

DRI Production Using Coke Oven Gas (COG): Results of the MIDREX[®] Thermal Reactor System[™] (TRS[®]) Testing and Future Commercial Application

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BACKGROUND

In the third quarter of 2014, Midrex Technologies, Inc. and Praxair, Inc., completed the final phase of development testing on the Thermal Reactor System[™] (TRS[®]) that will produce clean syngas from coke oven gas (COG) and other hydrocarbon sources for DRI production. The system utilizes Praxair's oxidation technology, the Hot Oxygen Burner (HOB), which offers the potential to do partial oxidation of hydrocarbons without steam injection. When HOB technology is combined with an extended reaction chamber, a preheated stream of coke oven gas can be converted into a product gas suitable for direct use as a reducing gas for the production of DRI. The Thermal Reactor System includes compression, preheating and processing of COG.

In all, the demonstration plant operated for three campaigns covering more than 2000 hours of operation during the 29 month project period. The plant operated on two major blends of COG feedstock, with toluene levels from 0 mol% to 1.9 mol%, and 100% natural gas as feed stock. It also used 4 different gas combinations for the firing fuel of the HOB.

DEMONSTRATION PLANT

To verify the required operating points of the Thermal Reactor System, Midrex and Praxair decided to construct a 1/10th scale demonstration facility at the Midrex Research and Technology Development Center in Pineville, NC. The scheme of the facility was to combine the primary gaseous components of coke oven gas, hydrogen, methane, nitrogen, and carbon dioxide from liquid bulk sources and recirculate a portion of the syngas generated to supply the carbon monoxide required. A separate stream of toluene would be added at varying levels to study the BTX component of coke oven gas and its effect on the system performance and syngas quality.

The demonstration plant has the following nominal design capacities:

- A. 1250 Nm³/h COG from compression
- B. 350 Nm³/h O₂ from liquid supply
- C. 450°C from feed stock heater
- D. 77 kg/h toluene from bulk tank
- E. 1800 Nm³/h syngas to flare
- F. Reactor pressure 2 bar-g (low nom.) and 7 bar-g (high nom.)

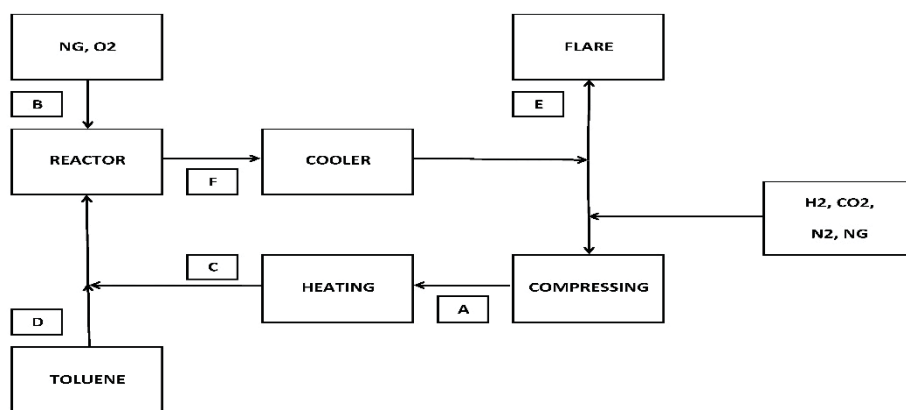


Figure 1 – Demonstration Plant Flow Sheet



Figure 2 – Thermal Reactor Demonstration Plant

CAMPAIGN PLANNING

The test plan for 2013 called for 2 test campaigns to establish clear parameters for operation of the TRS. Campaign 1 was expected to develop clear operating procedures for the demonstration facility as well as develop a preliminary understanding of the range of the operating envelope of the facility. Campaign 2 was to establish the critical operating points for commercial operation of the TRS units as well as turndown and upper limits on system capacity.

After the completion of campaign 2, a test plan for campaign 3 was developed. It required the use of different fuels in the HOB. To accomplish this, the flow sheet of the demonstration plant needed to be modified for additional gas metering and compression. These modifications and further commissioning corrections were completed by June of 2014. The HOB also required some independent testing, since its primary fuel had been only natural gas up to this point.

Campaign 1

Campaign 1 ran for 15 days in June of 2013 and tested numerous COG feedstock combinations with varying toluene content and varying oxygen rates, expressed as a stoichiometric ratio, or SR. The objectives were to determine the range of operation for this system and to begin to define the soot generation relationship with regard to the reactor temperature and SR.

