Application Guide – Syngas

Temperature Measurement, Low Temperature Shift Bed Safety and Optimization

Low Temperature Shift Process

The water gas shift reaction is a conversion process that converts Carbon Monoxide (CO) to Carbon Dioxide (CO_2) in the presence of water and is catalyzed by either iron or copper. The Water Gas Shift reaction is exothermic and favored by lower temperatures.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41.1 \text{ KJ mol}^{-1}$$

CO can be a poison to many catalysts and is difficult to remove. CO_2 is also a poison to some catalysts but is much easier to remove. In a traditional Syngas plant the Syngas is created in a partial oxidation unit or a steam methane reformer. Syngas is a blend of H_2, CO, CO_2 and residual H_2O and CH_4. The Syngas is then passed through one or a series of shift reactors to convert the CO to CO_2 and to generate some additional hydrogen. The stream then may be passed through a liquid CO_2 removal system and a methanator or to a Pressure Swing Absorber to clean up the gas.

The first shift bed is usually an iron based catalyst for bulk CO to CO_2 conversion. This is typically referred to as a high temperature shift reactor. A second reactor may follow the first and is typically loaded with a copper based catalyst. This reactor is operated at low temperature and is often referred to as a Low Temperature Shift Reactor. The copper shift catalyst is more active and can take advantage of lower SOR temperatures to maximize its CO conversion. It is also sensitive to high temperature which may increase the rate of sintering and age the catalyst.

The LTS catalyst is shipped in an oxide form. To be active for conversion the catalyst needs to be put into a reduced state and a reduction step is required. Once the catalyst is online the catalyst will deactivate over time due to process conditions and incoming contaminates.

Temperature Measurement

The Exothermic nature of the catalyzed reaction makes the measurement of temperature important in understanding the performance of the system and safely operating the reactor. It is important to understand the nature and limitations of the temperature measurement system so that proper start up and operating decisions can be made.

Types of Temperature Measurements Systems:

1. **Thermowells and Thermocouples;** These are traditional, old technologies that utilize a protection tube (thermowell) and a thermocouple inserted in to that thermowell. These systems are inexpensive and generally utilize standard, small gauge conductor wire, thermocouples. The temperature measurement is limited to the location and elevation of the thermowell.

2. **Pipewells and Multipoints;** A pipewell is a protection tube that is generally larger than the traditional thermowell and can accommodate either multiple thermocouples or a sliding thermocouple that provide a number of temperature measurements through a single reactor entry nozzle. There are a variety of types of multipoint and pipewell combinations. A typical fixed version would be a heat transfer block or button and guide tube. A block of metal is welded to the inside wall of the pipewell at the desired temperature measurement elevation. A guide tube is attached to the block so that the thermocouple can be inserted through the guide tube and make contact with the heat transfer block. This is an old technology that has a very long response time to changes in temperature. A more modern option for the multipoint assembly is to utilize a clean pipewell and insert a bundle of thermocouples supported by a rod or tube. The thermocouple measuring point is forced to the pipewell wall with bi metallic strips that change shape with temperature. The response time of these systems is more in line with traditional Thermowells and can allow for a greater number of temperature measurement points.
3. **Single Sheath Multipoints**: These multipoint assemblies utilize multiple conductors and thermocouple junctions at different levels inside a heavy walled sheath. This allows for 9 separate measuring points in a single thermocouple cable. The small metal mass gives a good response time to temperature changes, and a single cable is a good, low profile way to dramatically increase gradient points in a reactor. The ½" sheath OD allows for easy retrofits through very small nozzles.
4. **Flexible, Independent Thermocouples**: Flex – R, flexible independent thermocouples utilize large conductor size and a heavy walled sheath to provide a robust and durable thermocouple. The small metal mass provides the quickest response time and the independent nature of the thermocouple provides for near infinite measurement point locations. Most of the world's hydrocrackers have standardized on the Flex – R for radial and gradient temperature measurement.

Thermocouple response Time

Due mostly to the amount of metal mass in each system, the response to changes to temperature varies from system to system. Generally, the more metal mass in a system, the slower the response to temperature changes. The table below lists the approximate response time for the normal temperature measurement systems found in the LTS reactor. Response time is generally measured as the time it takes to see 63.2% of a temperature step change.

