Hydrogen Detection and Ignition

Walter Weiss – Process Engineer

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Hydrogen Detection

NASA Experience Focus

Corrosion Expectations

Example Acid Absorbing Tower Corrosion Exposure – alloy tower and piping

- 1 mpy corrosion rate (0.025 mm/y)
- 8000 h/yr (91% on stream time – 4 weeks of total planned and unplanned outage)

H_2 concentration in vent gas is << 1 ppmv

Unexpected Hydrogen Generation

Off Design Conditions

- Half rate – H_2 concentration in vent gas is still << 1 ppmv
- Operate with the acid concentration 1 - 2 percent lower than design
  - Corrosion rate is upwards of 3 – 4 mpy (0.075 – 0.100 mm/y)
  - Even at half rate, H_2 concentration in vent gas is still less than 1 ppmv

Even More Unexpected Corrosion Rate

Unusual corrosion rate is 15 mpy (0.375 mm/y)

96% acid at 290 F (143 C)

- Hydrogen concentration in the stack gas at full rate is about 1 ppmv
- Hydrogen concentration in the stack gas at half rate is less than 2 ppmv

Pick your own worst-case scenario in terms of corrosion rates and hydrogen evolution rate. Then calculate this in terms of gas flow rates to obtain a stack gas concentration.

Stack gas hydrogen content even at low acid strength and half the design gas flow is in a concentration range of single digit ppm.

Hydrogen Gas Monitoring

What about analyzing the gas for hydrogen?

- NASA uses a lot of hydrogen (space shuttle flight used 230,000 lbs in the external fuel tank and 375,000 lbs for the loading process)
- They have a need for hydrogen area monitoring
- Assumed to be mostly or completely for ambient air monitors
  - Maybe not good for sulfuric acid process temperatures, process contaminants such as acid mist, and process gases such as SO_2 and NO_x
  - May need to employ a gas conditioning system

Hydrogen Gas Monitoring – Cadillac

Gas chromatography / mass spectrometry (GC – MS) gives widest hydrogen concentration range and lowest detection limits.

- Detection as low as 1 ppmv.
- High investment. Especially for multiple locations in the plant.
- High maintenance – for the instrument itself and gas sampling system.

NASA – Hydrogen Monitoring

Four other monitor types considered by NASA:

Normally for ambient air at ambient temperatures or in cryogenic service

1) Catalytic Combustion Gas Sensor – needs 16% or more oxygen content in the gas to support combustion;

   100 ppmv minimum

2) Electrochemical Sensor – liquid or solid electrolytes; solid electrolytes need hydration or they dry out; ambient temperature

3) Semiconducting Oxide Sensors – 200 C minimum temperature; not selective to H_2

4) Thermal Conductivity Detectors – 100 C minimum temperature; not selective to H_2

Acid Plant Hydrogen Monitoring

People have asked about monitoring various points in the process. Is it practical?

Instrument needs to handle conditions of an acid plant. Acid droplets and sulfates, temperatures around 180 F (82 C), low oxygen conditions, and the presence of other gases – CO may report as a combustible for instance.

May choose multiple locations – atop drying tower, IPA absorbing tower and Final absorbing tower for instance and maybe the center core top (cupula) of a blooper plate converter.

Vacuum pump is needed to extract a sample as the blower may not always be in operation. And the greatest risk has been when the blower is not in operation.

Sample handling system will likely be needed to remove particulate and cool the gas.

For hydrogen monitoring – explosion proof equipment including the analyzer building may be specified by Engineering.

Monitoring Conclusions

No consensus to install. You must decide on your own merits.

- Where and how many instruments to place
  - Top of the two or three strong acid towers is a start
- What type of instruments to use
  - Normally will read zero even with low range instruments
  - Discipline will be needed to maintain these instruments even though they appear to do nothing
  - Real focus on instrument readings will be when the plant is down
    - not operator intuitive as this is a time alarms are normally ignored
    - following a weak acid incident, there will be plenty of other areas of focus
      - Again, the alarms may be ignored
      - Automated response?

