“Development of Ni-based Sulfur Resistant Catalyst for Diesel Reforming”

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ABSTRACT

In order for diesel fuel to be used in a solid oxide fuel cell auxiliary power unit, the diesel fuel must be reformed into hydrogen, carbon monoxide and carbon dioxide. One of the major problems facing catalytic reforming is that the level of sulfur found in low sulfur diesel can poison most catalysts. This report shows that a proprietary low cost Ni-based reforming catalyst can be used to reform a 7 and 50 ppm sulfur containing diesel fuel for over 500 hours of operation. Coking, which appears to be route of catalyst deactivation due to metal stripping, can be controlled by catalyst modifications, introduction of turbulence, and/or by application of an electromagnetic field with a frequency from ~ 50 kHz to 13.56 MHz with field strength greater than about 100 V/cm and more preferably greater about 500 V/cm.

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EXECUTIVE SUMMARY

In order for diesel fuel to be used in a solid oxide fuel cell auxiliary power unit, the diesel fuel must first be reformed into hydrogen, carbon monoxide, and carbon dioxide. One of the major problems is that even the 5 to 15 ppm sulfur found in ultra-low sulfur diesel in the US, Europe and Japan (by 2010) will poison “conventional” reforming catalysts resulting in loss of activity and excessive coking. The purpose of this research is to demonstrate that a low cost (and hence nickel based) catalyst can be used to reform these ultra-low sulfur diesel fuels, and to demonstrate that radio frequency coke suppression can be used to increase the life of the catalyst.

In the beginning of this project, a proprietary nickel based catalyst was shown too easy reform a 7 ppm sulfur diesel fuel under realistic conditions of an O to C ratio of 1.0 with a simulated recycle rate of 20 % (implying a steam to C ratio of 0.2). Unfortunately this same catalyst was readily poisoned by iron deposited from upstream components in the pilot plant. As a consequence, all source of iron were moved from the test apparatus and the project objectives were rewritten to focus on reforming a tougher 50 ppm S diesel fuel with and without radio frequency coke suppression.

With the 50 ppm S diesel fuel, the low cost Ni-based catalyst was shown to deactivate over the course of 360 hours due to metal catalyzed coking, which stripped nickel from the catalyst. Two different radio frequency electromagnetic fields at a frequency of 350 kHz (98 V/cm) and 50 kHz (92 V/cm) were then applied to the catalyst in two subsequent runs; in both cases the catalyst showed no or only minor loss of activity up to 500 hours of operation. The effect of radio frequency coke suppression on reducing coking on the catalyst was then measured as function of frequency and field strength. Not surprisingly, the RF coke suppression effect appeared to be linearly dependent upon the field strength (at least up to 800 V/cm), but was surprisingly independent of the frequency between 50 kHz and 13.56 MHz.

Initially it was thought that this Ni-based reforming catalyst was sulfur resistant due to free Ni which was stabilized on the surface of the proprietary support. Thus it was believed that the catalyst would adsorb sulfur in the front part of the reformer catalyst bed; thereby, allowing the remainder of the catalyst bed to reform the remaining hydrocarbons. This hypothesis was shown to be partially correct. With a 50 ppm S diesel fuel the sulfur loading capacity of the catalyst is reached in about 2 hours, however the catalyst reforming activity lines out at slightly lower activity at this point in time. By comparing the color changes of fresh and aged catalysts, it became clear that the surface Ni was being incorporated into the support to produce the sulfur resistant reforming catalyst. This is the same mechanism of sulfur resistance that Michael Krumpelt at Argonne National Laboratory had proposed for their series of perovskite based catalysts, and also imparts the sulfur resistance to “hexaaluminate” series of catalysts being developed by David Berry and co-workers at NETL in Morgantown.

Since the sulfur adsorption function of free Ni (or NiO) on the surface of the catalyst was too low to be practical in real world applications, and since it became obvious that this “free” Ni was actually contributed to coking, it became clear that the catalyst should be “reformulated” to reduce coking. In one “accidental” run, the O to C ratio was temporarily increased to over 1.0 for the first 172 hours. As a result the catalyst turned “blue”; indicating that all the nickel was “incorporated” into the structure. Surprisingly and quite fortunately, this “new” version of the catalyst had a coking rate that was 4 to 6 times less than the “base” case, and as a consequence did not need RF coke suppression to remain stable for 500 hours of operation.

