Development of Ni-Based Sulfur Resistant Catalyst for Diesel Reforming

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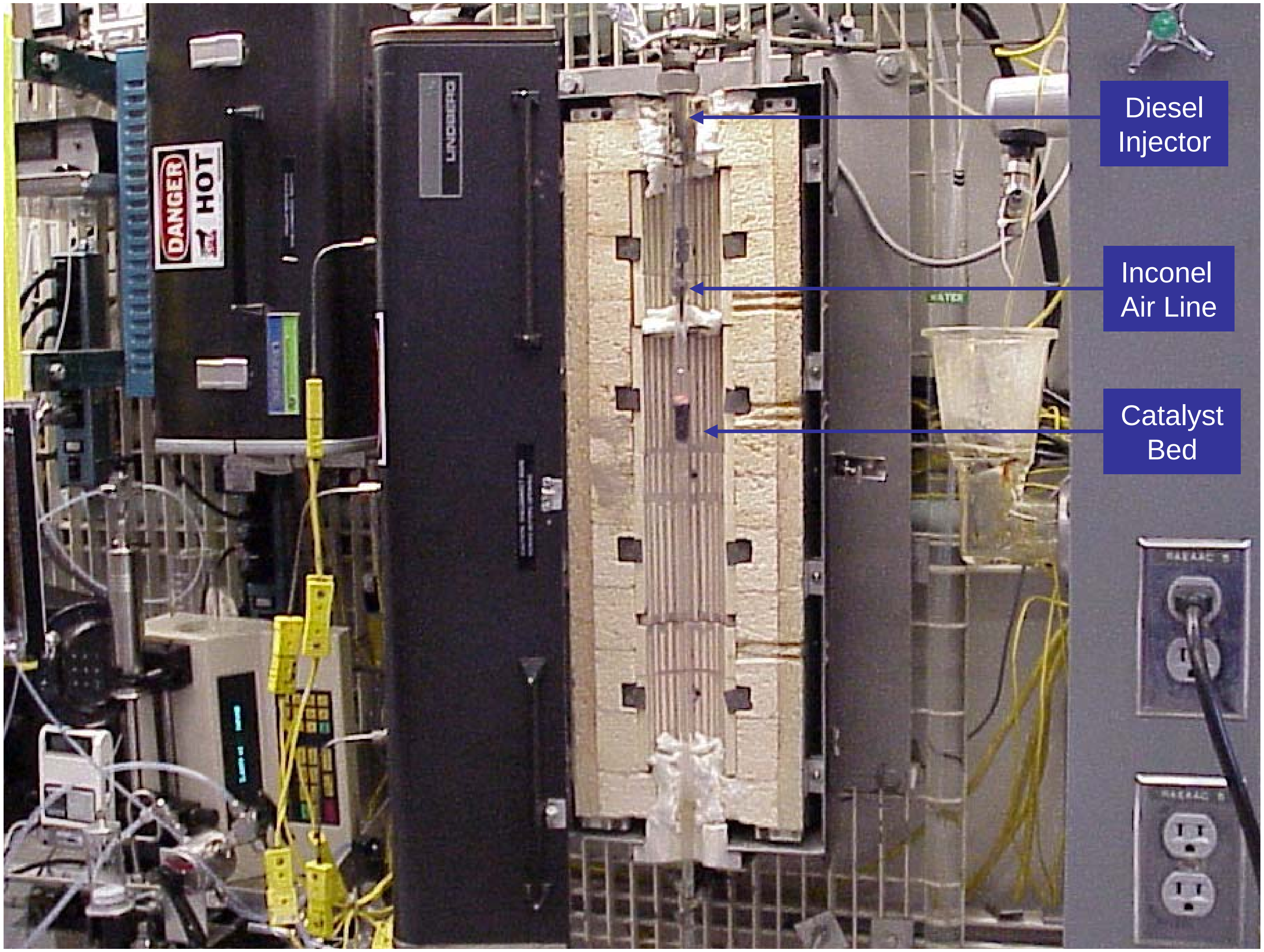
Technical Challenges

- Reform commercial sulfur containing diesel over low cost catalyst.
  - Only source of H_2O is in a 20% recycle stream from the SOFC anode.
- Low steam to carbon ratio may lead to coking. Thus deactivating the reformer catalyst, and thereby producing excessive C2+ molecules.
- Sulfur in the feed will readily poison most low cost Ni catalysts and Ni based SOFC anodes.