Hydrogen Properties

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Hydrogen Properties

Buoyancy

- Very light gas and tends to rise
- At standard conditions,
  - About 1/8th the density of natural gas
  - About 1/20th the density of nitrogen
  - About 1/25th the density of propane

Diffusivity

- Highly diffusive and tends to mix if given the opportunity
  - Three times the diffusivity rate of nitrogen in air

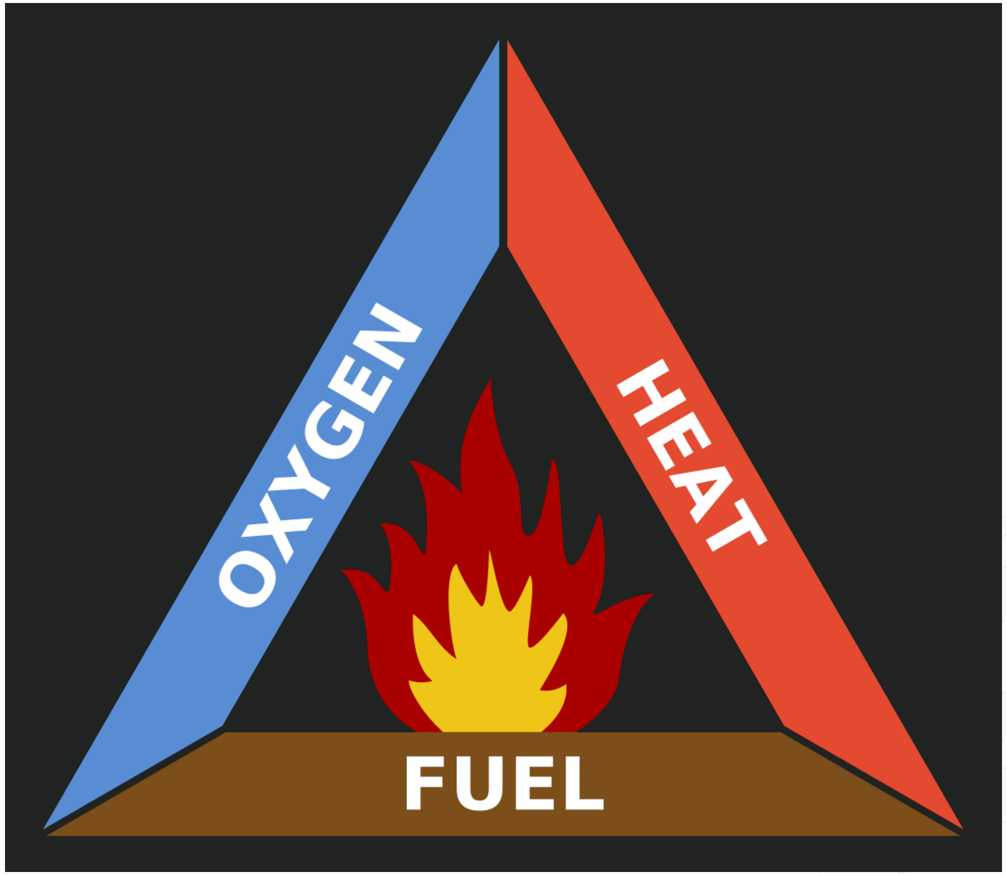
Fire Triangle – General

Needed for Combustion:

- Oxygen (as in air or process gas)
- Heat (ignition source)
- Fuel (hydrogen)

Acid Plant Considerations

- Oxygen consumed in the process
    - Normally 4-6% in the stack
    - Does this help reduce combustion risk?
- Can the ignition source (heat) be minimized?
- Can one purge hydrogen gas as it accumulates?



Hydrogen Combustion

$$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g) + Q$$

Beautiful in its simplicity. Powerful in its execution.

Q is heat of combustion (HHV) = 141.8 MJ/kg (61,000 Btu/lb)

Pressure release from ignition of a 4% hydrogen mix in air (at constant volume) can reach 20 psig and 55 psig at 20% hydrogen mix in air.

Minimum ignition energy for gaseous hydrogen in air = 0.02 mJ (1.9×10^{-08} Btu)

How Much Energy Is 0.02 mJ (1.9×10^{-08} Btu)

1 Btu heats 1 pound of water 1 degree F

- 1 average drop of water is about 0.05 grams – about 0.00011 pounds
- The energy needed to ignite this hydrogen gas mix is the same energy needed to heat one drop of water about 0.002 degrees F (0.001 degrees C)
- A gnat’s sneeze termed by others