In one final twist, it was also discovered that if “turbulence” was introduced into the flame front that the coking rate could be dropped by another 4 times.

Thus in summary it was demonstrated that a low cost Ni based catalyst can reform a 50 ppm diesel fuel with or without recycle gas and that if coking on the catalyst is controlled by proper catalyst formulation, introduction of turbulence into the flame front, and by possible application of a RF electromagnetic field, catalyst deactivation can be avoided for at least the first 500 hours of operation. This is a good step towards developing a long term stable catalyst capable of reforming ultra low diesel fuel for at least 5,000 to 10,000 hours. However it is important to realize that reforming diesel fuel is a very difficult process and that gas phase and metal catalyzed coking (particularly in the absence of steam) will deactivate any and all catalysts over the course of 24 to a few hundred hours. Thus this catalyst was specifically designed to tolerate periodic air regenerations.

REPORT DETAILS

Experimental Method: The apparatus used to reform diesel into hydrogen, carbon monoxide/dioxide, methane, and trace higher hydrocarbons for use in a SOFC (solid oxide fuel cell) APU (auxiliary power unit) is shown schematically in Figure 1, and consists of a fuel pump, a metered air supply, a metered nitrogen supply, water pump, and a fuel injection port. The “fuel injector” (shown in Figure 2) actually consists of three ports, (fuel, air and water), and is attached to the top of a 1” diameter quartz tube that extends through either a 3-zone furnace or 2 single zone furnaces placed in a vertical position (see Figure 3). The diesel fuel is injected at a pressure ranging from 3 to 5 psi through a 20 micron orifice that is contained in a heated stainless steel block set at 120°C into a 500°C or 600°C heated zone; thereby, allowing the diesel fuel to completely vaporize. Steam and nitrogen is also added to the top of the furnace, simulating a 20% recycle stream. The steam is created by pumping water through a 200 micron ID silica GC column onto a kaowool or sintered quartz pad. The “steam” ceramic pad was positioned by trial and error so that the steam rate was uniform. Air was injected into the vaporized diesel/steam/nitrogen mixture at a point approximately 8 cm above the catalyst bed (located in the center zone of the 3-zone furnace or in the lower furnace). The location of the air injection point is critical to the proper operation of the unit and was optimized by observation of the flame front and by minimizing both C1+ hydrocarbons left in the reformat stream and the coking rate on the catalyst. Placing the air injection point too high above the catalyst bed allows for too much pre-burning of the diesel fuel; thereby, lowering the temperature of the flame front and increasing both the residual C1+ compounds in the reformat stream as well as increasing the coking rate on the catalyst. Placement of the air injection point below the optimum point results in a non-uniform hot spot on the catalyst, thus allowing for a substantial slip of hydrocarbons around the catalyst bed. An ideal flame front is shown in Figure 4.

In the first few experiments, a 1/8” OD Inconel 600 line was used to inject air into the unit. Unfortunately, this line was subject to severe oxidation/reduction cycles right at the point where air and diesel met. This resulted in metal catalyzed coking which then deposited iron onto the catalyst. This line was later replaced with a 3 mm OD (1.9 mm ID quartz line so that iron contamination would not be a problem. The reformat gas from the furnace was passed through a water knockout pot and then analyzed on a calibrated Wassen GC. The entire system was leak tested at the beginning of each run, and a carbon mass closure of approximately 99 to 101% was obtained on each data point (unless noted). The sulfur content of the reformat gas for some of the runs were measured on a HP 5890 GC equipped with a Sievers 355 chemiluminescent sulfur detector.

A RF (radio frequency) field was applied to the catalyst bed by inserting a 3 mm OD or 10 mm OD quartz tube through the center of the catalyst bed. In the center of this quartz tube was run a 1/4” diameter stainless steel tube or a 1 mm OD Inconel 600 wire connected to an Advanced Energy LF5 variable frequency (50 to 460 kHz) or an

Advanced Energy RF5 (13.56 MHz) power supply. The outside ground consisted of a 1" OD Inconel 600 tube or Nichrome wire screen.

The diesel fuel used in these experiments were purchased at two different local gasoline stations and were either used as is (7 ppm fuel) or blended to obtain a 50 ppm S fuel. The properties of these fuels are listed in Table 1. The catalyst was prepared in-house, and consists of Ni supported on a proprietary support. The run conditions and catalyst bed parameters are listed in Table 2.