The system was run at 2.0 bar-g reactor pressure and was fed with a COG feedstock composition which fell into the following composition range:

| <u>Component</u> | <u>mol %</u> |
|-------------------------------|--------------|
| CO | 6.1 - 10.4 |
| CO ₂ | 2.2 - 2.7 |
| H ₂ | 54.3 - 59.7 |
| N ₂ | 1.0 - 4.2 |
| CH ₄ | 21.2 - 29.7 |
| C ₇ H ₈ | 0 - 1.9 |

In this first campaign, the SR was run over a wide range, from 0.14 to 0.21. The best raw syngas quality was obtained near the center of the test range. This represented a major improvement over the prior tests in the lab scale pilot facility, which ran best at an SR over 0.21. This improved SR is likely due to the reduced heat loss of the new reactor, 3.5% versus 40 to 50% for the prior lab scale test reactor.

Other developments which were applied in this first campaign included a laser opacity measuring arrangement designed to quantify and trend the soot generated within the reactor, and a sub-stoichiometric burner arrangement used to preheat and idle the system at temperatures in excess of the auto-ignition temperature.

After a follow up review, it was clear that one of the major objectives for campaign 2 would be to reduce the plant operating variations and bring a better understanding of the soot generating conditions.

Campaign 2

In campaign 2, which ran for 20 days from late July into August, the operating plan was targeted for a much tighter control of feedstock and reactor conditions. A soot sampling arrangement was established to verify the laser readings, and the laser opacity system was also modified to improve stability, in particular to overcome the system sensitivity to external temperature effects. The operating pressure of the reactor was increased to 3.3 bar-g to match the expected commercial design pressure then under consideration, and the COG feedstock target analysis was adjusted to:

| Component | mol % |
|-------------------------------|-------------|
| CO | 5.2 ± 1.5 |
| CO ₂ | 1.75 ± 0.5 |
| H ₂ | 64.0 ± 3.0 |
| N ₂ | 3.6 ± 1.0 |
| CH ₄ | 25.5 ± 3.0 |
| C ₇ H ₈ | 0.50 - 1.00 |

During the campaign, soot was filtered out of a slip stream of syngas from the reactor during 30 to 60 minutes sampling periods. The samples provided good spot validation of the laser opacity trends and the data needed to determine the critical SR for minimum soot formation. The soot data collected is shown in figure 3 and clearly shows the impact of toluene levels on soot generation.

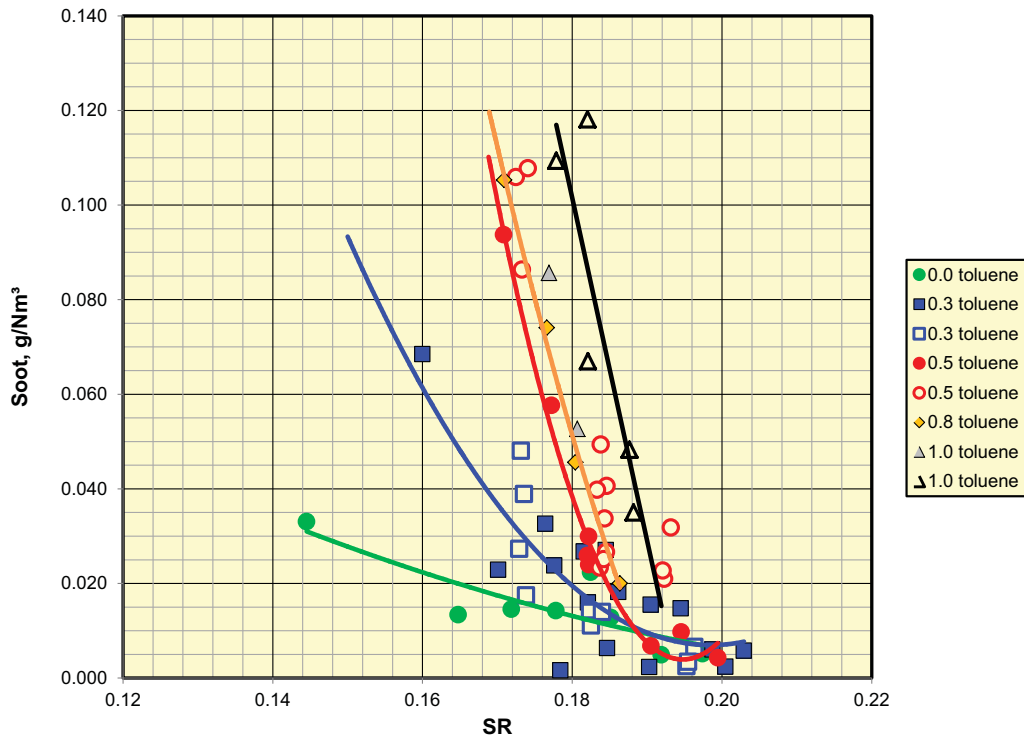


Figure 3 – TRS Soot Generation at Various Toluene Levels

Two additional pieces of important data for DRI production from syngas are the temperature of the syngas and the residual methane contained in that syngas. Their inter-relationship is shown on the following figures 4 and 5.