Temperature measurement Systems	Thermocouple & Thermowell	Pipewells and Multipoints (heat transfer block)	Pipewells and Multipoints (Flex – O)	Single Sheath Multipoints (GSS)	Flexible, Independent Thermocouples (Flex-R)
Response Time	60 Seconds	480 seconds	60 Seconds	16 Seconds	4-8 Seconds

Most LTS temperature measurement systems today have a 60 second response time. Advance Temperature Measurement Systems can dramatically improve that response time so that the operator can see changes to the system in real time.

Thermocouple Accuracy

Thermocouple accuracy is important to keep in mind when trying to determine performance of the LTS system or monitoring during reduction. Thermocouples purchased with a standard limits calibration may have a deviation of plus or minus 0.75% . For example a type K thermocouple at 700 ^{o}F could read 705 or 695 and be within the accepted specification.

A more selective process is special limits calibration. This only accepts thermocouples that are within plus or minus 0.4% .Again, in our example, type K thermocouples at 700 ^{o}F may differ from one another by 5.6^{o}F.

When looking at tight gradient or in trying to determine a radial temperature distribution, these calibrations my still be a bit wide. Gayesco has developed a special selection procedure to drive the allowable temperature spread even smaller. This process is utilized with the Flex-R flexible, independent thermocouples and each multipoint assemblies are accompanied by documentation that lists the calibration for each individual point.

Low Temperature Shift Catalyst Reduction

Process: The copper catalyst is generally shipped in an oxide form. To be active it must be placed in a reduced state. The reduction reaction is as follows

$$CuO + H2 \rightarrow Cu + H2O \qquad \Delta H = -80.8 \text{ kJ mol-1}$$

Procedures for the actual reduction should be developed in conjunction with the catalyst vendor. It is highly recommended that a representative from the catalyst company assist in the reduction. Generally, hydrogen is trickled through the reactor and the temperature reduction wave and effluent composition is monitored. This is often finished by a hydrogen soak to insure complete reduction of the catalyst.

Dangers The reduction process is exothermic. The more hydrogen that is available the quicker the reduction of the copper. This also means a greater amount of heat that is generated and must be carried off by the mass of the gas stream. Too much hydrogen too quickly, can over heat the catalyst, potentially damaging its activity. Conventional copper catalyst should not be heated too much in excess of 260 ^{o}C as they sinter and loose activity. In extreme cases it is possible to generate so much heat that the temperatures exceed the metallurgical limits of the vessel. This can lead to catastrophic failure.

Often the piping used for a reduction is not permanent or is used also in other service. Valves may be not sized correctly for reduction service and may be difficult to control in small increments. This heightens the danger that a wave of excess hydrogen may be introduced to the unreduced or partially reduced catalyst.

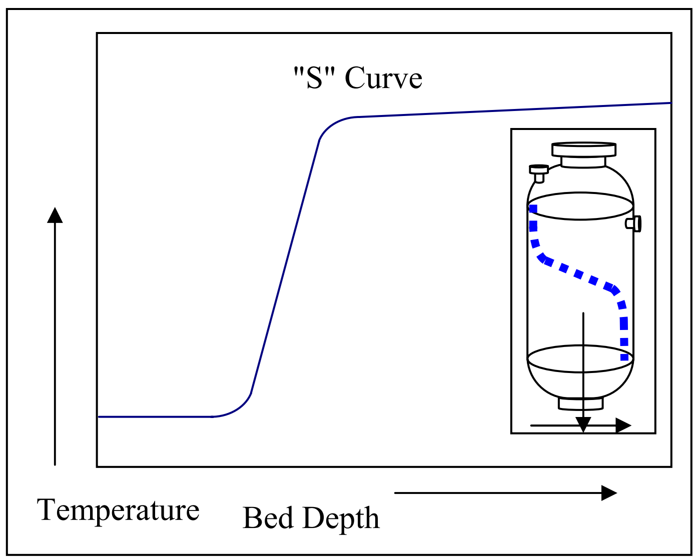
Thermocouple response Time: When performing a reduction, it is important to understand the limitations of the particular temperature measurement solution. Bed temperature changes with pipwells and Thermowells are not immediately reflected in reported temperature changes. Care should be taken to factor the response time of the temperature measurement system into decisions to change the rate of hydrogen addition. The small metal mass of the single sheath multipoints and the Flex-R flexible, independent thermocouples allows for a more real time response to temperature changes. The impact of response time can be determined by knowing the residence time of the reactor at the reduction conditions.

