Riding the Dragon: Sulfur Plant Thermal Reactor Temperature Measurement — Tools, Tips, and Tactics[†]

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Of all the fundamental measured process variables, temperature is perhaps the most reliable. Measurement of flow typically involves orifice plate meters which are susceptible to several operating and configuration issues. These flow meters also only extrapolate the flow based on differential pressure, which varies non-linearly with changes in flow. Pressure, which is perhaps slightly better than flow, still relies on load cells which also have non-linear outputs and have struggles with hysteresis, zero drift, and shock/overload damage. However, in most process applications temperature is measured by a thermocouple. A relatively simple junction of two dissimilar metals which produce a small voltage proportional to the difference in temperature between the junction where the temperature measurement is being taken and the point where the voltage is measured. Thermocouples are so cheap, accurate, and abundant that their use is normal in almost any application. Unfortunately, the Thermal Reactor of a Claus Sulfur Recovery Unit (SRU) is not a typical application.

The Thermal Reactor contains extremely high temperatures along with the presence of various sulfur compounds that can react with many metals, causing corrosion. The metals used in most thermocouples are particularly vulnerable to sulfidic corrosion, rendering them unusable in a very short time. This makes it impossible to use typical thermocouples for the long term in a Thermal Reactor. In fact, the useful life of a typical thermocouple at Thermal Reactor conditions can generally be measured in minutes to hours.

Temperature is still a critical process parameter to monitor in Claus SRU Thermal Reactors. The refractory lining is subject to failure if overheated (Figure 1), and it is very possible to accomplish this overheating given that the temperatures typically seen in the furnace are generated with a highly sub-stoichiometric combustion of the available fuel. Additionally, certain contaminant species (Ammonia, BTEX) can cause plugging/sooting problems downstream in the SRU if sufficient temperature is not maintained. These compounds need temperatures at the higher end of the normal operating range (2100–2300 ºF [1150–1260 ºC]) to be destroyed in the furnace. Therefore, special technologies and strategies are needed to measure and confirm the temperature in the Thermal Reactor.

Figure 1. Damaged furnace refractory, likely caused by high temperatures.

This paper discusses in greater detail the importance of temperature to the Thermal Reactor refractory lining; currently available options for field temperature measurement along with their drawbacks and limitations; and introduces a new semi-empirical tool developed by Optimized Gas Treating (OGT) to quickly, efficiently, and accurately determine Thermal Reactor temperature based on process parameters. Finally, the paper presents two case studies in which the new tool is used to estimate Thermal Reactor temperature in an operating facility before, during, and after a process upset and the estimates are compared against operating data.

Thermal Reactor Refractory Lining

Thermal Reactor temperatures can readily reach the 2800-3000 ºF [1500–1650 ºC] range, which is near, or above, the melting point for most carbon steels. Also, well before the melting point is reached, steel will enter a region of excessive corrosion due to the high H_2S content of the process gas. Ceramic refractory linings are therefore required to prevent equipment damage due to both these effects. These linings allow the steel shell to remain in a temperature range (400–650 ºF [200–1100 ºC]) that maximizes equipment life.

Although resilient, the Thermal Reactor refractory cannot withstand the most severe conditions that can exist in the reactor. Excessive heating can cause phase changes in the refractory which make it less strong and in the case of monolithic (castable) refractory, melt the stainless-steel anchors providing support to the lining. This ultimately leads to failure of both the lining and eventually the steel shell. Given extreme overheating (~3400 ºF [1875 ºC]) the refractory itself can melt and flow like lava. While atypical, it is possible to achieve these temperatures if near-stoichiometric combustion (of high H_2S content acid gas or fuel gas) is sustained for significant periods of time without appropriate mitigation (e.g., quench gas/steam injection). Extreme overheating can also be a side effect of contamination of process gas with heavy hydrocarbons, especially in the case of an oxygen-enriched Claus process.

Unfortunately, the dangers do not only lie at the very top of the temperature operating range. If the Thermal Reactor skin temperature drops too low (<375 ºF [190 ºC]), then it is possible for sulfuric and sulfurous acid to condense, quickly corroding the carbon steel shell of most Thermal Reactors and leading to rapid equipment failure. Operability and reliability concerns also exist with poor contaminant destruction at low process gas temperature. So, it is important for the responsible maintenance of equipment to know the Thermal Reactor temperature and be able to measure, or at least infer, what the steel skin temperature is.

Temperature Measurement Devices

Since, as discussed above, standard thermocouples are not an option for temperature measurement in the Thermal Reactor, what options are available for this service? There are two conventional choices, optical pyrometers, and ceramic shielded gas-purged thermocouples. Each of these choices has benefits and drawbacks to their use, which are discussed below.