Since units were not certified by the safety department to run unattended overnight, the catalyst was regenerated at the end of each day by turning off the hydrocarbon pump and then reversing the air flow so that it passed up through the bed.

Results and Discussion: Figures 5 and 6 show the temperature profile for the two test apparatuses running the 7 and 50 ppm diesel fuels under the test reforming conditions. Figure 6 also shows a "0" sulfur model diesel fuel which was n-dodecane, since the 7 ppm real diesel fuel was not further desulfurized using a Ni sulfur adsorbent from Sud-Chemie, C28-1-01RS run at 250°C.

There are a number of interesting aspects that can be seen in the temperature profiles. First of all, the temperature starts rising as soon as air and diesel fuel make contact, demonstrating that early pre-burn above the bed is still occurring, and secondly the high 50 ppm sulfur fuel shows a temperature drop of approximately 20° C immediately following the high temperature flame front. This demonstrates that in spite of the high level of sulfur in the feed, the catalyst is capable of steam reforming the light hydrocarbons created in the high temperature flame front. By the end of the bed there is very little reaction occurring. Also note that this endotherm is missing when the low 7 ppm sulfur fuel is reformed; implying that this fuel is mainly reformed in just the first 1 to 2 centimeters of the catalyst bed.

Figure 7 shows that a 7 ppm S diesel fuel is easily reformed over the Ni-based catalyst to H₂, CO, CO₂ and only a trace of methane. Note that the Figure 7 plots the mole % carbon in the fuel converted to methane and higher hydrocarbons versus time, and thus is really a plot of "unconverted" hydrocarbons versus time. The Ni-based catalyst was stable until about 65 hours, when in a one time incident, the steam and hydrocarbon feed streams were both turned off at the same time (normal operation was to turn off just the hydrocarbon feed). This "minor" change in procedure resulted in metal catalyzed coking of the Inconel line, since diesel was still dribbling into the unit through the orifice (i.e. the fuel pressure in the feed line would gradually drop normally over a period of 1 to 10 minutes). Once iron was "dumped" on the front of the catalyst bed, the concentration of methane started increasing. From this one time incident, the Inconel 600 air line was now sensitized to metal catalyzed coking, and thus continued to add more and more iron to the front of the catalyst bed. The run was stopped at 114 hours when it became clear

that the catalyst activity was on a steady decline. Figure 8 shows a 360 ppm Fe deposited on the Ni-based catalyst from this low sulfur run. What is really surprising is that a small amount of iron can cause a lot of trouble.

Figure 7 also shows that it is possible to reform a significantly higher sulfur diesel fuel. Given these two sets of data, the project objects were then modified to focus on reforming a 50 ppm diesel fuel with and without radio frequency coke suppression. Both units were also modified so that iron contamination would no longer be an issue.

Figure 9 shows the initial activity of the Ni-based catalyst as a function of time reforming the 50 ppm S diesel fuel. It is interesting to note that the activity of the catalyst is dramatically lost after the first regeneration. However by the 4th to 5th day of operation, the concentration of undesirable C2+ products in the reformat gas has lined out after the first 2-3 hours of operation.

Figure 10 shows the long term deactivation of the Ni-based catalyst reforming the 50 ppm S diesel fuel with and without RF coke suppression. Clearly RF coke suppression allows the catalyst to survive for more than 500 hours of operation. Without RF, the catalyst clearly showing signs of deactivation by 200 hours of operation, and rapidly deactivates thereafter (in black). The major effect of applying a RF field easily seen in the length in time it takes the coke to burn off the catalyst at the end of the day. With application of a 350 kHz 98 V/cm (in red) or a 50 kHz 92 V/cm (in yellow) RF field, the coke on the catalyst would burn off in about 5 minutes (climbing to about 8 -12 minutes near the end of the aging run); whereas, in the RF off case, the catalyst was substantially coked, and required more than 20 to 30 minutes of regeneration for the coke to burn off the catalyst after a 8 to 10 hour run. The “repeat RF off run” (in green) showed no deactivation due to excess air that leaked into the reactor during the first 172 hours (see discussion below).

Figure 11 shows the aged catalyst from the RF off case (black data in Figure 10) while it was still in the reactor. Note the color of the catalyst is no longer green as in Figure 8, but has changed to blue on one side and gray on the other. This run was stopped at 366 hours because the coking on the gray side of the catalyst bed was becoming progressively worse and the activity was rapidly degrading at this point in time. It is clear that severe coking had stripped both free surface NiO as well as bound Ni (III) nickel from the catalyst.