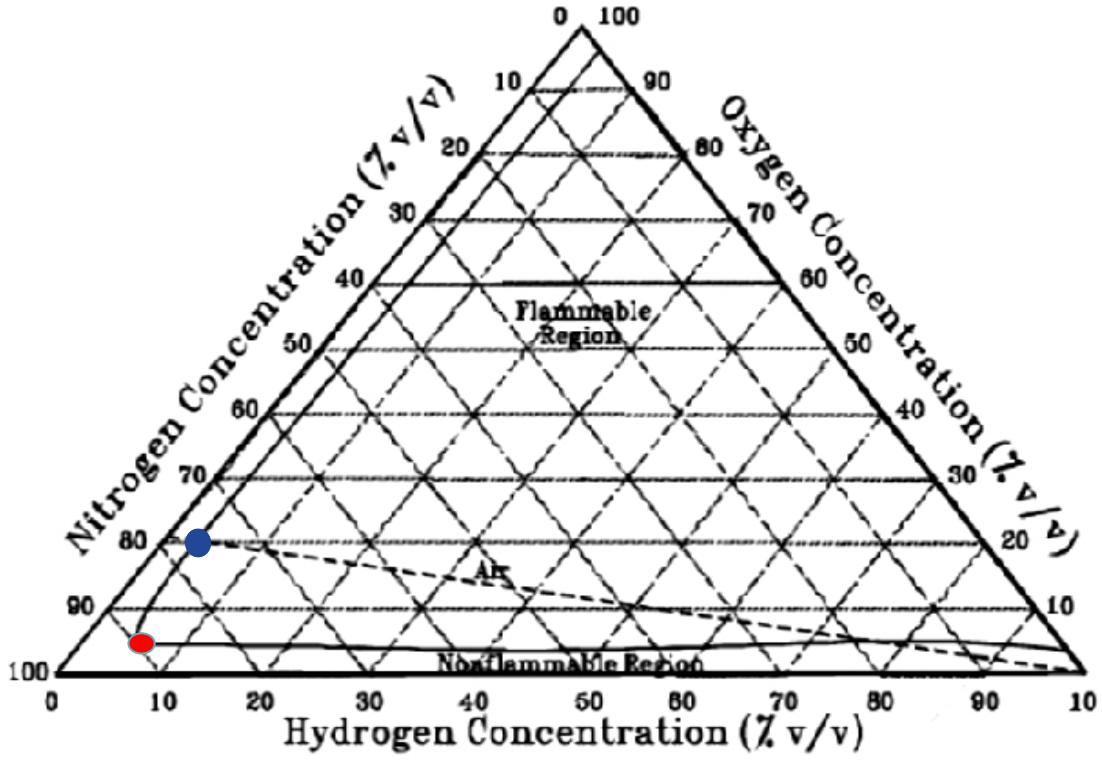
Ignition need not be by weld torch, or spark, or hot surfaces. It may be caused by something as small as static build up on droplets.

Hydrogen Ignition

Hydrogen Fire Triangle

Flammable region of hydrogen is noted here. Ambient temperature!

- Air is shown as the dashed line.
- The blue point shows the LFL at about 4% hydrogen in air at ambient temperature
- Remove oxygen by process chemistry to stack gas levels - shown as the red point
- Same: LFL is about 4 - 6% hydrogen in acid plant vent gas
- LFL decreases with increasing temperature
  - At 100 C, the LFL decreases by 0.5% H_2 concentration



H_2-O_2-N_2 flammable limits [15]

Oxygen Role In Hydrogen Flammability

Fire Triangle is showing Oxygen, Hydrogen and Nitrogen – the latter as an inert.

- In the acid plant, the nitrogen side of the triangle might include SO_2, SO_3, and NO_x. But these are NOT inerts as they contain removable oxygen and can assist in the ignition of hydrogen and can change the energy release from the reaction.
- There is not any meaningful change in hydrogen LFL for 21% oxygen and 5% oxygen. Concerns with purging to avoid adding extra oxygen and increasing explosion risk are not warranted.
- Air purging reduces the hydrogen content and also removes other oxidizers as noted above.
- Air purging prevents heat from backing up into the top of the tower.