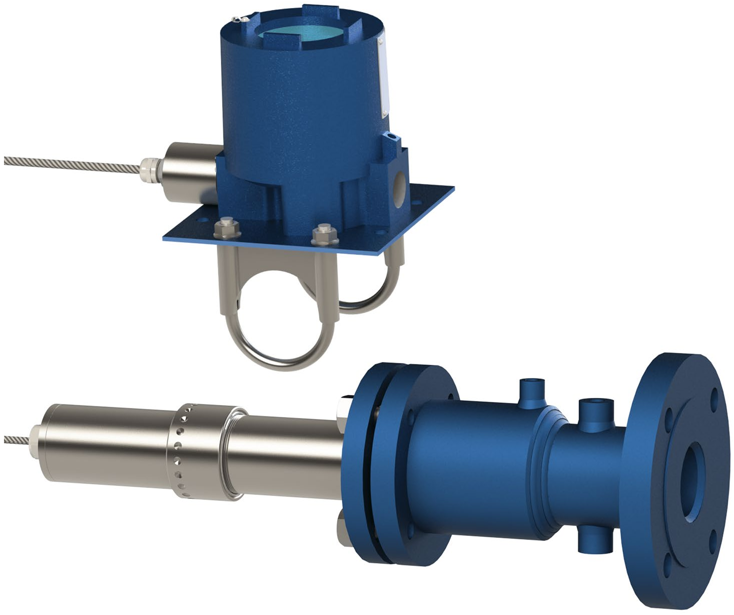


Figure 2. Optical Pyrometer Lens Assembly & Process Connection (Bottom) with Remote Electronics Unit (Top)

Optical pyrometers are devices that are positioned in such way as to observe emitted radiation from an object, and then analyze the intensity of that radiation to infer temperature of the object using the Stefan-Boltzman law. In the case of Thermal Reactors, the optical pyrometer is typically set up to observe infrared band electromagnetic (EM) radiation over a target area, which usually is a section of refractory opposite the pyrometer in the Thermal Reactor. The choice of specific frequencies is important since gases in the furnace can absorb some EM radiation and thus affect the resulting indicated temperature. Careful choice of frequencies, along with certain compositional requirements can allow the pyrometer to indicate the approximate gas temperature in the Thermal Reactor as opposed to the refractory temperature. This can seem useful since the large mass of the refractory acts as a thermal capacitor and keep operators from seeing the full effect of process changes over a reasonable time scale. However, since the refractory brick, in general, has low emissivity and high reflectivity, the temperature indicated when in refractory mode is more representative of average internal temperature. Therefore, it is often recommended to use the refractory temperature mode unless other concerns dictate use of the gas temperature mode.

There are, however, a few drawbacks to using an optical pyrometer to measure Thermal Reactor temperature. The first drawback is that since all emitted radiation that is “viewed” by the pyrometer is used to infer temperature the device naturally indicates an average temperature along the view path of the pyrometer. While useful, the average temperature can disguise the actual maximum temperature which might be a point of concern when operating a unit on the edge of the temperature envelope.

Another drawback is that the pyrometer can only give information about what the radiation detector can “see”. This has a couple of practical implications. First, if there is an obstruction of the field of view, the obstruction’s temperature will be averaged into the calculation, even if the object is at ambient temperature. This can lead to a far cooler observed versus actual temperature reading. Common causes of this type of error involve misalignment of the pyrometer where part of the nitrogen-purged nozzle is in the pyrometers view path. In the most extreme case, the temperature error can be due to the lens of the pyrometer being completely occluded with sulfur or soot leading to a to false indication of unrealistically cool temperatures. The use of a two-color pyrometer system can help alleviate the problem of lens occlusion since it uses the ratio of two different wavelengths to infer temperature. However, operating a two-color pyrometer in this way usually means sacrificing the ability to measure both gas and refractory temperature simultaneously. Second, the pyrometer can only give information about the temperature in the region it can see. If the burner is not providing good mixing, or if any other effect creates hot and/or cold spots in the Thermal Reactor, then the pyrometer will only provide information to the extent that the spot occurs inside the device’s view.

Finally, configuration and calibration of the pyrometer can be tricky. Any pyrometer that attempts to measure gas temperature must assume a water concentration. This is often problematic as the actual water concentration changes with the process and ambient conditions. Also, to indicate the correct temperature, the effective emissivity of the system must be known. Determining this quantity is not a trivial exercise because the effective emissivity varies with chosen wavelength, furnace gas composition, and refractory surface conditions. To approximate, a thermocouple is often inserted into the pyrometer nozzle, a reading is taken, then the emissivity is adjusted to make the pyrometer indicated temperature match the thermocouple. This approach has many sources of error. For example, pyrometer nozzles are purged with nitrogen (or less commonly air) at ambient temperature with the purge gas exiting at the nozzle right where the thermocouple is taking its reference measurement. Even if neglecting the purge, the thermocouple is taking a point measurement of the gas temperature very near the point the pyrometer nozzle joins the Thermal Reactor shell. This is not an average temperature across the entire line of sight of the pyrometer. Therefore, it is common for there to be disagreement between theoretical calculations of temperature and indicated values of 1.5-2% of the indicated reading.

The other common option for Thermal Reactor temperature measurement is a purged thermocouple. Since typical thermocouple/thermowell systems are not resilient enough for the Thermal Reactor operating atmosphere, the industry has developed thermal measurement systems consisting of a ceramic thermowell (which can survive the Thermal Reactor atmosphere) with an integral inert gas purge. This serves to protect the thermocouple junction (which is highly susceptible to corrosion upon exposure to even small amounts of Thermal Reactor process gases).