Technical Approach

- Spray/vaporize diesel fuel into a heated simulated 20% recycle stream consisting of steam in N_2. H_2O to C = 0.2
- Blend vaporized diesel with air at the catalyst bed at an O to C = 1.0.
- Sulfur in the feed is adsorbed by the front part of the catalyst bed so that Ni on the catalyst is not poisoned.
- The catalyst is periodically regenerated by burning off the coke/adsorbed sulfur in air.

Autothermal Reactor



Results to Date

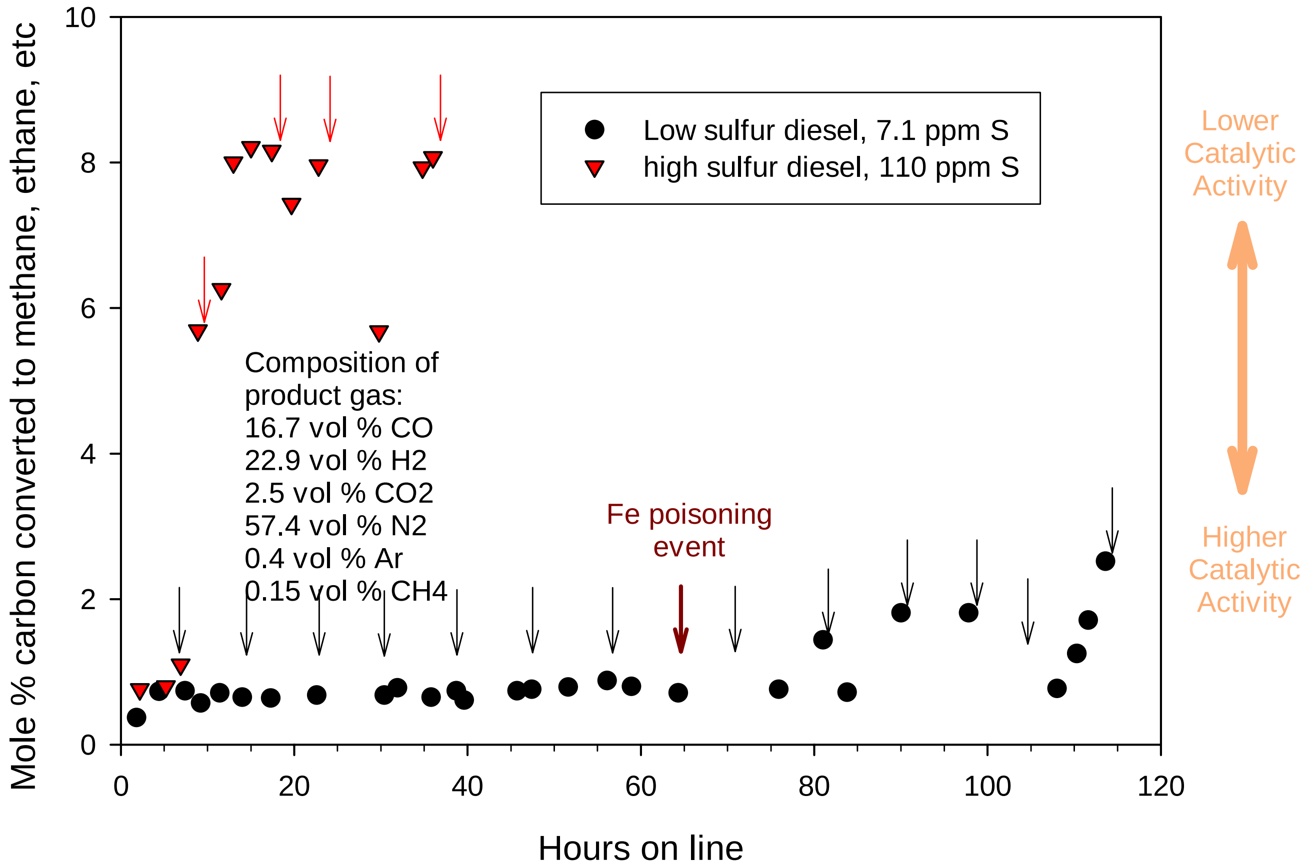
- ChevronTexaco's Ni based catalyst (CARCAT104) readily reformed a 7 ppm low sulfur diesel. Subsequent tests will use a 50 ppm S diesel.