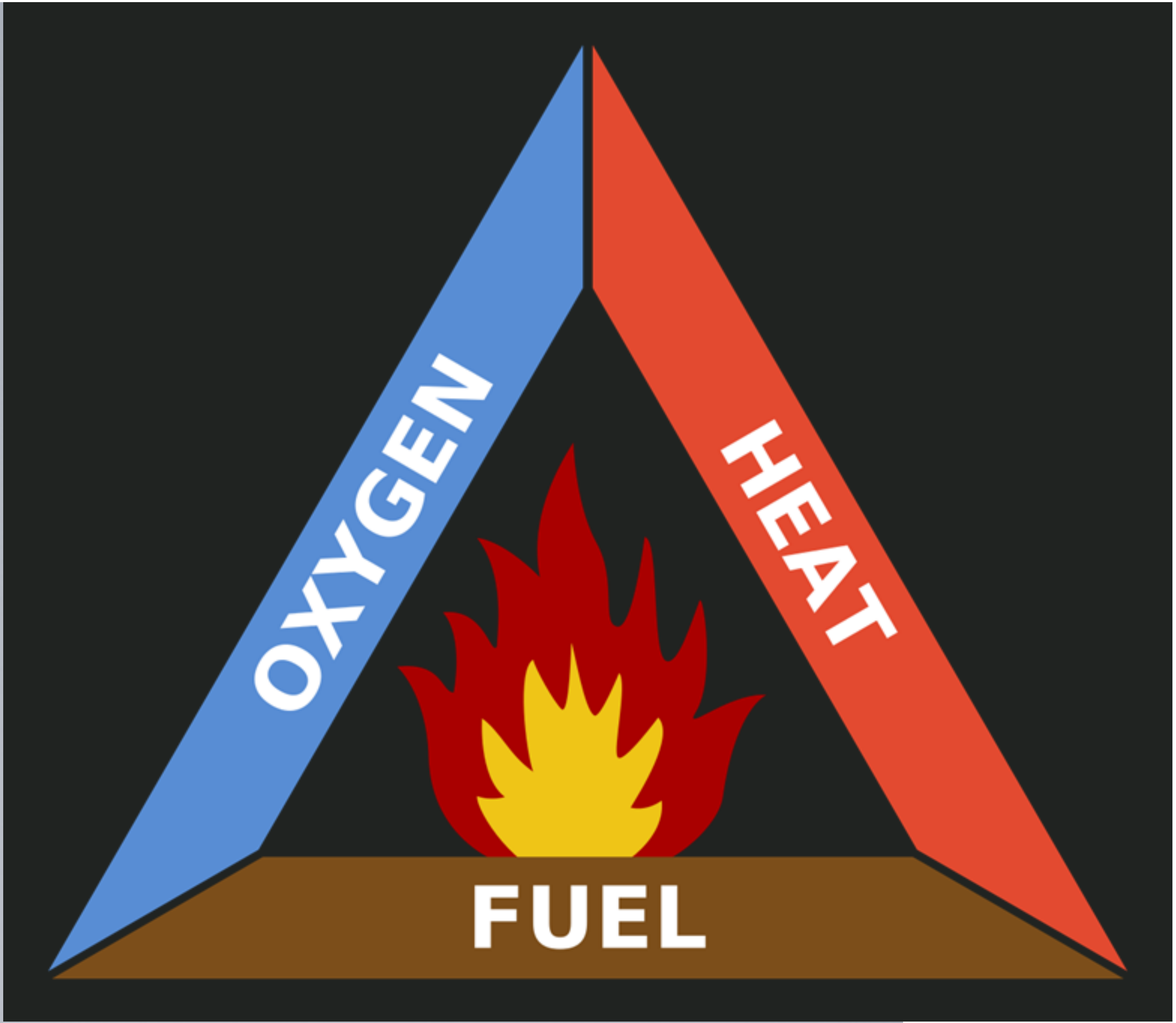
Nitrogen Role In Hydrogen Flammability

Inerting has been discussed. Use of nitrogen as an inert gas is possible and carbon dioxide is also an inert gas.

Inert gas addition to a volume displaces the hydrogen and other oxygen bearing gases from that given volume as well as oxygen. In other words, it can remove both of the reactants.

I have not ever seen this done. Only discussed. Rate of inerting I think is important.

- Hydrogen is buoyant and collects in the high spots.
- Inert gas injection is needed where the high spots are. There will be multiple locations. Depending on the source of the weak acid incident it may be a selective high spot.
- Large volume in an acid plant. Even a small acid plant. Inerting the entire acid plant is not practical nor timely.
- May be possible to inert selective sections of the plant. May be possible to automate the inerting process in the context of a hydrogen response protocol.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Reducing Risk

- Ignition source cannot be minimized enough by practical means
- Maintaining low oxygen content at normal plant levels is not helpful
- Inerting may offer localized reduction in both hydrogen and oxygen concentrations
- Maintaining blower operation even at reduced flow will keep hydrogen diffused in the bulk gas and purged to the stack
- Maintaining blower operation even at reduced flow will prevent increasing temperature from reducing LFL.
- High point vent valves if properly located, with or without blower purge, will allow hydrogen from building up to LFL levels. These should be automated.

Thank you for your kind attention.

Questions???

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