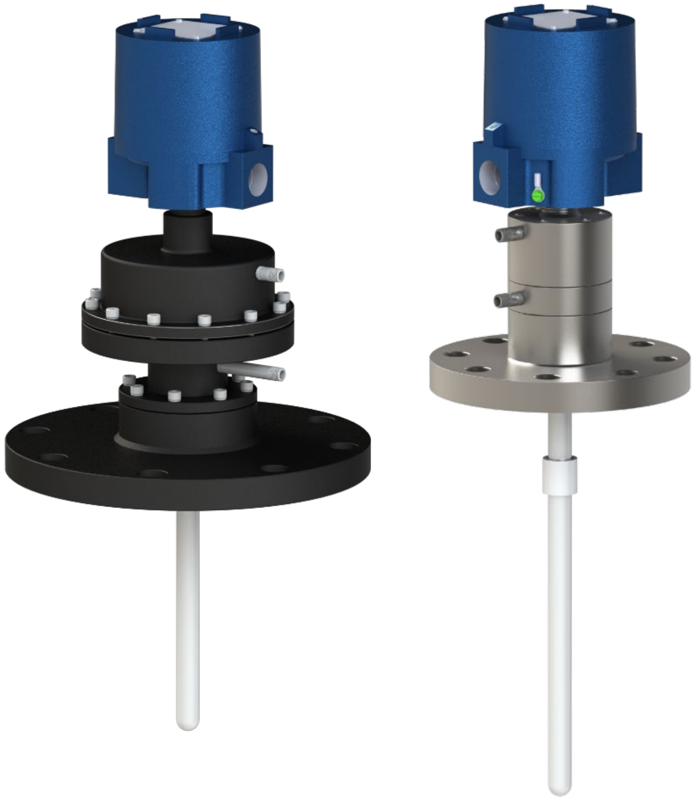


Figure 3. Two Examples of Purged Thermocouples for typical (left) and compact (right) installations.

However, this method of temperature measurement also has its own set of drawbacks. First and foremost, installation of the ceramic thermowell is a delicate and complicated process. Usually, a hole must be drilled for the thermowell through the completed furnace refractory lining, without compromising its integrity. Then the thermowell must be installed and affixed to the Thermal Reactor without damaging the ceramic thermowell, which is not as robust or forgiving of rough handling as a typical metallic material would be. Also, compared to typical thermowell materials the ceramic thermowell has a relatively high heat transfer resistance. So, this means there is some delay between changes in the Thermal Reactor temperature and being able to observe the temperature change. Finally, thermocouples are a spot measurement of temperature precisely at the hot junction, which is located (if installed properly) at the hot face of the refractory brick. As with the optical pyrometer the thermocouple will only be able to sense a temperature anomaly if it occurs at the precise location the thermocouple is installed.

Recently, Delta Controls Corporation has offered a specially designed, unpurged thermocouple for use in SRU Thermal Reactors, which utilizes a proprietary set of features branded as QSeal® (primary silicon carbide thermowell, secondary monocrystalline sapphire thermowell, along with other proprietary sealing technologies.) The combination of features allows for thermocouple operation without access to a source of purge gas. In general, purged thermocouples are still preferred, but there is an alternative for installations unable to accommodate a purged thermocouple’s installation requirements.

Calculated Temperatures

Given the multiple failure modes and sources of error present for each of the Thermal Reactor temperature measurement technologies, it is prudent to have a check of the indicated values. The best check would be to completely model the chemistry of the Thermal Reactor and as a result, the temperature would be known. The model would only depend on various commonly monitored process parameters (compositions, flows, pressures, and temperatures). There are several commercially available process simulators on the market which can claim to provide a solution which accomplishes the calculations described.

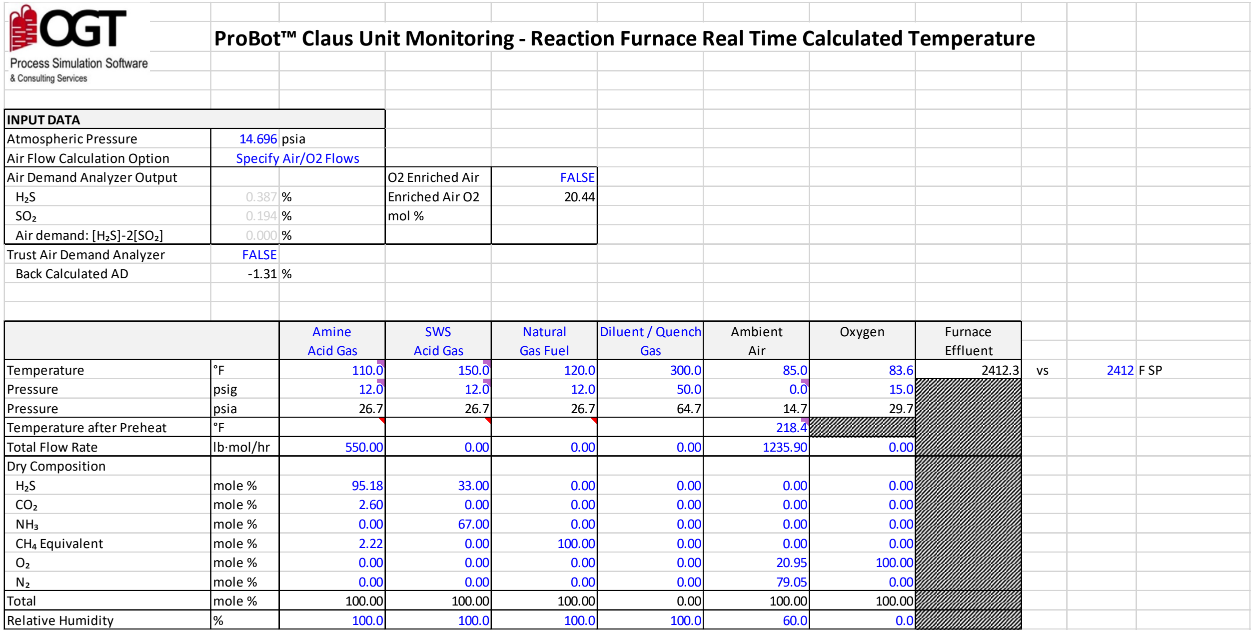
However, even the best simulators available only approximate reality. There are various assumptions implicit in any simulation model which impact its reliability and accuracy. For example, virtually all models assume that good mixing is taking place regardless of reality. Model calculations are also subject to plant metering and laboratory errors which impact the results of modeling. All these factors must be kept in mind when utilizing any computationally derived temperature values.