Thermocouple Accuracy: During the reduction process, we are watching the temperature wave move through the bed. A larger number of points in the reactor give you a better profile and depth of that reaction wave but it also means that you are comparing two different thermocouples. It is important to understand at what calibration limits were those thermocouples specified. When trying to compare absolute numbers between systems and looking for small changes it is essential to factor in the potential, acceptable, thermocouple deviation.

Catalyst Monitoring

Catalyst Modeling and Approach to Equilibrium (ATE)

Approach to equilibrium (ATE) for the outlet of a catalyst bed is difference between the actual outlet temperature and the theoretical equilibrium outlet temperature for the outlet composition. The more accurate the input data for the model, ie the outlet composition and temperature, the more accurate the ATE is a reflection of catalyst activity at that temperature.



“S” Curve Temperature Graph

A basic way to track the performance of an exothermic fixed bed catalyst is to examine the temperature profile of the exotherm. The more temperature points that are available for profiling the catalyst provides for a more detailed picture of catalyst performance, historical change and catalyst life predictions.

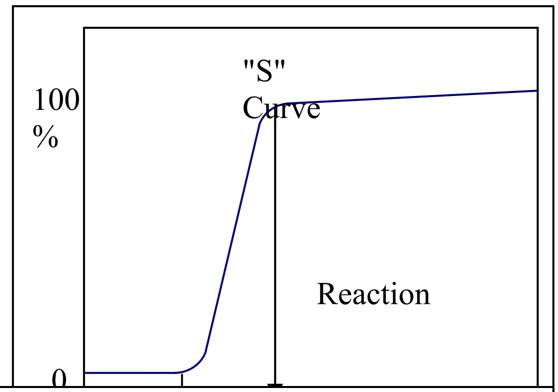
If you graph the temperatures of the LTS bed thermocouples versus bed depth you will create an “S” shaped graph. The initial flat section at low temperature represents little or no temperature increase and no reaction. We can infer that the catalyst represented in this section is inactive. The upward sweeping section is the reacting section of catalyst. The final flat section of the graph is a section of catalyst that is not yet necessary for the reaction.

% Exotherm Graphs

Since the inlet temperature of the shift bed may change over time, straight temperature analysis may fluctuate too much to give a clear picture of the reactor over time. It is useful then to transform the temperature data by looking at the exotherm, the total temperature change in the reactor. By taking each temperature measurement point and expressing it as a % of the total exotherm you can minimize much of the noise that is caused in the data by the varying inlet temperature.

"S" Distance - minimum Catalyst Reaction Depth

One of the first things that can be estimated from the "S" curve exotherm graph is the minimum catalyst volume for the particular reaction at a particular CO slip. The more thermocouples available for measurement the tighter the estimate can be. Since the thermocouples are at a known depth, the volume of catalyst between them can be calculated.



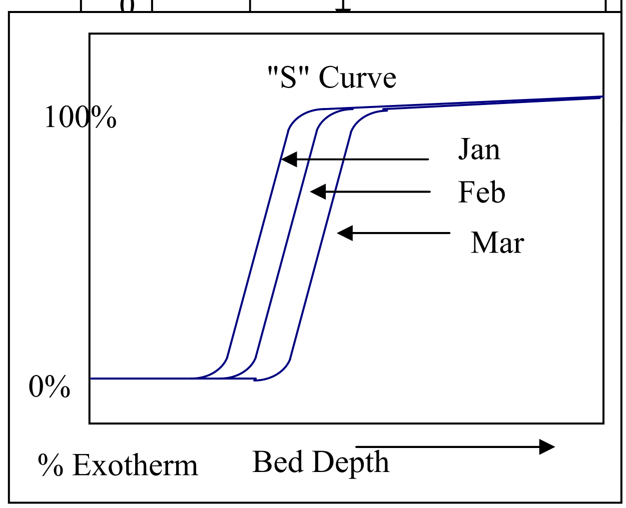
Catalyst Event Prediction (Graph shifting and Shape Changing)