The “repeat RF off run” was actually not a repeat of the first RF off base case. By 172 hours, it was clear that this “repeat” run was completely different from the first RF off (base) case, carbon closure was less than 97%, the coking rate was substantially reduced and it was observed that the flame front on the catalyst would sometimes “glow” very brightly, particularly when the hood system was pulling very strongly. In this unit the product gases from this unit was fed to the hood system so that the reactor was normally under reduced pressure but would vary from time to time depending upon changes in the building ventilation system. Thus at 172 hours of operation, the reactor was pressure tested, only to discover that the inner quartz liner for the RF probe had chipped, probably

as a result of metal expansion/twisting of RF antenna during the initial heat-up (see Figure 12). This inner quartz liner was carefully removed so as to minimize disturbance of the catalyst bed, and the run continued to 475 hours. As a result of the cracked inner quartz liner for the RF antenna, the catalyst was run with an O to C ratio greater than 1.0 for the first 172 hours, but at 1.0 from 172 hours to end of run. At 172 hours the color of the catalyst was blue indicating that all of the free surface NiO was now incorporated into the structure. This resulted in catalyst that was as stable and active as CARCAT 104 under RF coke suppression. In other words, RF coke suppression may not be necessary for most applications, since the coking rate on the catalyst can be readily dropped simply by increasing the calcination temperature of the CARCAT catalyst during preparation.

Figure 13 compares the effect of RF on maintaining surface NiO. The blue catalyst on the left is from the “repeat RF off run” after 475 hours online and shows that only substituted Ni (III) can be found in the catalyst. The “green” catalyst on the right is from the 50 kHz 92 V/cm aging run after 380 hours online. The color of the aged catalyst clearly shows that application of RF prevents Ni stripping.

This is also supported by the data in Figure 14, which shows the sulfur breakthrough curves for both fresh and RF aged catalyst (350 kHz 98 V/cm run) as a concentration of sulfur (as H₂S) in the reformat gas. Note that the Ni-based catalyst is capable of adsorbing sulfur produced when reforming a 50 ppm diesel fuel, but that this effect only lasts for about the first 2 hours. After roughly 3 to 4 hours online the catalyst is completely saturated and cannot adsorb any more sulfur. Thus the concentration of sulfur reaches the theoretical limit based on fuel sulfur content. Note that RF coke suppression (at 350 kHz 98 V/cm) has prevented Ni stripping so that even a well aged (450 hr) catalyst is still capable of absorbing sulfur just as well as the fresh catalyst.

Figures 15 and 16 show the effect of RF coke suppression as a function of field strength and frequency on coke yield. In these runs, the 50 ppm S diesel fuel was reformed over CARCAT 104 at an O to C ratio of 1.1 with no added steam. Eliminating the recycle component in the testing, greatly reduced the amount of coke formed by metal catalyzed coking on the catalyst, and allowed for more stable and reproducible operation, and also mimicked the more commercially feasible “no recycle” case of operation. Figure 15 shows that RF coke suppression effect depends upon the field strength, but appears to be independent of the frequency over a range of 50 to 460 kHz.

To try and expand the range of field strengths and frequencies, the unit was modified by increasing the inner diameter of the RF electrode. This surprisingly resulted in introducing turbulence into the flame front on the catalyst, as the high velocity air struck the center electrode and randomly moved around the catalyst, resulting in a “flickering” flame front. This effect dramatically reduced the coking rate by more than 5 X. In hindsight, this makes a lot of sense. Normally, most coke is formed just behind the flame front, and it is this area that suffers most from metal catalyzed coking. If the O to C ratio is temporally varied; any coke that is deposited at one moment will soon burn off in the next moment. Thus turbulence can be an important tool improving the life of these

reforming catalysts. One can imagine that one could design an air inlet that could be pulsed or chopped to introduce this same effect over a larger range of flow conditions.

Figure 16 shows the effect of RF coke suppression under these unusual high turbulent conditions. Again, RF coke suppression is linearly reduced by increasing the field strength, and that frequency over the range of 50 kHz to 13.56MHz showed no variation in improvement. However at 60 Hz at field strength of 180 V/cm, RF coke suppression was either very small or not existent. This project came to an end before we could obtain a RF power supply in the 500 to 20,000 Hz range that could match the output of our other power supplies. However it is clear that somewhere between 60 Hz to 50 kHz RF coke suppression effect starts appearing.