The various simulation models also differ in in their approach and rigor. In the simplest case, Thermal Reactor chemical reactions are modeled as simple conversion reactions (either from correlation or specified). Slightly more sophisticated and flexible models might use a method to determine the complex chemical equilibrium of the various reactions of interest (e.g., Gibbs Free Energy Minimization). Still, others may use rate-based chemical kinetics to determine the conversion of reacting species as a function of reactor conditions and time spent in the reactor. Such kinetic models have seen significant steps forward in the last few years with a better understanding of and a model for complex side reactions in the Thermal Reactor (e.g., direct H_2S cracking and recombination). Some hybrid combination of two or more of the above methods might also be used depending on data availability and modeler's preference.

Obviously, more rigorous methods are expected to deliver more accurate and reliable results. Unfortunately, more rigorous models often require more data and can be cumbersome to set up for real-time monitoring. Additionally, the computational cost for each of the methods also goes up with the level of rigor. For a single simulation run, the difference in time spent waiting for the model to calculate is negligible. However, when expanded over many data points, this multiplied differential computational time can become significant. For example, with a dataset of 2000 points a difference in run time of only 5 seconds per run leads to a difference of 2.75 hours. Which is a long time to sit and wait on a computer.

OGT's Realtime RF Monitoring Tool

Realizing the need for a straight-forward, speedy, and flexible Thermal Reactor temperature estimation tool, OGT has developed a focused model to provide real-time feedback to plant operations. This tool uses field measured temperatures, pressures, and % water saturation of the Amine Acid Gas, Sour Water Stripper Gas, Natural/Fuel Gas (for startup or co-firing), Diluent/Quench Gas (N_2, Steam, COPE® recycle, etc.), Ambient Air, and Supplemental Oxygen along with assumed dry-basis compositions.



Process Simulation Software
& Consulting Services

ProBot™ Claus Unit Monitoring - Reaction Furnace Real Time Calculated Temperature

INPUT DATA				
Atmospheric Pressure	14.696	psia		
Air Flow Calculation Option	Specify Air/O2 Flows			
Air Demand Analyzer Output			O2 Enriched Air	FALSE
H_2S	0.387	%	Enriched Air O2	20.44
SO_2	0.194	%	mol %	
Air demand: $[H_2S]-2[SO_2]$	0.000	%		
Trust Air Demand Analyzer	FALSE			
Back Calculated AD	-1.31	%		

		Amine Acid Gas	SWS Acid Gas	Natural Gas Fuel	Diluent / Quench Gas	Ambient Air	Oxygen	Furnace Effluent		
Temperature	°F	110.0	150.0	120.0	300.0	85.0	83.6	2412.3	vs	2412 F SP
Pressure	psig	12.0	12.0	12.0	50.0	0.0	15.0	▨		
Pressure	psia	26.7	26.7	26.7	64.7	14.7	29.7	▨		
Temperature after Preheat	°F					218.4	▨	▨		
Total Flow Rate	lb·mol/hr	550.00	0.00	0.00	0.00	1235.90	0.00	▨		
Dry Composition								▨		
H_2S	mole %	95.18	33.00	0.00	0.00	0.00	0.00	▨		
CO_2	mole %	2.60	0.00	0.00	0.00	0.00	0.00	▨		
NH_3	mole %	0.00	67.00	0.00	0.00	0.00	0.00	▨		
CH_4 Equivalent	mole %	2.22	0.00	100.00	0.00	0.00	0.00	▨		
O_2	mole %	0.00	0.00	0.00	0.00	20.95	100.00	▨		
N_2	mole %	0.00	0.00	0.00	0.00	79.05	0.00	▨		
Total	mole %	100.00	100.00	100.00	0.00	100.00	100.00	▨		
Relative Humidity	%	100.0	100.0	100.0	100.0	60.0	0.0	▨		

Figure 4. Screenshot of the Microsoft Excel® interface to OGT's Real-time model

The model was constructed using hundreds of Thermal Reactor simulation runs using the rate-based kinetic model implemented in the OGT|SulphurPro® product. Through the clever choice of independent variables, the model attempts to correctly capture some of the finer points of determining the Thermal Reactor temperature. These include reactor feed stream superheating correction (for pre-heated feeds), water saturation effects for the acid gases, and providing a means to identify and correct questionable feed compositions based on air demand analyzer reading.

Since the industry is generally concerned about a furnace operating at the top of the safe operating window (1800–3000 ºF [980–1650 °C]), particular care was taken to improve the fit of the model in that range. The Table below shows other limits of the correlation data used to generate the model.