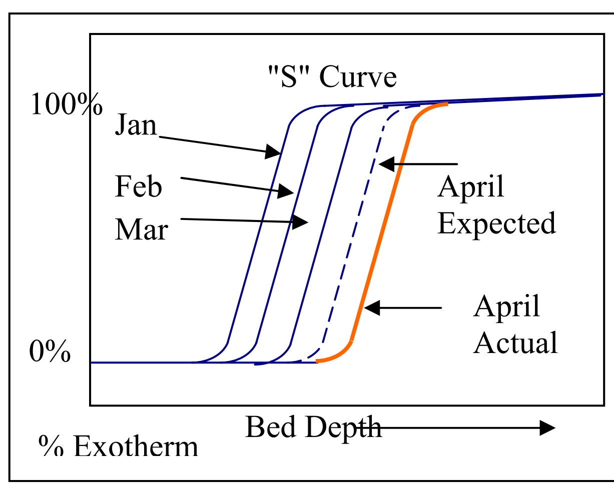
By looking at the "S" curve graphs over regular time intervals you can begin to see a pattern of shifting "S" curves. As catalyst near the inlet of the bed deactivates it causes less and less exotherm. The reaction profile moved deeper into the bed and fresher catalyst. If conditions remain relatively stable, you would expect the same shape and movement of the "s" curve. Detailed analysis of the shift bed exotherm curves should be performed in conjunction with experts from your catalyst company. They are in the best position to determine if the performance is within expected parameters and can make recommendations for future operation.

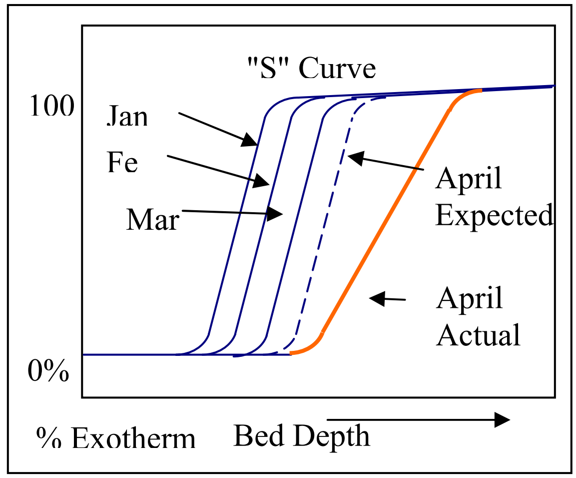
Generally, for the shift bed, monitoring once per month gives enough regular data to be useful. It is important not to use monthly averages but to use actual plant data.

In the example to the right, if the plant conditions have remain stable you would expect that the February curve would be the same shape as the January curve only shifted slightly to the right (increase in bed depth). The March curve should also retain the same shape and should shift an equal amount. If everything remains the same this pattern should repeat through the whole catalyst bed until the minimum reaction depth is reached. At that time the exit CO Slip will start to increase.

This type of analysis begins to become powerful when conditions change. In the example to the right we would expect that the April curve would mirror the February and March Curves and shift an equal amount to the right. But instead, the graph has shifted by double the expected amount. Since the shape of the graph has not changed, we would expect that the current

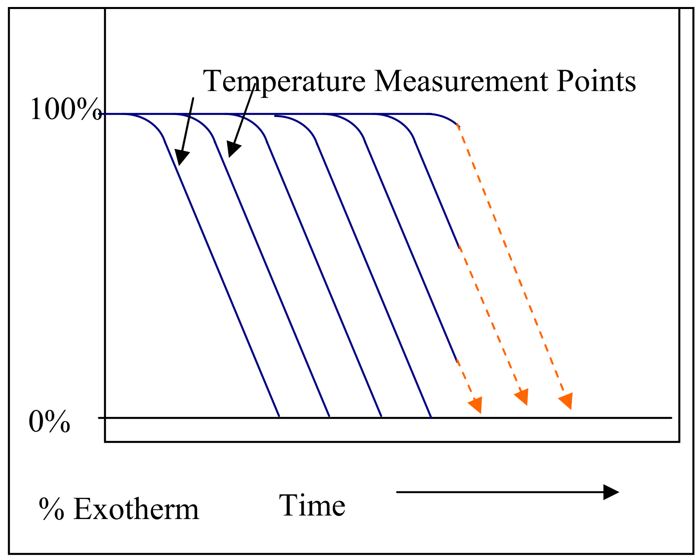






conditions are equivalent to the conditions during January through March. However, it looks like there was some event that has caused and extra amount of catalyst to deactivate. This might have been a slug of contaminate or some event surrounding a plant rate change. This does however give us a tool to flag up events in a catalyst bed's history that effect the life and performance of the catalyst bed.

Now, lets suppose that the "S" curve graph for April had also changed shape as in the example to the right. The curve has not only shifted far more than expected but also flattened out. This would seem to indicate that more of the bed than expected has deactivated and it is taking more reaction depth to accomplish the reaction. This might indicate a rate change or a change in composition to the reactor. This would also indicate that this is an ongoing change of condition and not a one time event. This is a good flag to have the current conditions reviewed by your catalyst company .