Conclusion: At the start of this project, the mechanism of sulfur resistance in this proprietary Ni-based catalyst was a mystery. One assumption was that the sulfur resistance was due to “free” Ni (or NiO) supported on the proprietary surface that allowed adsorption of sulfur in the front part of the catalyst bed; thereby, allowing the back part of the catalyst bed to reform the fuel. This mechanism only applies to very low sulfur fuels.

From the data, it is now clear that the sulfur resistance of this Ni-based catalyst is a result of the same mechanism that Michael Krumpelt and co-workers at Argonne National Laboratory has ascribed to their sulfur resistant perovskite series of catalysts, and is also the same mechanism that imparts the sulfur resistance to the hexaaluminate series of catalysts being developed by David Berry and co-workers at NETL in Morgantown. Michael Krumpelt has advocated that sulfur resistance is obtained when the active reforming metal such as nickel “dissolves” into the structure to partially occupy the “B” site in the perovskite structure.

In a conventional reforming catalyst, Ni is supported on Ca (or Mg) doped alumina, and that these catalysts are readily poisoned by even 1 ppm S in the feed, and furthermore these catalysts can never be exposed to air at high temperatures, since NiO then dissolves into the structure to irreversibly form very stable NiAl_2O_4 . In other words conventional Ni-based reforming catalysts can never be regenerated by burning the coke off in air.

The Ni-based catalyst used in this project was developed to allow free Ni or NiO to remain on the surface even after air regeneration. Comparing Figure 14, which shows the sulfur breakthrough curve for the Ni-based catalyst versus time against the initial activity curves for the same catalyst shown in Figure 9, we see that the catalyst is still capable of reforming the 50 ppm diesel fuel even after 4 hours when the support appears to be completely saturated with sulfur. In other words, the hypothesis that “free” Ni on the support can be used to adsorb the sulfur; thereby, allowing subsequent hydrocarbon reforming to occur in the back part of the reformer bed is partially right and partially wrong. This mechanism is only active for the first 2 hours of operation when reforming a 50 ppm diesel fuel at a weight hourly space velocity of 1.5 (6700 GHSV). It is interesting to note that the data in Figures 9 and 14 are completely compatible, in that

when the Ni-based catalyst can no longer adsorb sulfur, the catalyst loses activity; lining out in about 4 hours at a lower activity.

We were initially hoping that CARCAT 104 could be used to serve a dual function of reforming the sulfur laden fuel as well as adsorbing the sulfur so that anode catalyst would not be poisoned by sulfur. Unfortunately, the sulfur capacity of CARCAT 104 is too small to be practical in most applications. For example, a 15 ppm S diesel fuel would start “slipping” sulfur is less than 7 hours at the same space velocity. Unless one designs an expensive and complex dual bed system, where one catalyst bed reforms the fuel while the second is regenerating, CARCAT 104 cannot be used as a practical dual sulfur absorber/reformer system.

This calls into question the current CARCAT 104 formulation, which is loaded with “free” Ni on the surface. Based on the four aging runs in Figure 10, it appears that the major role of “free” Ni on the surface is to increase the coking rate; thereby reducing the life of the catalyst. If this free surface Ni is not useful in absorbing sulfur since its sulfur loading capacity is too small to be practical in most applications, CARCAT 104 should be modified by calcining the catalyst at a higher temperature to drive Ni into the structure to reduce its coking rate. This is exactly what happened in the “repeat RF off run” in Figure 10 when the O to C ratio exceeded 1.0 for the first 172 hours.

In the normal reforming process, Ni slowly diffuses into the structure if coking rate is not too extreme. Looking closely at both RF aging runs in Figure 10 (red and yellow data), we see that CARCAT 104 actually loses activity in the first 20 hours, and then starts increasing in activity up to about 100 hours, when the catalyst finally lines out. Again, we interpret this data based on the slow incorporation of part of the Ni into the CARCAT 104 support. Application of RF coke suppression is useful only that it prevents the stripping of Ni from the catalyst. When CARCAT 104 reforms a “high” 50 ppm sulfur diesel fuel without RF coke suppression, the coking rate is so severe that Ni may not be able to dissolve into the support in time before it is lost to the coke, and swept off the catalyst when the catalyst is regenerated. With a 7 ppm S diesel fuel, the coking rate is substantially reduced, so that application of RF will have little impact.

