples? We use a pyrometer but would like some form of continuous monitoring that ties back to the DCS
- A43. Tube skin thermocouples only provide a spot measurement, typically only employed on a limited number of tubes and do not tend to have long lives. The benefit of the pyrometer measurements is that it encourages operators to also make a visually assessment of the reformer, which is particularly important for identifying signs of reformer issues that can influence carbon laydown.
- Q44. Can steaming too long damage catalyst?
- A44. Excessive steaming can have negative effects, please see Q40.
- Q45. We saw some spikes in sulfur in the feed and got some hot spots in the reformer. Is this carbon and can this can be removed?
- A45. Sulphur is a poison for reforming catalyst. The subsequent loss of activity and hence decrease in endothermic reforming reaction, may be observed as hot spots/bands. The reduced hydrogen partial pressure and the increased temperatures can then lead to carbon deposition in these zones. Steaming can help to remove the sulphur poisoning as well as the carbon, however in such circumstances it is important that the source of the sulphur is first stopped so that the catalyst is not poisoned again after the steaming.
- Q46. What's the best way to detect for early signs of carbon formation?
- A46. Generally, hot spots/bands on the reformer tube during operation is the first sign of carbon formation issues. The tube appearance should be checked following any known plant upset where you suspect carbon laydown may have occurred.
- Q47. Is C deposition an issue with Naphtha - Steam Reforming and not at all likely for Natural Gas - Steam Reforming?
- A47. Carbon formation issues can happen with all types of hydrocarbon feeds including natural gas and naphtha. Generally, there is greater challenges of preventing carbon with heavier feeds because they are more prone to cracking at lower temperatures.
- Q48. Are there any systems for continuous online TWT measurements?
- A48. Yes, there are several continuous monitoring systems for TWTs, such as the NIR Borescope provided by Ametek Land. These types of systems are not commonly used at present, however there is a growing interest in these systems for improving reliability and as part of digitisation initiatives.
- Q49. What are some common causes of burner issues on top-fires reformers?
- A49. Burners can suffer from issues such as erratic flames, tip erosion, fouling, misalignment and as circulation problems. Hence it is important to ensure burners are well maintained. Fuel and combustion air can also be prone to maldistribution challenges due to the low pressures of these systems.
- Q50. What is the longest you are allowed to steam the reformer?
- A50. Please see A40.

- Q51. For non-top fired reformers (e.g. bottom fired and terrace wall), is the main zone of susceptibility still 1/3 down? Or does it = the highest heat flux zone?
- A51. The location of carbon formation can vary depending on the reformer geometry. Most issues with carbon formation during normal operation occur at a third of the distance heated length from the process gas inlet side of the tube, whether the reformer is downflow or upflow. However, this is not always the case and the position of carbon formation may differ depending on the root cause of the carbon laydown and the operating mode of the reformer at the time.
- Q52. What should be the operating optimum temperature for steaming? For how long can we steam, is oxidation of catalyst a concern while steaming?
- A52. The aim is to obtain a high inlet temperature to increase the potential for carbon gasification in the inlet section. However, a steaming process should always be discussed with the catalyst supplier before it is attempted. Please also see Q40.
- Q53. We look at TWT, reformer outlet temp, flue gas temp, natural gas compressor spill back (to help determine if we have dP) and feed/product PCs. Any other ideas?
- A53. It is also advisable to have occasional analysis of the feed and effluent gases, to check for changes in feed and to confirm the unit performance. If the pressure drop measurement is over several units, it may not provide the most effective means of assessing issues and problems with the reformer. Ensuring the measured parameters are not only measured but also appropriately recorded and actively checked for trends is vital. Good operator training is also an important tool for managing the reformer and ensuring reliable operation.
- Q54. Can JM predict whether carbon will form for varying feed composition?
- A54. Johnson Matthey has an advanced reformer simulation with an integrated carbon model which has been developed from years of experience and analytical data. This is one of the tools we use to provide guidance on catalyst selection and suitable operating conditions.
- Q55. What would be a conservative S:C ratio to prevent carbon deposition for methane concentrations <92%, or heavier hydrocarbons in the range of 6-8% or higher?
- A55. Most plants operating with a natural gas feed will operate with a S:C ratio of 2.8-3.5 mol/mol. However please consult your catalyst supplier for specific advice.
- Q56. Effect of olefins in the feed gas on carbon formation? What level is acceptable?
- A56. Olefins would normally be hydrogenated in the HDS upstream of the reformer in most syngas plants. In the absence of a HDS unit, the olefins would increase the potential for carbon formation and are highly reactive to form carbon at the reformer operating conditions.
- Q57. What temperature and max duration should steam only operation is recommended for potash promoter catalyst?
- A57. For effective gasification of the carbon, it is important to try and get the inlet temperature as hot as possible. Excessive steam can have negative effects and hence we would always advice consulting your catalyst vendor before attempting the process. Please also see Q40.
- Q58. What is the least steam to carbon ratio that catalyst can be save from carbon deposition in a certain trouble shooting?
- A58. The onset for carbon laydown varies from plant to plant. Also, duration has an effect. Under aggressive conditions carbon laydown can be significant and happen quickly, or alternatively under mild conditions the carbon laydown slight but build up gradually over time. Hence the range of S:C ratios that can be recovered from can be wide. Please also see Q14.

- Q59. For steam to carbon, we have had success with 92-94% methane keeping the s:c no less than 3.3?
- A59. Many plants operating with a natural gas feed can get to S:C ratios lower than 3.3, however many factors influence the minimum S:C ratio that is achievable other than the feed composition. Please also see Q14.
- Q60. What if the purpose of reforming is to optimize production of Carbon Monoxide, how to operate to avoid/ decrease the chance of carbon deposition?
- A60. HyCO plants generally operate at lower S:C ratios than hydrogen plants, and often have recycle or other streams of CO₂ added to the feed. The CO₂ aid in preventing carbon formation and hence why HyCO plants can get to much lower S:C ratios. Nevertheless, even with HyCO plants, alkalised catalysts can still provide value.

Audience Poll Results

How often do you take measurements of the TWTs on your plant?

Continuous online monitoring	4%
Every day	32%
Every week	50%
Every month	7%
Less than once a month	7%