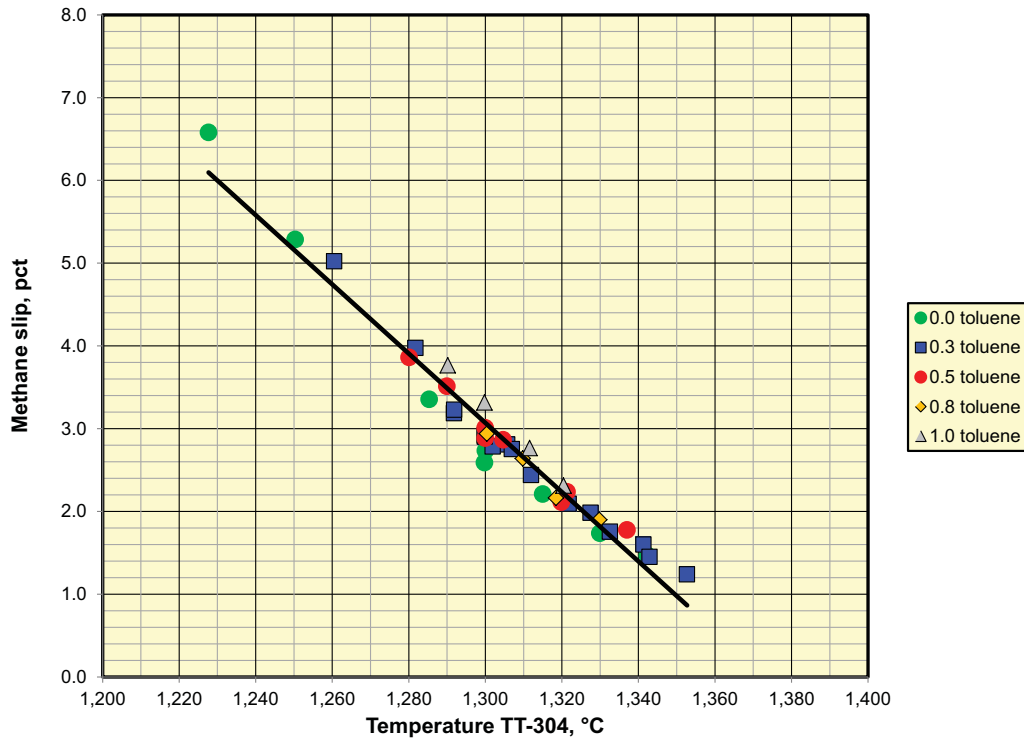


Figure 4 –Peak Reactor Temperature vs SR in Campaign 2

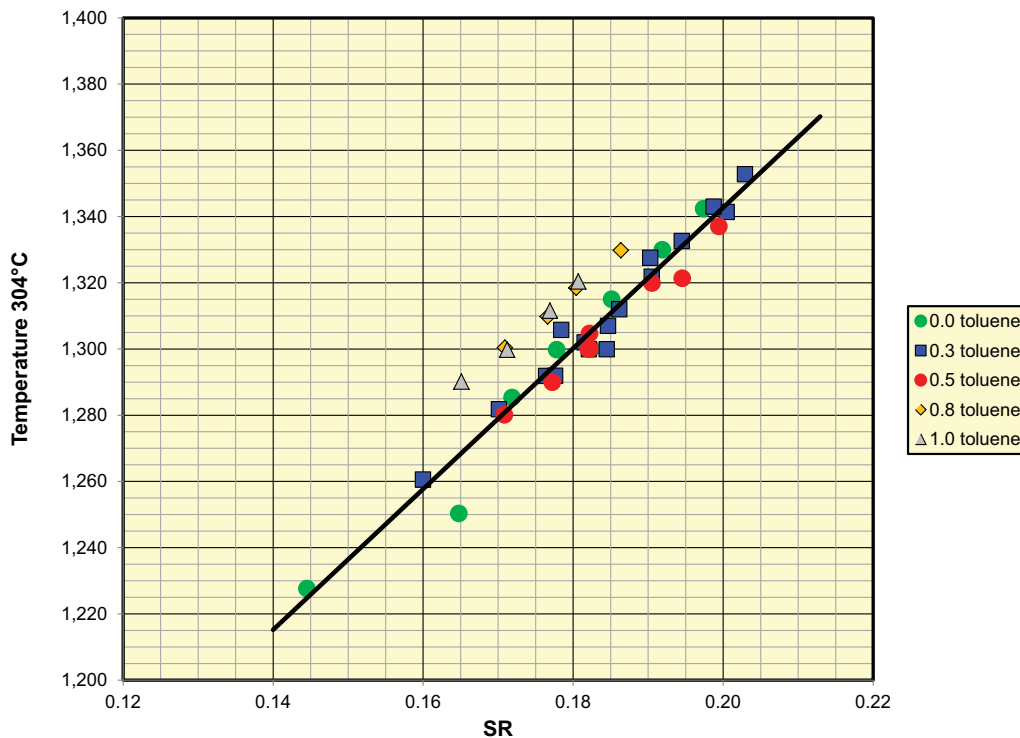


Figure 5 – Peak Reactor Temperature versus Methane Slip from TRS in Campaign 2

Based on the operating data from campaign 2, the raw syngas produced from the TRS reactor, fed by the COG identified earlier, would have a typical reductants-to-oxidants ratio $[(H_2+CO)/(H_2O+CO_2)]$ of about 6 for the uncooled raw syngas at 1340 °C, as shown below:

| <u>Component</u> | <u>mol %</u> |
|-------------------------------|---------------------------------|
| CO | 21.8 |
| CO ₂ | 1.66 |
| H ₂ | 56.07 |
| H ₂ O | 11.95 |
| CH ₄ | 1.36 |
| N ₂ | 7.05 |
| C ₂ H ₆ | 0.02 |
| C ₃ H ₈ | 0.003 |
| C ₂ H ₂ | 0.020 |
| C ₂ H ₄ | 0.040 |
| Gas Quality | 5.72 = $[(H_2+CO)/(H_2O+CO_2)]$ |

The reductants-to-oxidants ratio increases to about 15 when the raw syngas is quenched to about 40°C to reduce the H₂O content. As a rule of thumb, for every 100 Nm³ of COG the TRS produces 175-180 Nm³ of the raw syngas at approximately 1340°C.

Campaign 3

For campaign 3 the remaining issue to be demonstrated was the use of the low heating value fuels in the HOB. Two different hot oxygen temperatures were also tested. The fuel compositions run during the test period ranged from Top Gas Fuel (TGF), typical of spent reducing gas available in the DRI plant, to COG taken from the feed stock to the TRS:

| | TGF | COG | NG |
|--------------------------------|--------------|--------------|--------------|
| <u>Component</u> | <u>mol %</u> | <u>mol %</u> | <u>mol %</u> |