Thus metal catalyzed coking appears to be the major route of deactivation of CARCAT 104, and probably all other Ni-based sulfur resistant catalysts. The higher the coking rate, the faster the catalyst deactivates. Furthermore, coke appears to be capable of removing or stripping not only the free Ni from a catalyst support, but also the “embedded” or structurally bound Ni that is critical for sulfur resistance. We come this to conclusion from a number of experiments. First, in the 366 hour aging run of CARCAT 104 without RF (black data in Figure 10), one side of the catalyst was completely stripped of Ni and that this stripping seemed to occur gradually over the last 100 hours of operation as the catalyst bed started failing/coking more on that one side. However this process of coke stripping the structurally bound Ni can also be very fast. We had an unfortunate situation, where the feed rate was accidentally set at too high so that the O to C ratio was at 0.55 instead of 1.1. In a matter of less than 2 hours, the catalyst was completely destroyed. Even after burning off the coke (which took ~ 1

hour), the regenerated catalyst had turned gray, and became quickly coked even when subsequently run under the proper conditions.

Consequently, controlling coking is critical to maintaining catalyst life. In this work, we have discovered a number of methods that can be used to reduce coking. (1) The easiest way is to calcine the catalyst in the manufacturing step so that Ni is already incorporated into the structure. This is easily monitored by looking for the “blue” color of Ni (III). (2) Change the O to C ratio to 1.05 to 1.1. At this ratio, recycle of SOFC anode gas as a means of introducing a tiny amount of steam appears to be unnecessary. (3) Introduce turbulence into the flame front. One way to vary the O to C ratio at the flame front would be to pulse the air steam that is pointed at the catalyst bed, or to install a moving fan or chopper. The major penalty of introducing turbulence into the flame front is that the concentration of C₂+ material in the product stream will increase. (4) Finally, we have demonstrated that application of a 50 kHz to 13.56 MHz electromagnetic field at a field strength greater than ~ 100 V/cm and more preferably greater than 500 V/cm can reduce coking anywhere from 40% to over 600% over the base case. However the application of RF coke suppression is of minimal use when the prior coke reduction technologies have been applied (see Figure 16).

Given the cost and difficulty of producing RF fields (\$50 to \$100 per APU), and dealing with electrical inputs to a hot catalyst bed, I can only recommend RF coke suppression for extreme applications such as the military may encounter. However for most civilian applications, it should be cheaper to simply throw away the low cost Ni based reformer catalyst if it is ever damaged during the run by a low O to C ratio for example.

Thus it appears that a low cost sulfur resistant Ni-based catalyst can be produced that can reform diesel fuel up to 50 ppm S to produce syngas for SOFC and other applications.

Table 1
Diesel Fuel Properties

	7 ppm S	50 ppm S
Aromatics	18.6 vol %	16.2 vol %
Paraffins	70.6 vol %	70.7 vol %
Naphthenes	10.8 vol %	13.1 vol %
Simulated Distillation		
Initial boiling point	257 F	237 F
10 wt %	367 F	371 F
50 wt %	487 F	549 F
90 wt %	633 F	668 F
99 wt %	736 F	746 F
Final boiling point	760 F	766 F

Table 2
Run/Catalyst Properties

O to C ratio = 1.0 H₂O to C ratio = 0.2 20 % simulated recycle gas
 Catalyst Furnace Temp = 750 C Upper Furnace or Zone = 500 C or 600 C
 Catalyst: 1.5 WHSV, hr-1 (based on diesel injected) or 6700 GHSV
 6.5 grams CARCAT 104 (8-14 mesh on top)
 1.0 grams CARCAT 104 (5-8 mesh on bottom)

Catalyst bed approximate dimensions: 5 cm long x 2 cm in diameter

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Figure 1: Schematic of the Autothermal Reformer

Figure 2: Fuel Injector

Figure 3: Autothermal Reactor

**Figure 4: Ideal Flame Front in the Autothermal Reactor
with 1.9 mm ID air line.**

Figure 5: Temperature Profile of BSU 977
 Reforming a 7 ppm & 50 ppm S diesel fuels at 750 C
 O/C ratio 1.0, H₂O/C = 0.2 20% simulated recycle
 Catalyst: CARCAT 104 1.5 WHSV hr⁻¹

Figure 6: Temperature Profile of BSU 979
Reforming a "0", 7 & 50 ppm S diesel fuels at 750 C
O/C ratio 1.0, H₂O/C = 0.2 20% simulated recycle
Catalyst: CARCAT 104 1.5 WHSV hr⁻¹

Figure 7: Autothermal Reforming of 7 and 110 ppm S diesel fuel

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.