- Exceptions/cautions:
  - Fe from upstream reactor components poisoned the catalyst, as a result of a one time incident involving metal catalyzed coking of Inconel 600 air line and 316 SS steam line.

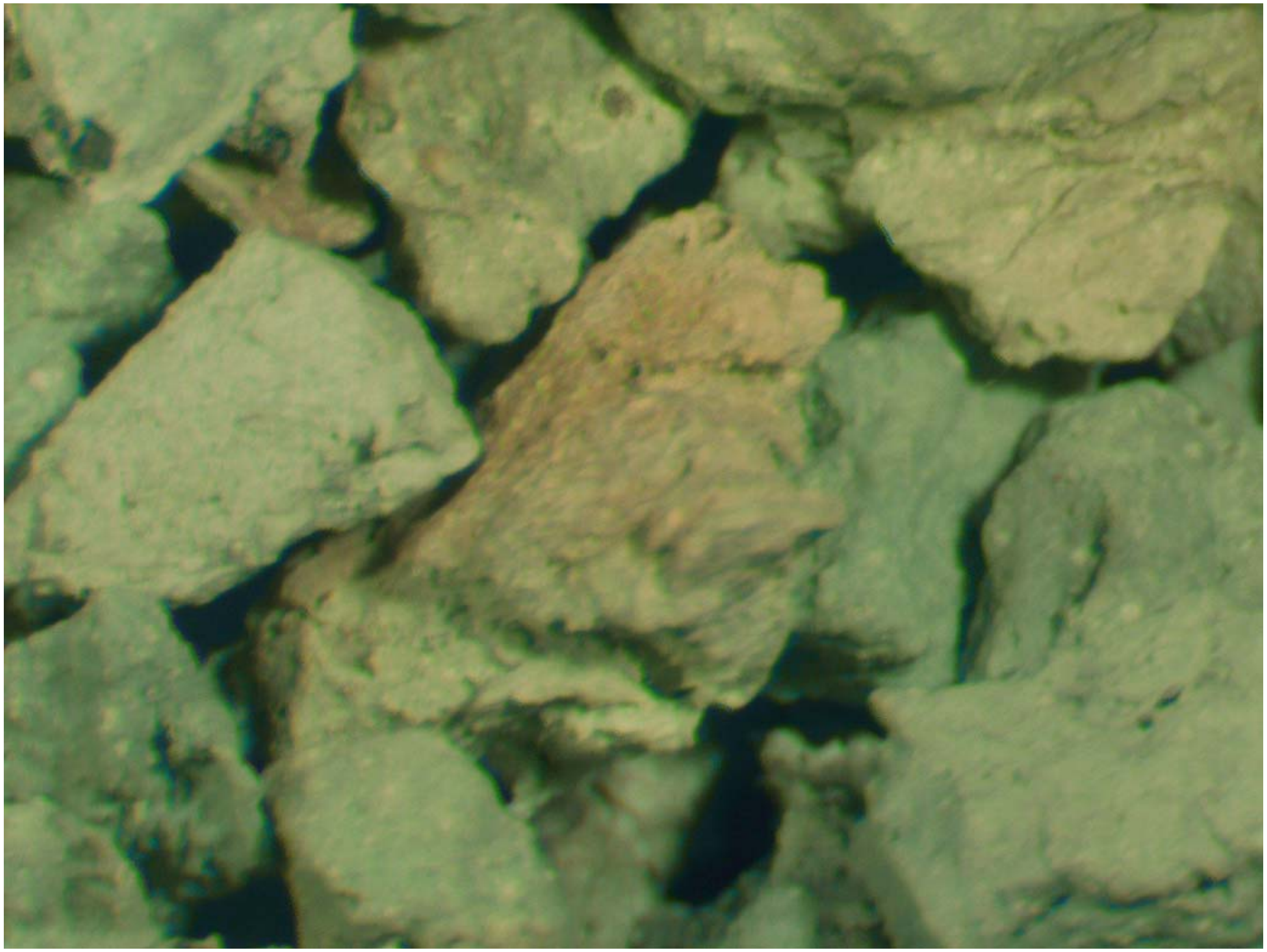
  - excessive mixing of diesel and air above the catalyst bed may lead to pre-burning and poor performance.