| CO | 20.5 | 11.7 | - |
| CO ₂ | 14.6 | 3.2 | 1.35 |
| H ₂ | 46.1 | 55.3 | - |
| H ₂ O | 0.7 | 1.2 | - |
| N ₂ | 13.4 | 3.9 | 0.31 |
| CH ₄ | 4.6 | 23.6 | 95.40 |
| C ₂ H ₆ | - | 0.7 | 2.34 |
| C ₃ H ₈ | - | - | 0.60 |
| C ₇ H ₈ | - | 0.3 | - |
| LHV (kcal/Nm ³) | 2201 | 4032 | 8649 |

For campaign 3, the TRS feedstock analysis target was reverted back to the target from campaign 1 and resulted in the following composition:

| <u>Component</u> | <u>mol %</u> | Std. Dev. | |
|-------------------------------|--------------|--------------|------|
| | | <u>mol %</u> | |
| CO | 10.6 | ± | 1.3 |
| CO ₂ | 3.4 | ± | 1.1 |
| H ₂ | 54.3 | ± | 1.3 |
| H ₂ O | 0.8 | ± | 0.1 |
| N ₂ | 3.8 | ± | 0.6 |
| CH ₄ | 25.6 | ± | 0.2 |
| C ₂ H ₆ | 0.8 | ± | 0.01 |
| C ₇ H ₈ | 0.1 – 0.5 | ± | 0.02 |

The resulting syngas, produced from the above range of HOB gases and TRS feedstock was as follows:

| <u>Component</u> | From TGF | From COG | From NG |
|---|--------------|--------------|--------------|
| | <u>mol %</u> | <u>mol %</u> | <u>mol %</u> |
| CO | 23.76 | 23.10 | 21.81 |
| CO ₂ | 2.40 | 1.99 | 1.66 |
| H ₂ | 48.07 | 51.46 | 56.07 |
| H ₂ O | 14.65 | 12.93 | 11.95 |
| N ₂ | 10.22 | 8.39 | 7.05 |
| CH ₄ | 0.85 | 2.06 | 1.36 |
| C ₂ H ₆ | 0.045 | 0.044 | 0.024 |
| C ₃ H ₈ | 0.006 | 0.005 | 0.003 |
| Gas Quality [(H ₂ +CO)/(H ₂ O+CO ₂)] | 4.21 | 5.00 | 5.72 |

As with the previous campaigns, the major issues focused on the control of the peak gas temperature, the methane slip, and the potential for soot generation in the reactor. These are each summarized in the figures 6, 7, and 8.