Figure 8

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 diesel at 1.1 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. Average concentration of Fe on the catalyst is 360 ppm

Figure 9

Initial activity of CARCAT 104 over the first 5 days reforming a 50 ppm S diesel at 750 C, O/C = 1.0, H₂O/C = 0.2 1.5 WHSV

Figure 10

Autothermal reforming of 50 ppm S diesel fuel using CARCAT 104 under SECA conditions: 750 C, O/C = 1.0, H₂O/C = 0.2, 1.5 WHSV (6700 GHSV) with 20% recycle stream symmulated using nitrogen/steam. The catalyst was typically run for 8 - 10 hours before regeneration. The catalyst was regenerated by passing air up through the bed.

Figure 11

Comparative photos showing the different colored side of aged CARCAT 104 without RF coke suppression (black data points in Figure 10) in the quartz reactor after running 50 ppm S diesel for 366 hours. The “free” Ni on the surface has been stripped off the catalyst leaving only “bound” Ni on the “blue” side of the catalyst bed and no Ni on the “gray” side.

Figure 12

**Inner Quartz RF antenna liner from “Repeat RF off Run”
from Figure 10.**

Chipped quartz RF antenna liner
allowed “extra” air to be pulled
into the catalyst bed during the
first 172 hours, thus increasing
the O to C ratio to > 1.0 .

Figure 13

Comparison of CARCAT 104 at end of run showing that application of RF maintains the “green” color of Ni^{2+} supported on the CARCAT proprietary support.

Aged CARCAT 104 catalyst from “repeat RF off run” from Figure 10 after 475 hours on line with no RF coke suppression showing only blue color of Ni^{+3} incorporated into the support.

Aged CARCAT 104 under 50 kHz RF at 92 V/cm after 380 hours online. Clearly showing that application of RF has prevented stripping of Ni^{2+} from the catalyst surface.

Figure 14: Sulfur breakthrough curve versus time online reforming a 50 ppm S diesel fuel.

Figure 15: Effect of RF field strength on coke deposition rate at 13.56 MHz
The coke is measured by the amount of time it takes to burn the coke off the catalyst after reforming a 50 ppm S diesel fuel over CARCAT 104 for 2 hours.

WHSV 1.1 O to C ratio 1.10 Catalyst bed temperature 750 C no added steam.

Figure 16: Effect of Field Strength and Frequency on Coking Rate of CARCAT 104 reforming a 50 ppm S diesel fuel under high turbulence (low coking) conditions. Catalyst was run for 3 hours, then the time to burn off the coke was recorded as the coking rate.

Figure 17

NETL's (Morgantown WV) hexaaluminate sulfur resistant reforming catalyst; $\text{SrAl}_{11.6}\text{Ni}_{0.4}\text{O}_{18.8}$ illustrating the blue color of structurally bound Ni (III).

LIST OF ACRONYMS AND ABBREVIATIONS

APU	auxiliary power unit
BSU 977	bench scale unit 977 (Chevron test apparatus)
BSU 979	bench scale unit 979 (Chevron test apparatus)
°C	Centigrade
C1+	all higher molecular weight hydrocarbons starting from methane
C2+	all higher molecular weight hydrocarbons starting from two carbon species such as ethane or ethylene
Ca	calcium
CARCAT 104	proprietary nickel based catalyst used to reform diesel fuel
cm	centimeter
F	Fahrenheit
ID	inner diameter
GC	gas chromatograph
GHSV	gas hourly space velocity
kHz	kilo Hertz or kilo cycles per second
Mg	magnesium
MHz	mega Hertz or mega cycles per second
NETL	National Energy Technology Laboratory
Ni	nickel
NiAl ₂ O ₄	nickel aluminum oxide (spinel)
NiO	nickel oxide
Ni III	nickel in the plus three oxidation state
OD	outer diameter
ppm	part per million (weight basis)
RF	radio frequency
S	sulfur
SOFC	solid oxide fuel cell
WHSV	weight hourly space velocity
V	volt
V/cm	volts per centimeter