HYDROGEN AND AMMONIA: ZERO-CARBON FUELS FOR STEAM CRACKERS

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AGENDA

Introduction

Production and transport of zero-carbon fuel

Fuel characteristics

Performance impacts:

- Burners and radiant section
- Convection section

Other design considerations

Conclusions

The majority of the emissions from steam crackers are due to use of hydrocarbon fuel obtained from the process as methane-rich offgas

One of the methods to eliminate the CO_2 emissions from steam cracking heater is to use fuel source that does not contain any hydrocarbons

Two fuel sources have drawn significant attention because of the simple fact that they don't produce CO_2:

<u>Hydrogen</u>

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

<u>Ammonia</u>

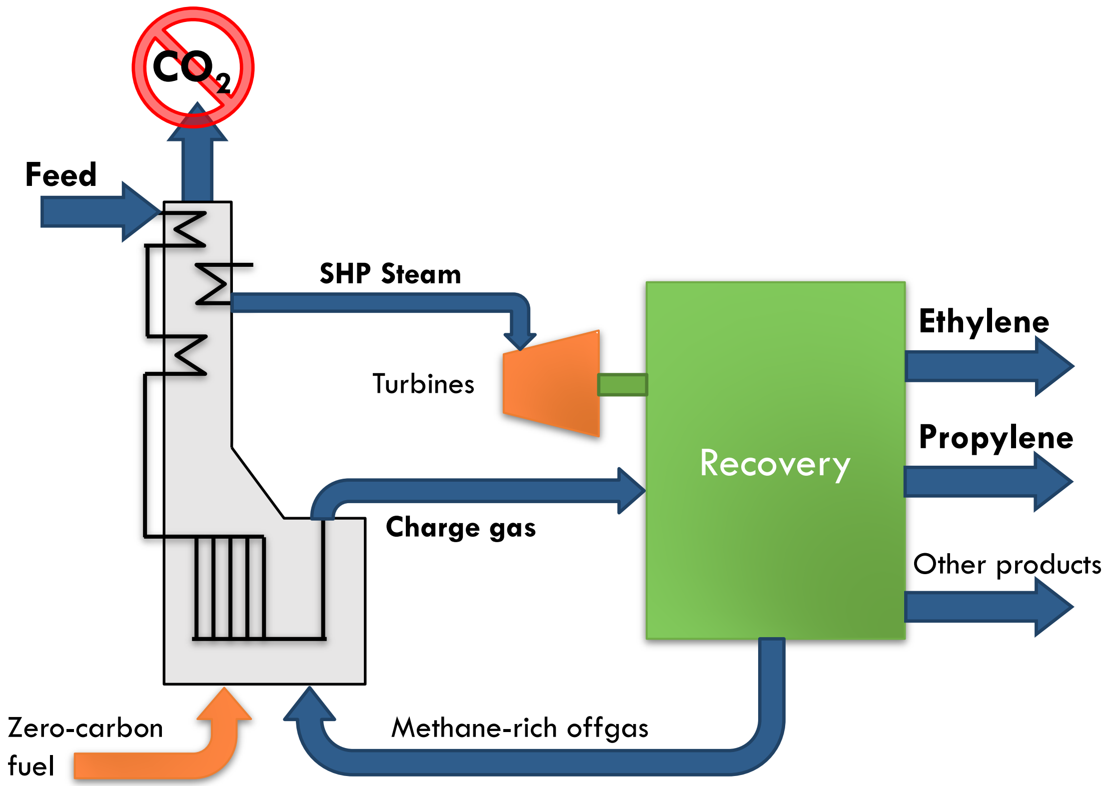
$$NH_3 + \frac{3}{4}O_2 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O$$

Advantage over other CO_2 reduction methods is that there are no major equipment modifications or electrical infrastructure needed

- Maintain SHP steam production to drive compressor turbines

Designers and operators must consider performance impacts:

- Burners and radiant section
- Convection section



PRODUCTION AND TRANSPORT OF ZERO-CARBON FUEL

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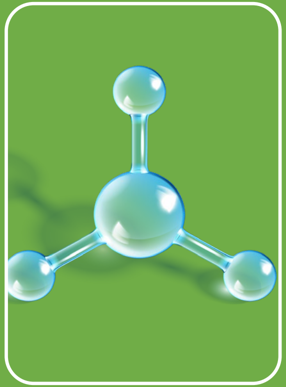
Hydrogen

- Ethane crackers already produce hydrogen-rich fuel gas (70-85 mol% H_2)
- Impact is well understood
- Extremely light gas, challenging to store and transport long distances
- Produced close to consumer, or via pipeline