The use of lower heating value fuels was successful in generating a reducing quality gas with low CO₂ content and free from significant soot generation. As would be expected the lower the fuel heating value, the oxidant level in the raw gas is higher for the same peak operating temperature. The resulting gas qualities are easily improved with full or partial cooling of the hot syngas streams. The typical resulting H₂O content would be between 9%- 10% for partial quench and 1.5% – 2.0% for a full quench.

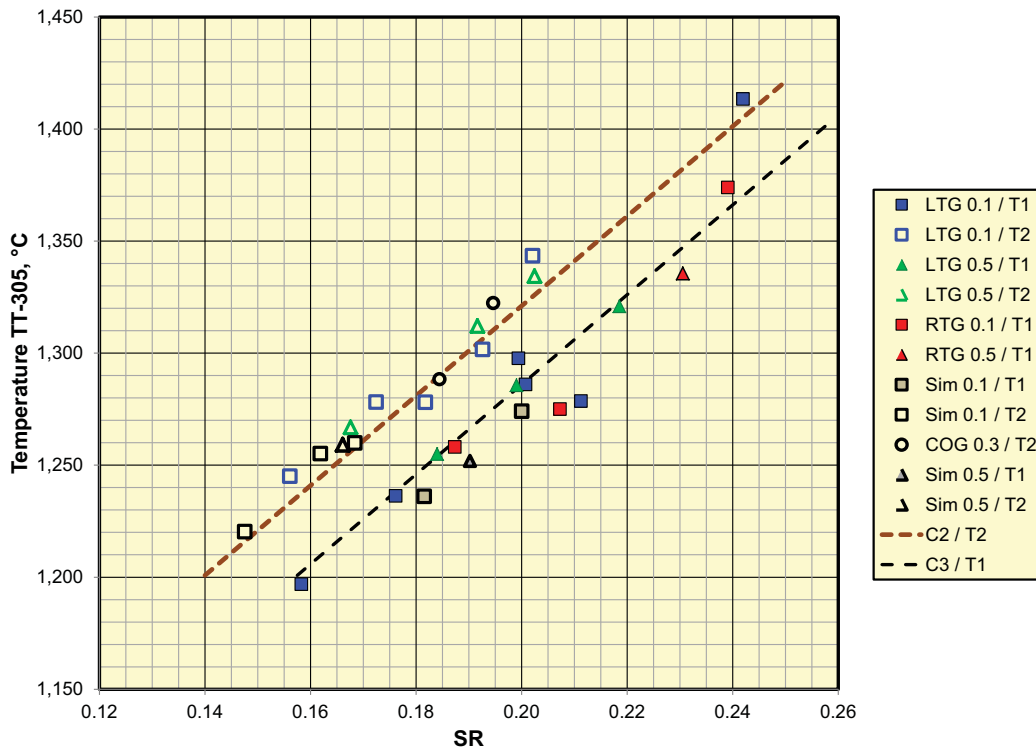


Figure 6 – Peak Reactor Temperature vs SR in Campaign 3.
T1 < T2 are hot oxygen temperatures