Limitation	Range
H_2S Content	48.6 % - 90.6 %
Acid Gas Pre-Heat Temperature	0 - 450°F
Hydrocarbon Content (Methane)	0 – 10 %
Ammonia	0 – 25 %
Air Flow Ratio to Stoichiometric	0.5 – 2.0
Oxygen Enrichment	21 – 99 %

Data outside of these ranges will not necessarily generate incorrect results, but no information outside this range was used to correlate the data so the model fit might give unexpected or incorrect results. The focus for the model was not necessarily to develop a high precision model with an exact match to simulated results, but to develop one that produced values with an accuracy on the order of field instrumentation (±1% of value).

The following set of plots display data for three different scenarios each of which demonstrates the model's performance for a different operating condition.

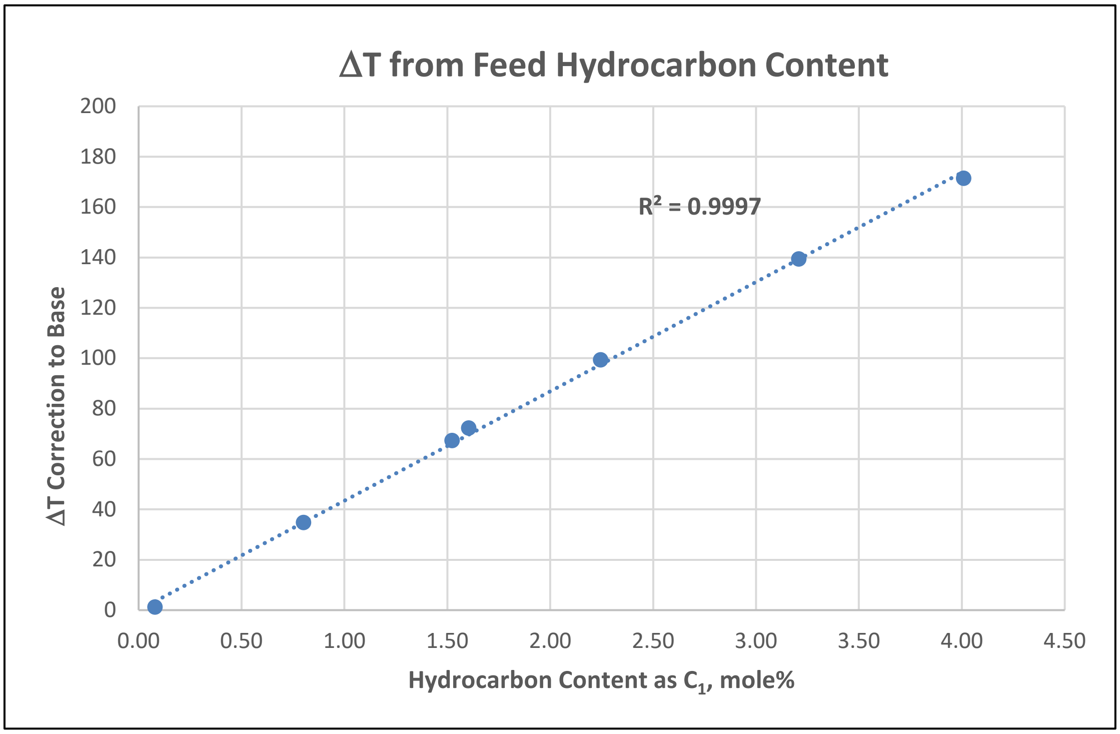


Figure 5. Plot showing performance of model over various hydrocarbon concentrations.

Figure 5 shows that as hydrocarbon content of the combined Thermal Reactor feeds goes up, the modeled temperature difference (dashed line) from the no hydrocarbon case temperature has a good fit to the simulator-generated data points. This shows that the real-time model explains 99.97% of the simulator Thermal Reactor temperature data variation with feed hydrocarbon contents of up to 4 mole% (as C_1 equivalent).