Ammonia



- *New fuel for steam cracking*
- Haber-Bosch process:
  $3H_2 + N_2 \rightarrow 2NH_3$ (with Fe catalyst @ high T&P)
- One of the largest volume chemicals produced globally
  - ✓ Established infrastructure and experience
- Easier to ship and store than hydrogen
  (9.2 bar @ ambient temp)

H_2 & NH_3 Production

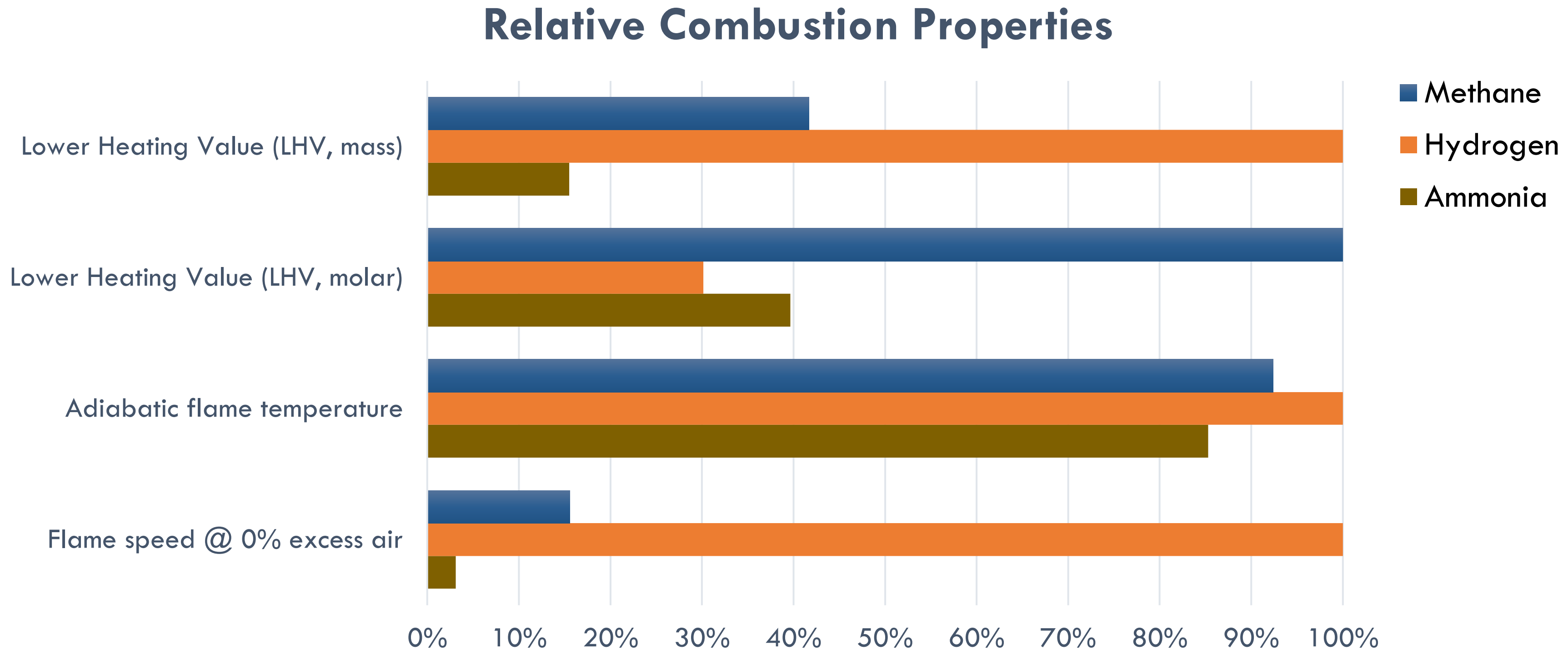
- CO_2 footprint must be considered:
  - **Gray** – from reforming of natural gas
  - **Blue** – from reforming of fossil fuels, *with CO_2 capture*
  - **Green** – from renewable electricity, via electrolysis

  < 1% today
- Many projects in development could increase green and blue hydrogen up to ~20% of total demand by 2030

NH_3 has a higher potential as import fuel where hydrogen pipelines don't exist

FUEL CHARACTERISTICS

➢Hydrogen and ammonia have vastly different fuel properties from methane that will impact cracking heater performance



➢These differences in combustion properties will impact:

- **Burner design** and radiant coil **heat flux**
- **NO_x formation**
- **Heat recovery**