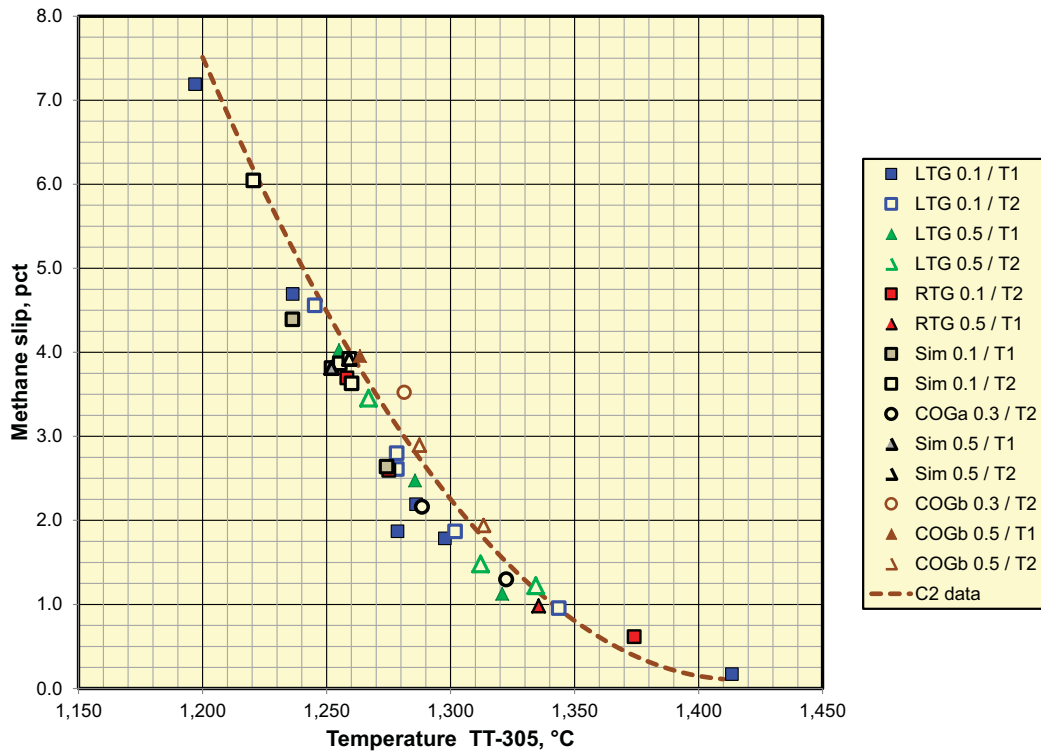


Figure 7 – Peak Reactor Temperature versus Methane Slip from TRS in Campaign 3

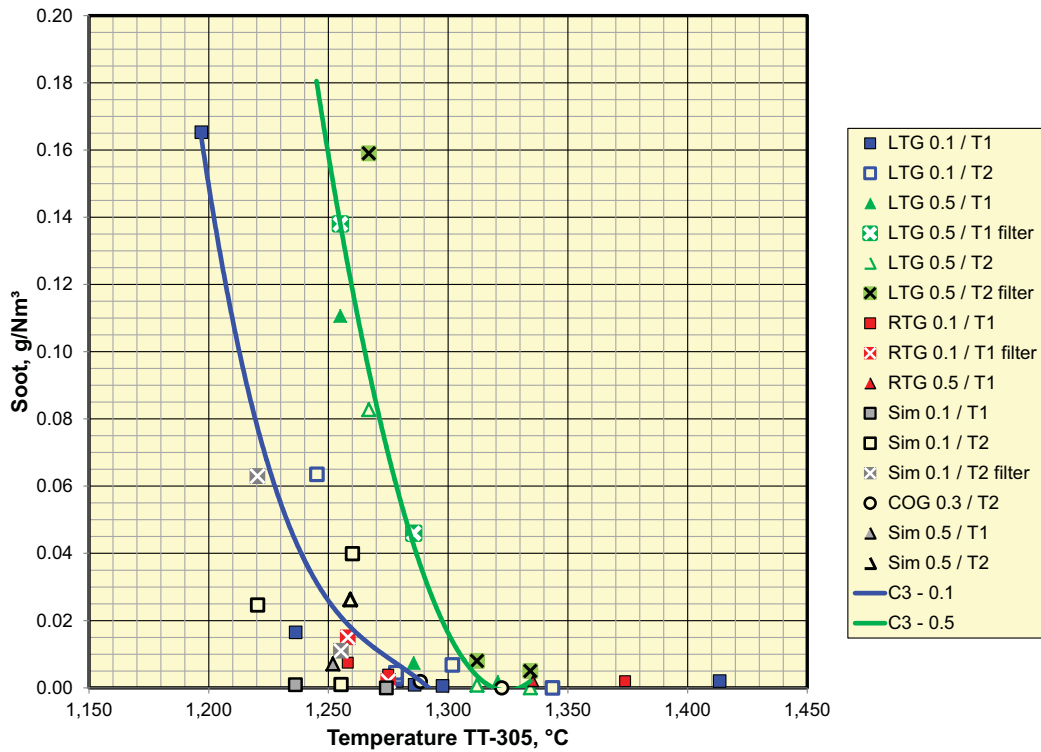


Figure 8 –Soot Generation versus Peak Reactor Temperature in Campaigns 2 and 3

TRS FLOW SHEET INTEGRATION

There are two TRS flow sheet options which will be used to add the syngas and produce high quality DRI from the COG. Both arrangements use the MXCOL[®] flow sheet as the principle arrangement of equipment for managing the removal of the oxidants (H₂O and CO₂) from the process stream. The two flow sheet options are the Feed Gas TRS[®] and the Bustle Gas TRS[®], which are shown below in the figures 9 and 10.