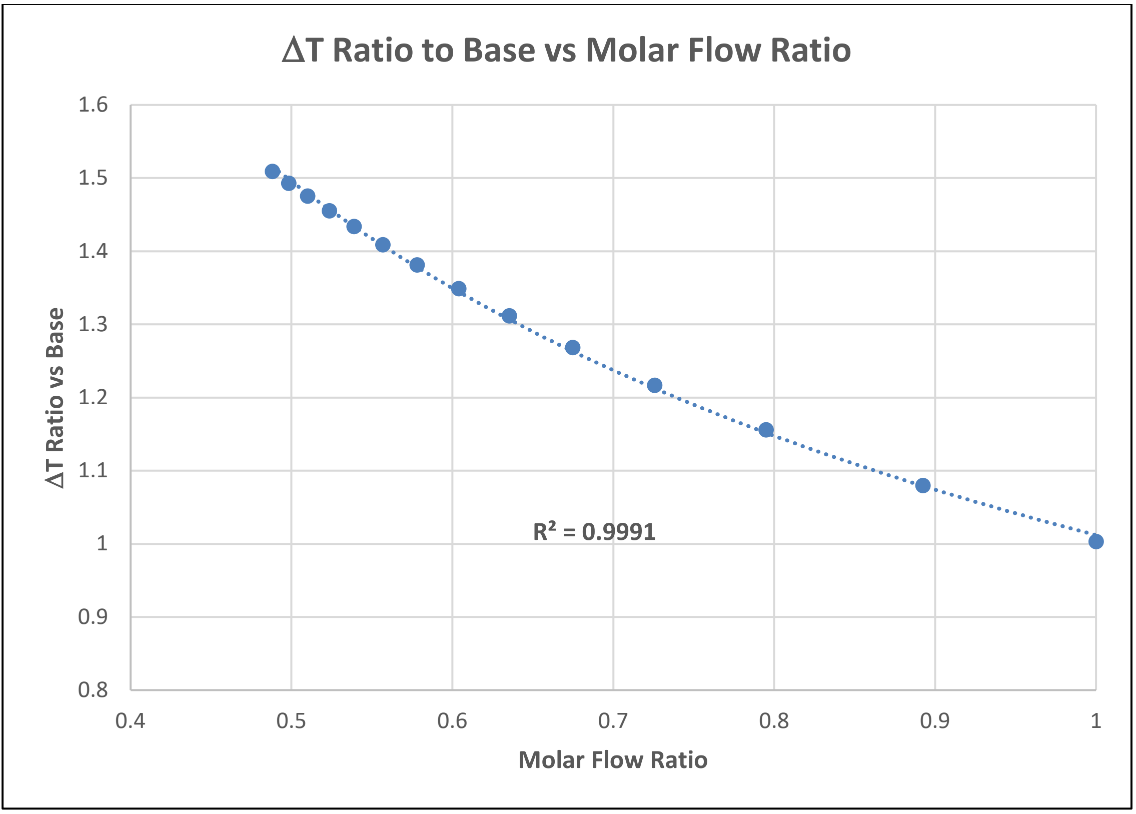


Figure 6. Plot relating O_2 enriched air with change in temperature versus a non-O_2 enriched case.

Figure 6 shows how the ratio of Thermal Reactor ΔT varies with the molar flow ratio for an oxygen enriched air inlet ratioed to a base ambient air case. As the molar flow ratio drops, the oxygen enrichment percentage goes up, and the temperature should rise accordingly. This shows that the model handles a wide range of oxygen concentrations and is suitable for typical oxygen enriched conditions. The real-time model accounts for 99.91% of the simulator data variation.

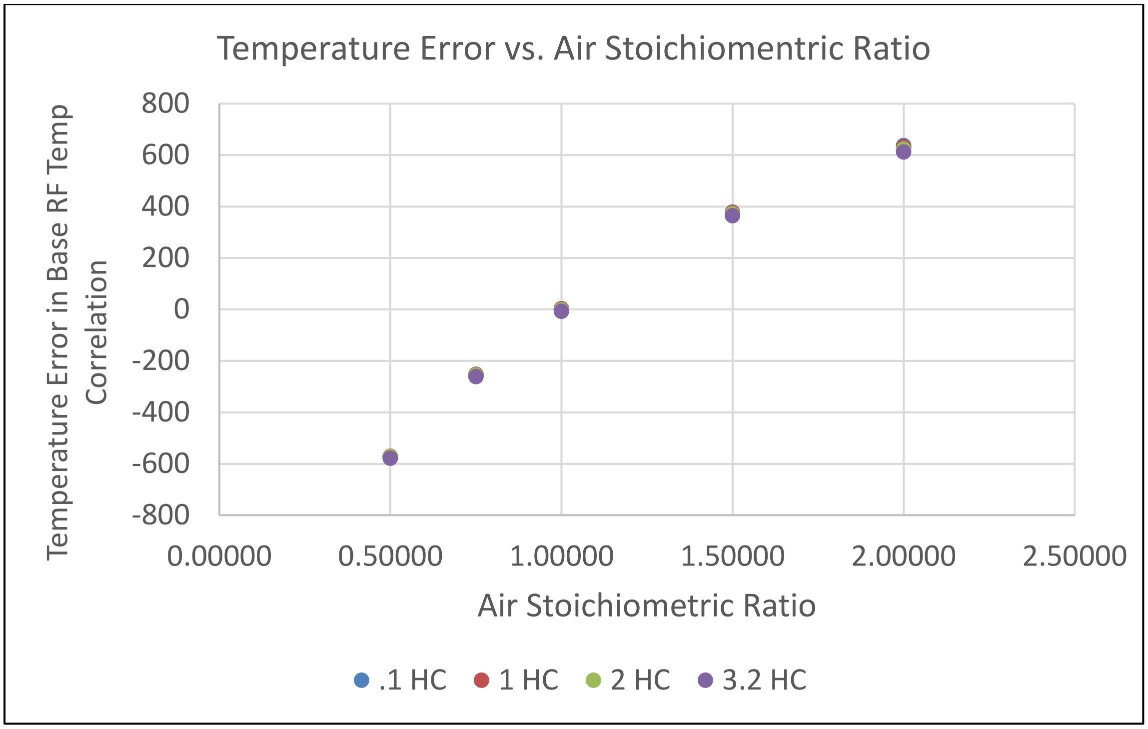


Figure 7. Plot showing difference between correlation and simulation vs. % stoic. air and several hydrocarbon contents.