This which calls for a careful review of the cracking heater design

Introduction

- Typical crackers are using one of the following combustion system set-ups:
  - All radiant wall burners fired units
  - All floor fired units
  - Floor burners with a limited number of rows of radiant wall burners units
- Floor burners are in general non-premixed Low NO_x or Ultra Low NO_x burners.
- Radiant wall burners are often premixed burners

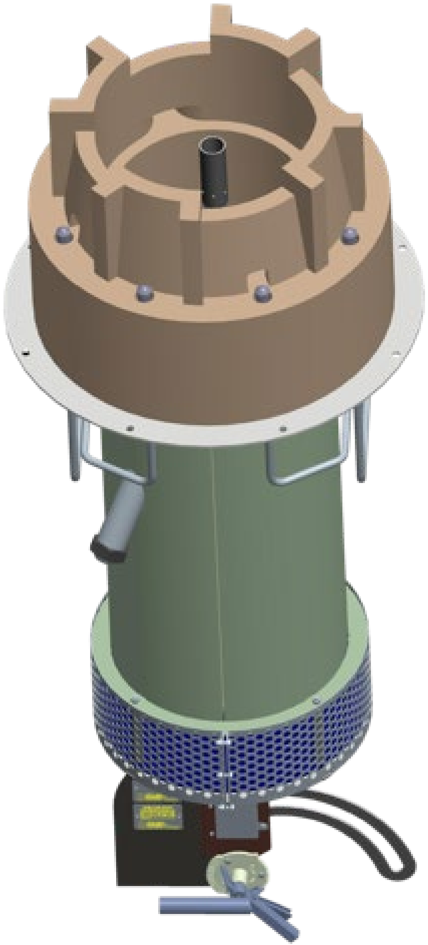
→Pure hydrogen or ammonia fuel operation will significantly vary by burner technology: Floor & Radiant wall

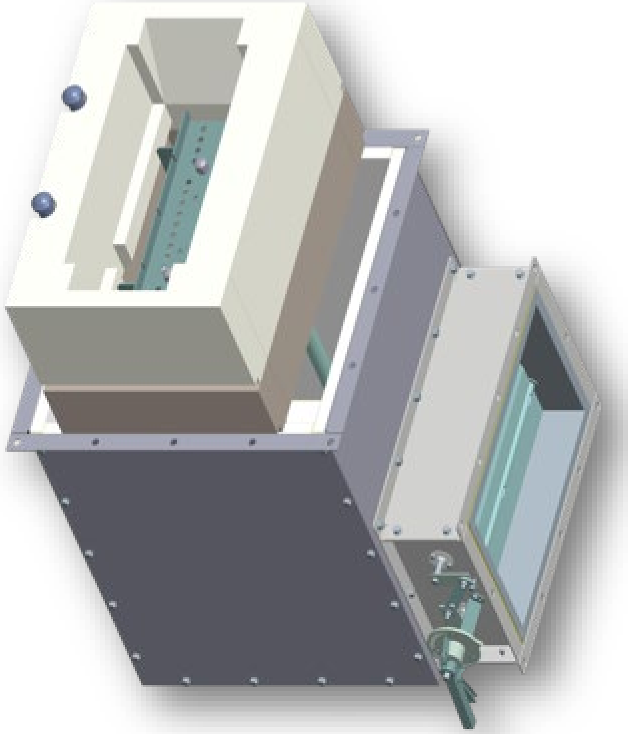
PLSFFR Burners Floor fired

Impact of hydrogen and ammonia on non-premixed floor burners (combustion, NO_x and heat flux)