Autothermal reforming of low and high sulfur diesel fuels using CARCAT 104 under SECA conditions: 750 C, O/C = 1.0, H2O/C = 0.2, 1.1 WHSV (5000 GHSV) with 20% recycle stream symmulated using nitrogen/steam. The catalyst was typically run for 8 hours and regenerated using steam and air, except for the regeneration at 65 hours. The regeneration points are marked with an arrow.

The regeneration at 65 hours only used air. Since diesel fuel was still slowly dripping in, metal catalyzed coke formed on the 316 SS steam injection line and on the Inconel 600 air line; thereby, depositing 360 ppm Fe (on average) onto the catalyst. As a consequence the catalyst now shows a daily decline in activity due to coke building up on the front part of the catalyst bed following this one time event.



CARCAT 104 (Ni-based sulfur resistant reforming catalyst) showing the deposition of iron on one particle after 114 hours on line at 750 C, O to C ratio 1.0, H2O to C ratio 0.2, 20% simulated recycle running a 7.06 ppm S 2006 US type diesel at 1.0 WHSV. Iron from upstream components in the reactor had broke free due to metal catalyzed coking and deposited on the top layer of 8 to 14 mesh catalyst particles effecting the performance of the catalyst.

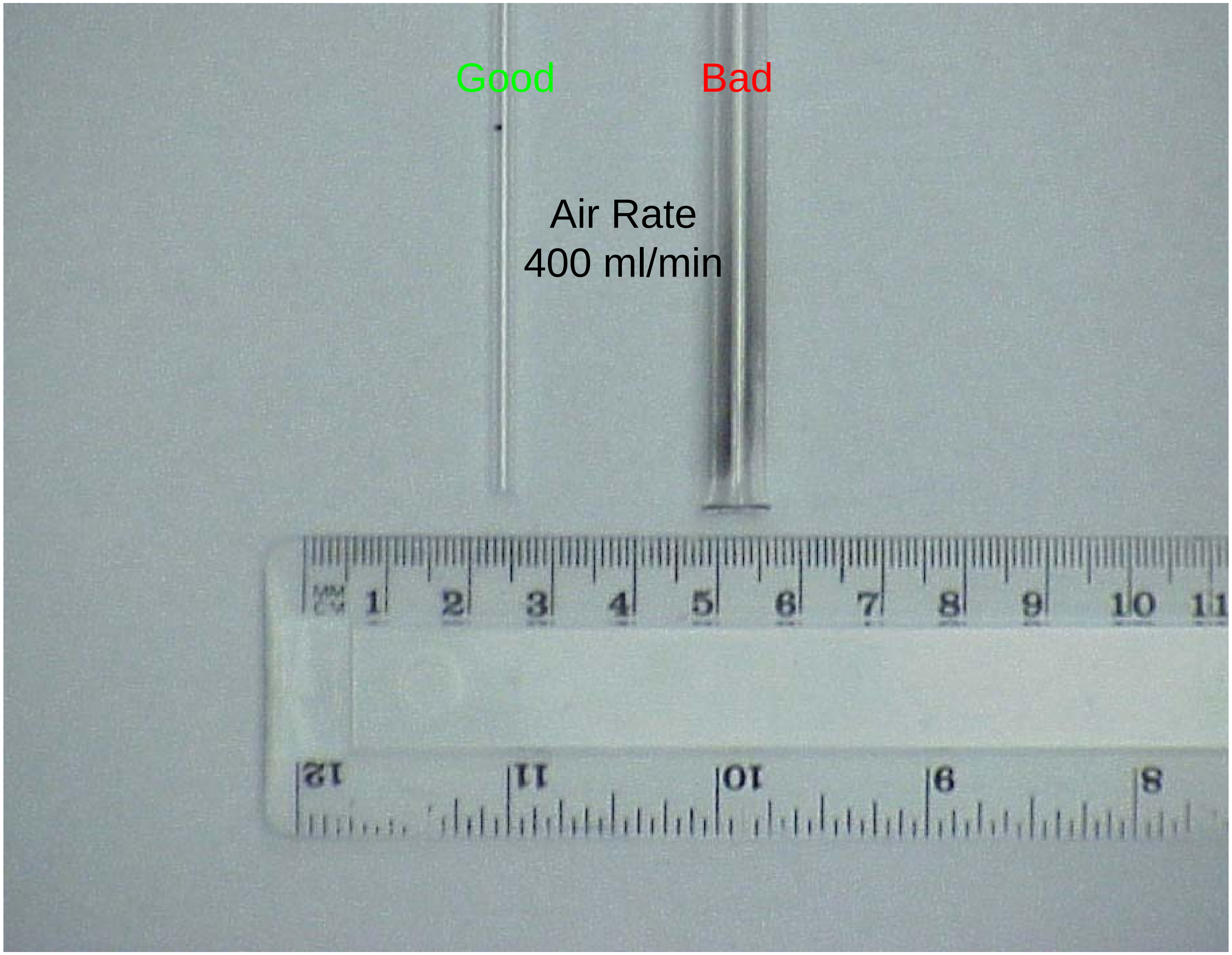


Solutions to the Fe Deposition Problem

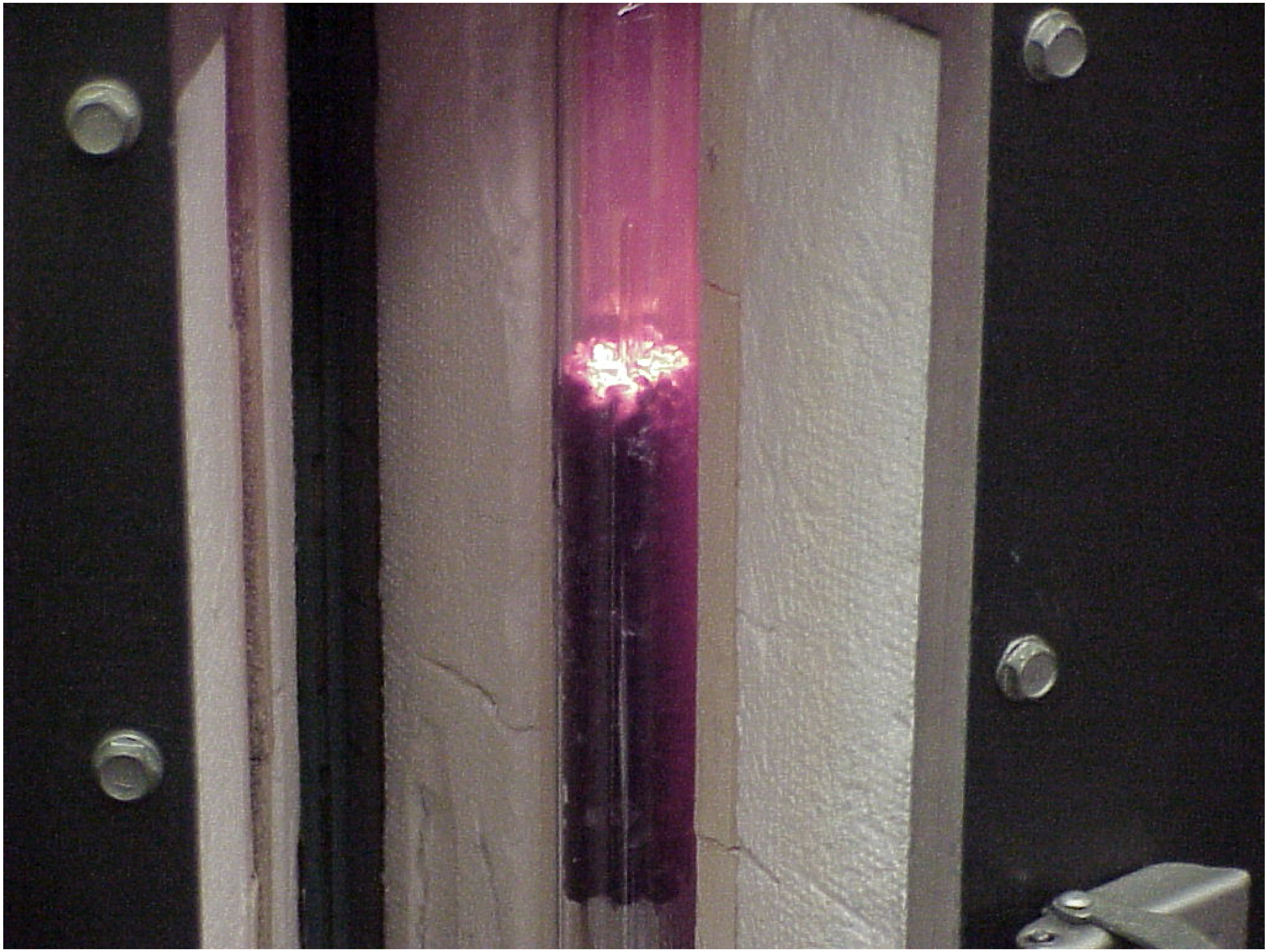
- In the laboratory:
  - build the reactor from quartz glass with no metal parts
- In the real world:
  - select low coking metallurgy or coat the reactor with an aluminide coating (see U.S. Patent 6,803,029). There is a trade-off between preheating the diesel fuel and the temperature at which metal catalyzed coking will occur.

Diameter of the air inlet line is critical!