Figure 7 shows differences between simulation values and real-time model values for various percentages of stoichiometric air and different feed hydrocarbon content. One expected effect (given Figure 5) is that hydrocarbon content has relatively little impact on the observed error. In fact, at this scale it is difficult for most of the points to distinguish between the different hydrocarbon content values. The error vs. stoichiometric ratio (with 1.0 being airflow related to a perfect 2:1 H_2S:SO_2 ratio) shows that the further away from the stoichiometric point the base case model is pushed the more error can be expected. However, all well operated plants will operate near the stoichiometric point even when deliberately raising the ratio of H_2S:SO_2 to a value greater than 2:1 to protect the overall sulfur block from upsets. This is because the air demand analyzers typically used loosely indicate full scale (-5%–+5%) over approximately 10% of the inlet air flow. The plot above not only covers all normal operating cases with a good match to simulated data, but it also acceptably covers a very wide range that would likely correspond with most plant upsets.

Field Case Studies

OGT had the opportunity to test the real-time model against two actual operating plants, complete with times of significant upset. Both units are refinery style sulfur units. For the first data set, historian data was provided for essentially an entire year of operation and the unit was a typical SRU operating at low flow.

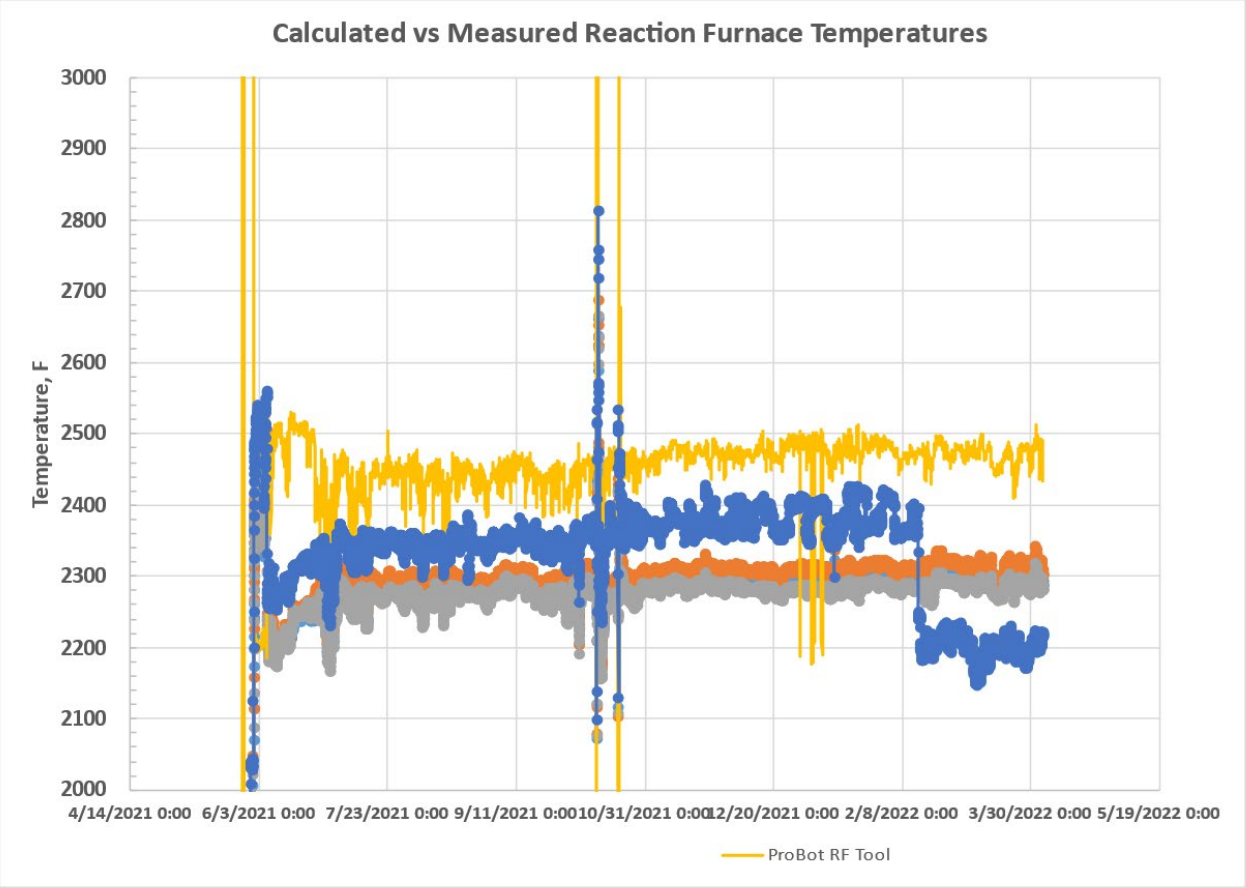


Figure 8. Case Study #1 Operating Data and Real-time model output

There are several notable items in this plot. First, the tool tracks well while indicating a ~150 ºF higher temperatures than the field optical pyrometer. This is mostly likely due to the very low rates being processed by the unit during this time, leading to significant heat loss in the Thermal Reactor. This heat loss is not an effect currently integrated into the real time model. Another interesting point is that the model tends to overshoot the measurements during excursions (both high and low). This is not unexpected since the model calculates temperature changes immediately, as soon as the input compositions, conditions, or flow rates change. In an actual Thermal Reactor, there is a great deal of mass that provides thermal capacitance and therefore resists a sudden change in temperature. Finally, in the last month or so of operation a sudden threshold shift in the pyrometer temperature reading is observed while none of the other temperature measurements or the real-time model show a similar shift. While in this case the thermocouples also point out the fact that the optical pyrometer is having issues, the real-time model could be used alone to call into question the sudden shift.