The preferred option is the Bustle Gas TRS flow sheet, in that it retains the residual heat from the TRS reactions and utilizes it directly in the DRI production process. The heat helps convert the lower quality syngas and feed gas, typically about 8.5 quality (reductant/oxidant) ratio, to a 12.0 quality ratio at equilibrated conditions. Typical MIDREX[®] reformed gas has a quality ratio of 10.5 and after equilibration reaches a 12.0-12.5 quality ratio. So as can be seen, the production performance from the TRS syngas fits well into the normal performance curves for a MIDREX[®] Direct Reduction Plant.

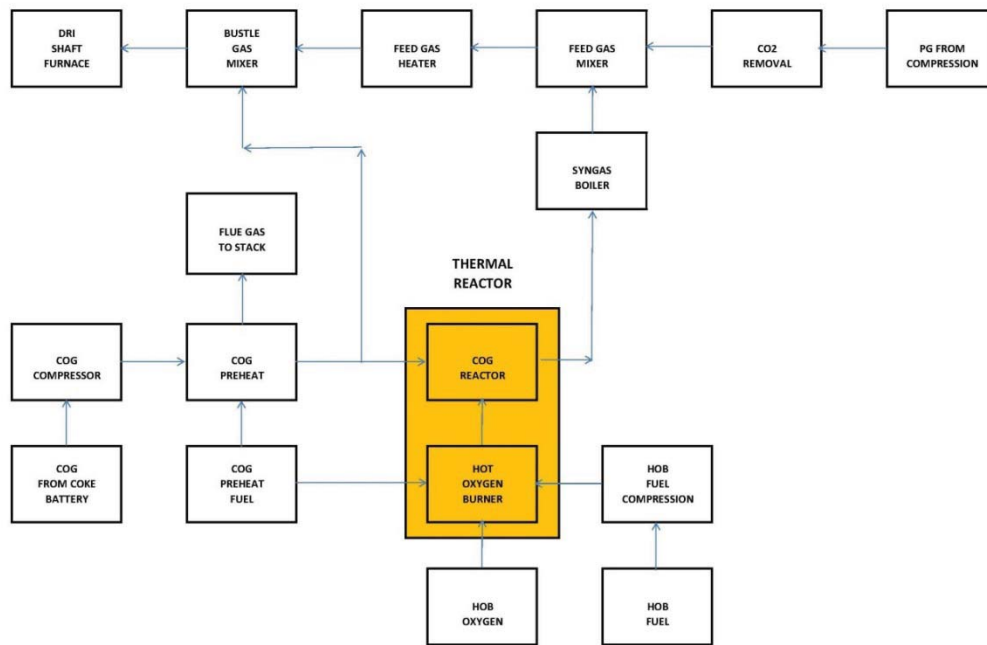


Figure 9 – Feed Gas TRS Flow Sheet

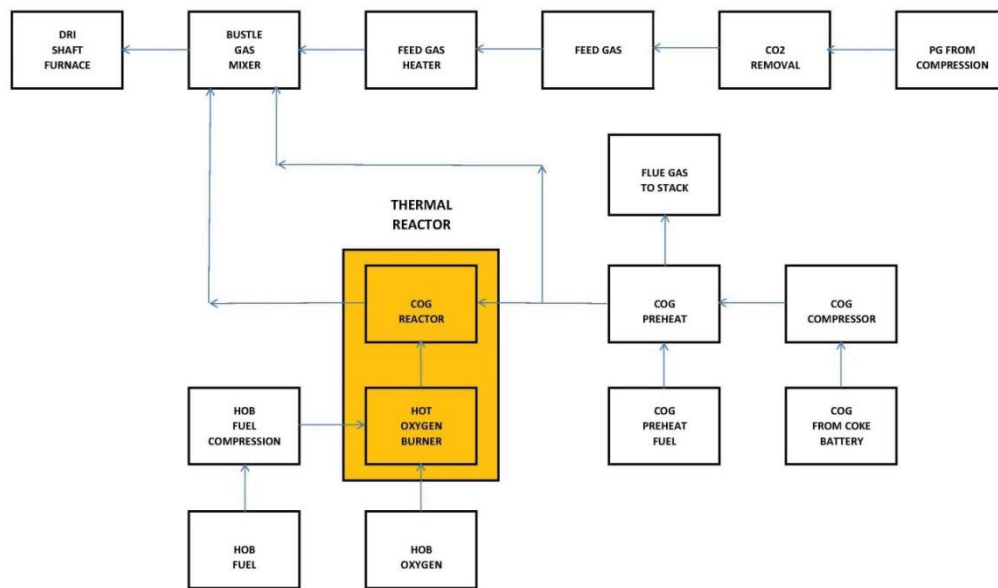


Figure 10 – Bustle Gas TRS Flow Sheet

Midrex has also developed a flow sheet which does not incorporate a recycle of spent process gases but rather exports the gases for use as burner fuels in other plant operating sections. This flow sheet requires approximately twice the COG per ton of DRI produced but yields about a 60%-65% return of heating value in the export gas volumes. This option would fit best in larger integrated facilities where the DRI needs are less and the need for additional in process furnace fuels is significant.

CONCLUSION