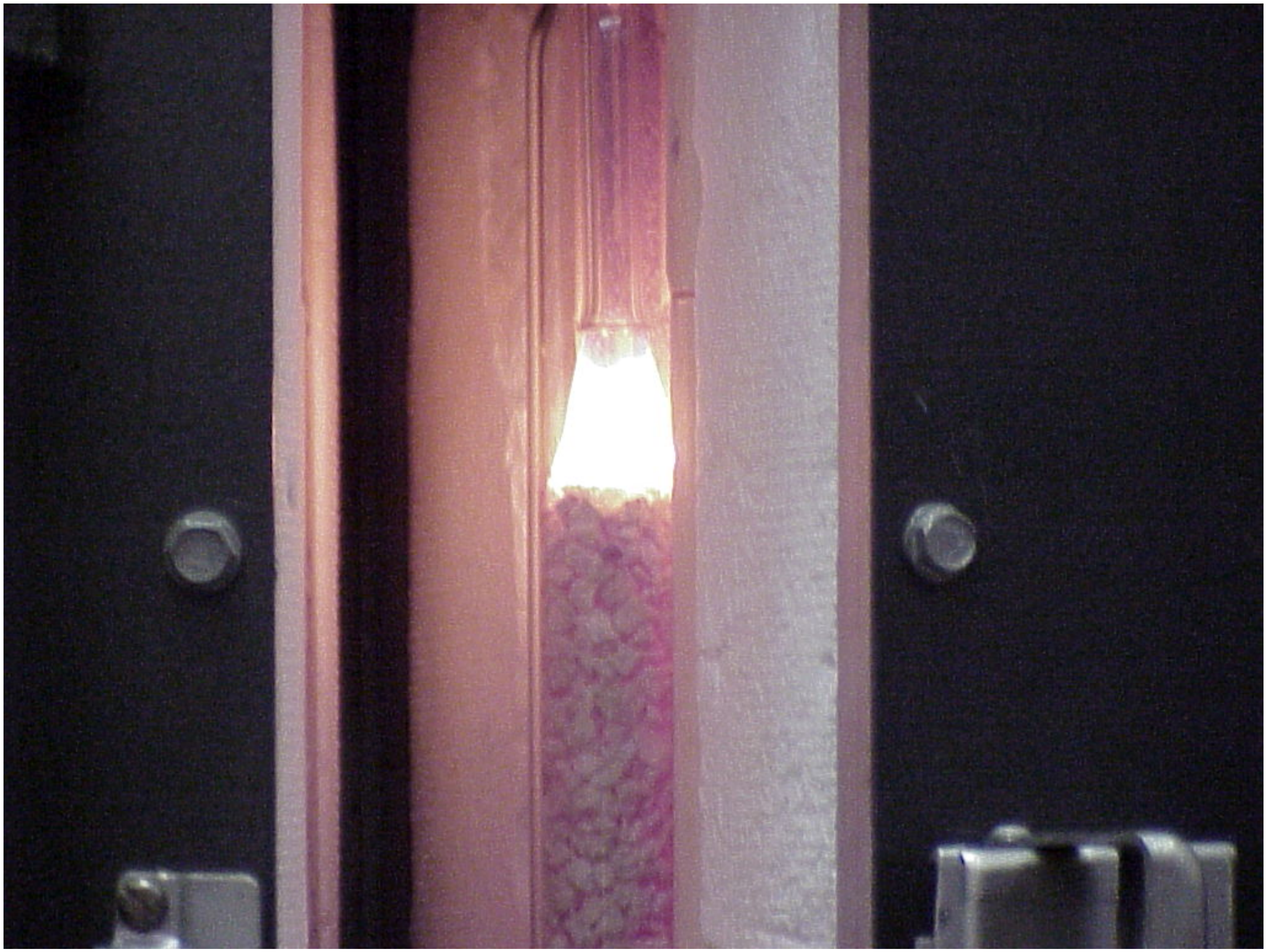
High air velocity prevents pre-combustion



Autothermal Reactor with 1.9 mm ID air line located 6 cm above the catalyst bed. Note the even flame front.



Autothermal Reactor with 5.1 mm ID air line located 2.5 cm above the catalyst bed. The diesel fuel has just started to burn above the bed.



Autothermal Reactor with 5.1 mm ID air line located 2.5 cm above the catalyst bed. Note the coke/soot that has quickly formed on the catalyst bed after ~ 2 minutes of operation.

Reformer Design Elements to Optimize Catalytic Performance

- Prevent upstream Fe creation and deposition

- Allow diesel fuel and air to mix and burn at the catalyst surface.
  - vaporize diesel in recycle stream at as high a temperature as possible (limited by metal catalyzed coking).
  - use a high velocity air stream to avoid "pre-burning" the diesel fuel above the catalyst bed.
  - 3 dimensional catalyst bed allows rapid mixing and hot even flame front.

Future Activities

- Task 2: Evaluate and characterize the system
  - Eliminate sources of iron upstream of the catalyst bed
  - Measure temperature profile with and without sulfur in the feed.
- Task 3: determine effectiveness of radio frequency coke suppression (see U.S. Patent 6,790,547)
  - Identify conditions/feeds that rapidly deactivate the catalyst
  - Conduct aging/deactivation studies at different frequencies.
  - Conduct aging/deactivation studies at varying electric field strengths