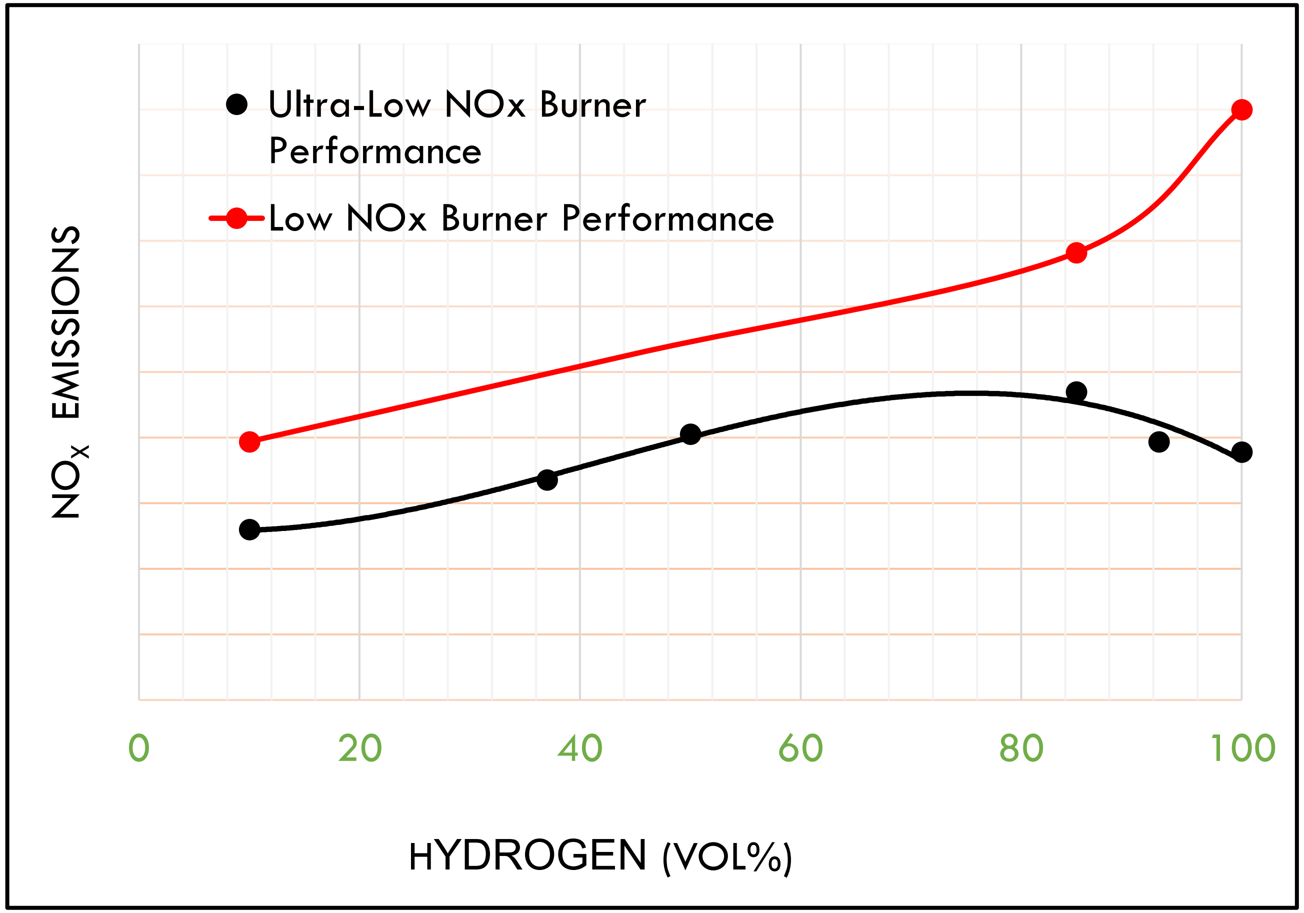
Impact of hydrogen fuel

- Hydrogen firing in ethylene crackers has been done for years
  - Hydrogen is a byproduct of the steam cracking process
- For gas crackers it is common to see H_2 concentration around 85 vol.% in the fuel
- Most floor non-premixed burners are able to fire 100% H_2 with some modifications
  - Fuel pressure might increase to obtain same heat liberation
  - Lifetime of materials may be impacted (Refractory, flame stabilizer,…)
  - Noise will increase