Midrex and Praxair are confident that the TRS will be able to produce clean syngas from COG (and other hydrocarbon sources) for DRI production in a MIDREX® Direct Reduction Shaft Furnace. The commercial applications for the steel industry are numerous. The TRS offers a solution for producing quality reducing gas in regions with limited access to natural gas for production of DRI. The ability to use COG to replace natural gas as a source for reducing gas may be the only way regions like India can continue to produce higher quality DRI products.

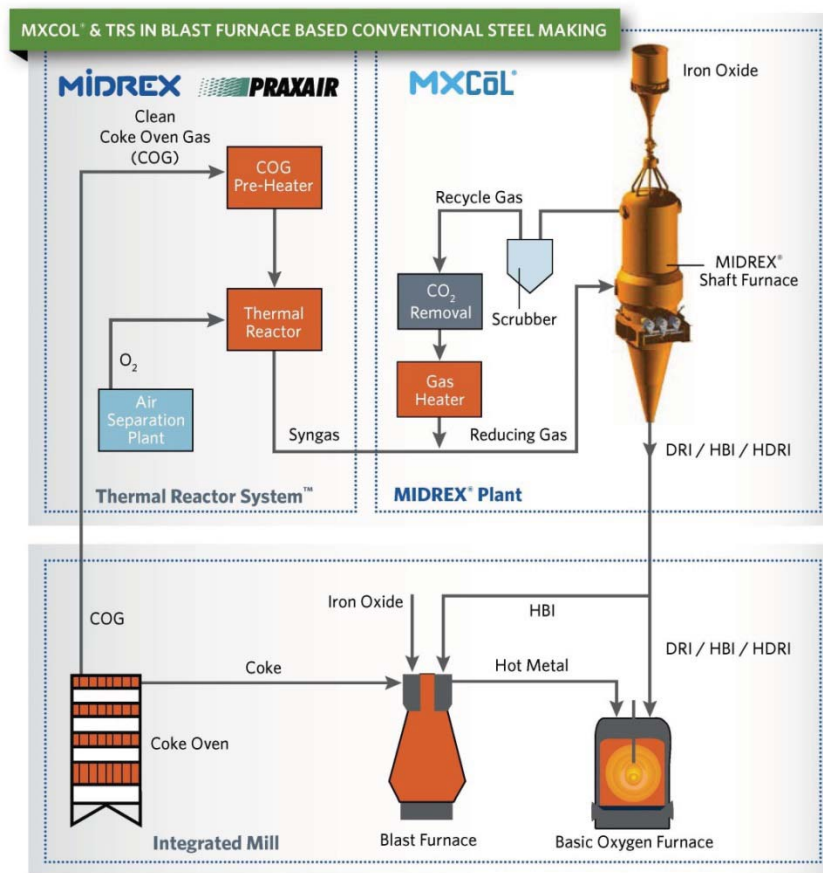


Figure 11 – TRS® in Integrated Mill

This technology can be retrofitted to existing plants as well as new projects. In addition, the TRS not only opens up new DRI production by being able to use COG for up to 100% of reducing gas, the long term implications of the technology will have an impact upon integrated mills, as seen in figure 11. Using the TRS technology to produce DRI in a MIDREX® Furnace can also help integrated steel producers sustainability by maximizing iron and steel production through optimum coke usage. The TRS allows integrated steel producers to take even greater advantage of their resources. More iron could be produced for the same amount of coke and that iron in the form of hot briquetted iron (HBI) could then be fed to a blast furnace or a BOF within the same integrated works. This would increase hot metal production reducing the specific coke consumption, greatly reducing the environmental impact of the steel produced, and perhaps be an alternative for purchased scrap in the BOF.