The second plot shows operating data for an oxygen enriched SRU. The data set covers a day and a half of operations before, during, and in the recovery from a low air flow excursion. The low flow excursion was caused by a loss of indication for one of the feed meters causing feed forward air control to cut air flow unnecessarily.

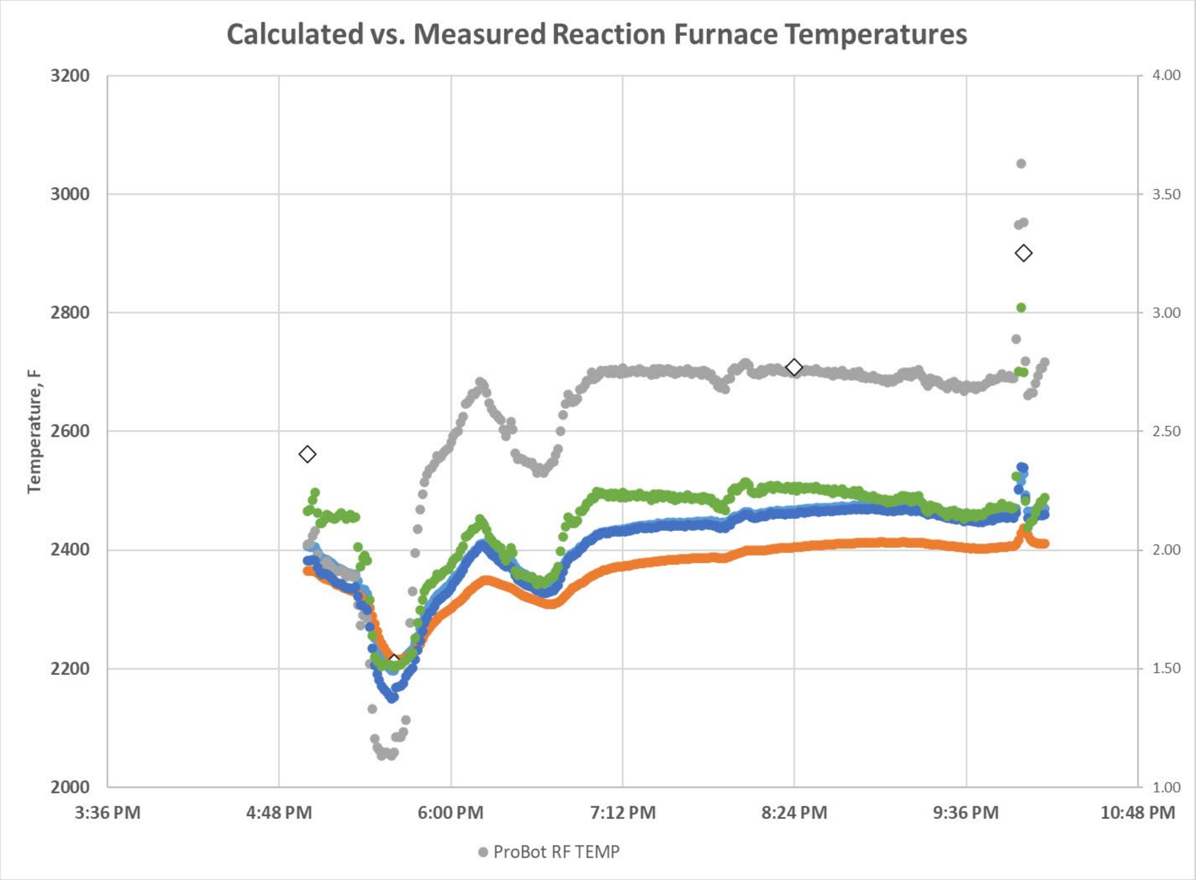


Figure 9. Case Study #2 Operating Data and Real-time model output

This plot shows some of the same features as the previous plot. In particular, the overshooting of temperatures during excursions is still observed and for the same reason. Once again there is a constant temperature offset with the real-time model reading ~150 ºF hotter than the other temperature indications. In this case, the offset may be the result of a recycle flow (which is a feature of some oxygen enriched process) for which no flow rate data are available. The recycle could be quenching, the temperature from a value nearer the real-time model. Also, just as before there could also be unaccounted for heat loss which possibly leading to a lower real-time model calculated temperature, and a better match with the field data. In any case, the real-time model is within 4% of the thermocouple indicated temperatures without any corrections.

Summary

Thermal Reactor temperature measurement is a complicated endeavor. There are multiple options, all of them customized/specialized for use in an SRU. Unfortunately, all the technologies have drawbacks which can lead to incorrect indication. OGT has developed a tool to provide real-time temperature estimation to quickly, efficiently, and accurately double check and diagnose other measurement technologies. The model has been verified against both a state-of-the-art simulation model and actual plant data from a field study consisting of two SRUs in different facilities and different configurations. This comparison shows that OGT's real-time temperature model accurately and efficiently estimates Thermal Reactor temperature using only the process variables commonly monitored in operating facilities. This is a valued addition to the industry because it can serve as a double check to field instruments to protect equipment and be used in the analysis of past plant performance data and planned future operations.