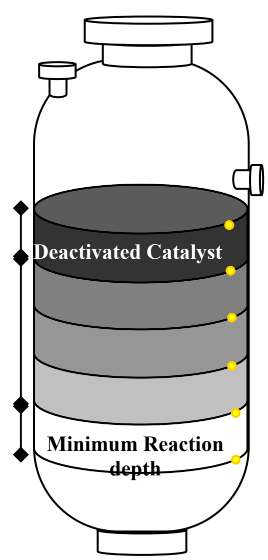
Die off Graphs

The "S" curve graphs are a plot of all the temperature measurement points at one particular time. If we now look at each temperature point over time we can actually see the change in activity in that zone of the catalyst bed. Again, temperatures should be converted to % exotherm.

As the catalyst above a temperature measurement point deactivates, the % exotherm to that point will decline to 0%. When the exotherm is 0% the catalyst is not active for the reaction at that particular inlet temperature.

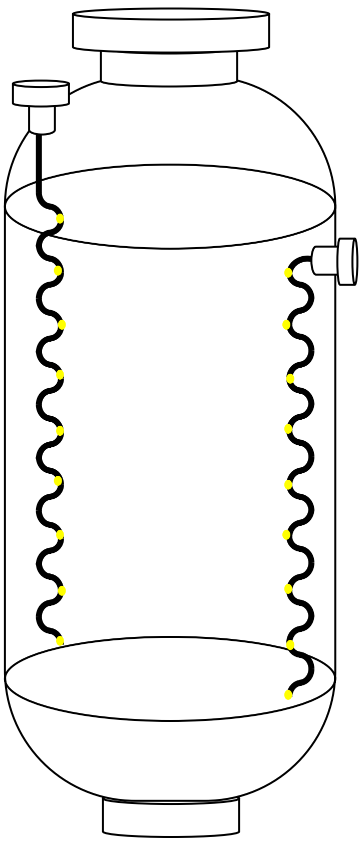
Since the temperature measurement point is at a known bed depth, the volume of catalyst associated with its exotherm can be determined. The time online for that temperature measurement point to reach 0% exotherm is also known. This now gives us enough information to calculate a catalyst die off rate.

Once you calculate a bed die off rate, you can now estimate your remaining bed life if conditions remain constant. First determine your minimum reaction depth from the "S" Curve graph. This is the volume of catalyst that is required to maintain your CO Slip. When the temperature measurement point at this height reaches a 0% exotherm you will need to decide how high you CO slip can go before requiring a change of catalyst. By trending the temperature measurement point you can estimate a date when the exotherm will reach 0%.



End of Run Decisions

The die off rate calculations really help determine if your current operating conditions will give you the bed life that you need. If it is unacceptable it may be possible to increase the inlet temperature of the bed to gain back more activity. Higher temperatures may cause a higher rate of deactivation. Changes in operation should be considered in conjunction with your catalyst company. They will be able to predict how a given change in temperature will effect the operation and life of your catalyst bed.



Retrofit options

Simple Gradient

For most reactors, monitoring the temperature changes down the bed is sufficient to help optimize performance, aid in safe reduction, and predict bed life. Advances in thermocouple assemblies that have taken place for Hydroprocessing units can now be applied to other fixed bed reactors for quick and simple retrofits. The Gayesco Single Sheath is a multipoint thermocouple in a ½" heavy wall sheath. Basically a single sheath or multiple sheaths can be run through an existing nozzle, replacing a single thermowell/thermocouple combination with 9 temperature measurement points. Since the single sheath is flexible, it will bend similar to stainless steel bar stock, it can enter through any nozzle orientation.

Similar systems have been used in Hydroprocessing units over the past 5 years. The systems are designed to survive multiple catalyst loadings and unloading and should give many years of temperature measurement life.

Radial Spread

Some problem reactors may benefit from a higher level of instrumentation than a simple gradient. A radial temperature measurement system greatly increases the number of measurement points and can be useful in diagnosing reactor mal distribution and channeling. Gayesco introduced the Flex – R flexible thermocouple in 1987 and it has since become the recognized standard for hydrocracking service around the world. Each point is independent and can be routed to anywhere in the reactor where a temperature measurement point is desired. It utilizes a heavy wall sheath and large conductor size and is designed to survive multiple catalyst loadings and un loadings.

For more information on temperature measurement solutions contact

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