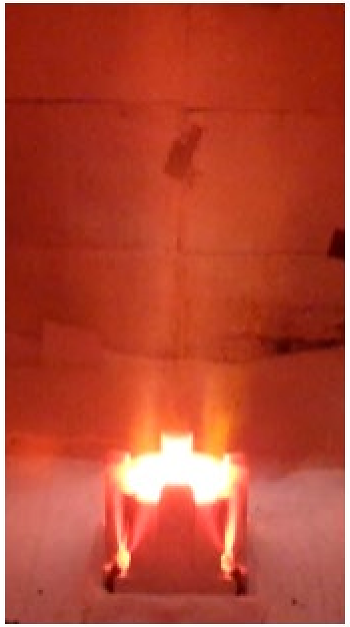




Impact of hydrogen fuel: NO_x emissions



100% NG

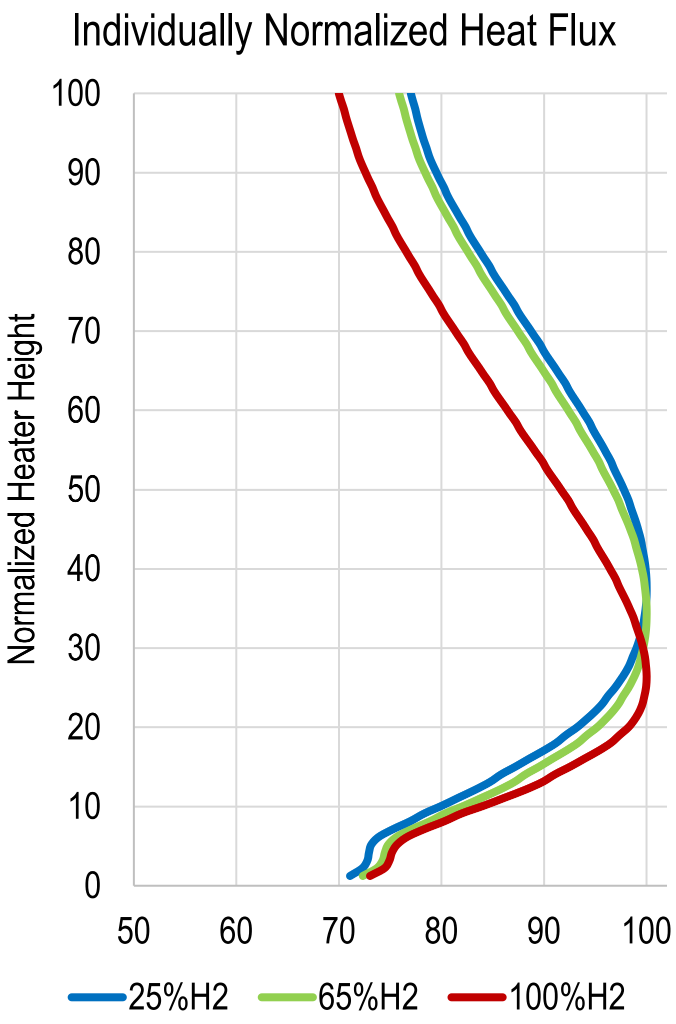


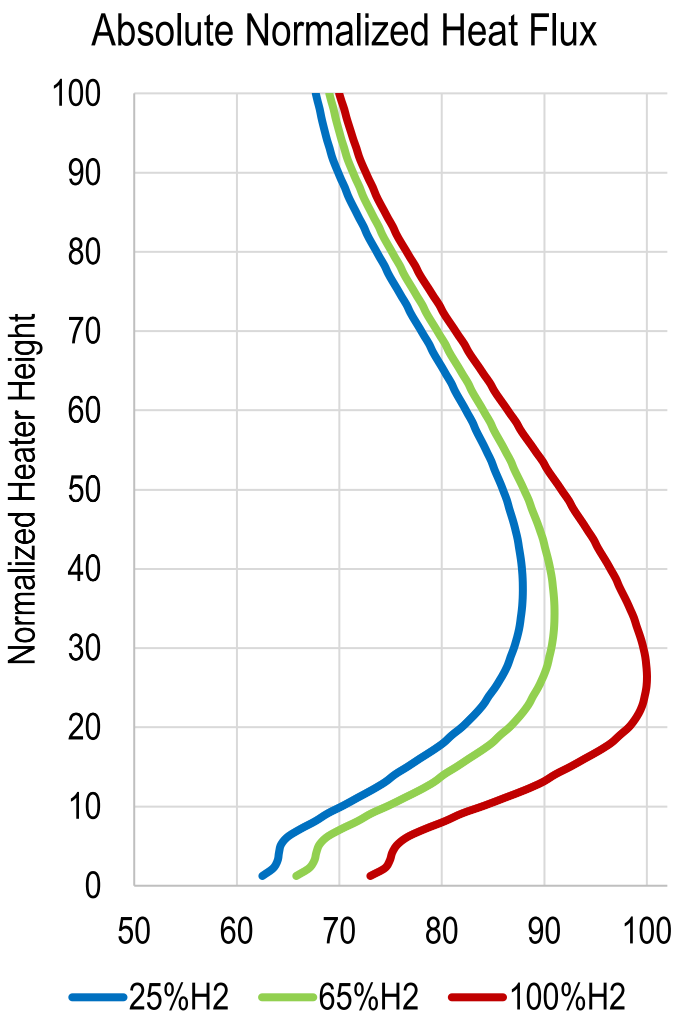
100% H_2

→ *Thermal NO_x emissions will increase while prompt NO_x will reduce*

Impact of hydrogen fuel: Heat flux impact

- Flame length decreases with increasing H_2 content
- Peak heat flux elevation shifts downwards with increasing H_2 content
- Peak heat flux increases with increasing H_2 content
- Overall absorbed heat of radiant coils increases with increasing H_2 content





Impact of ammonia fuel

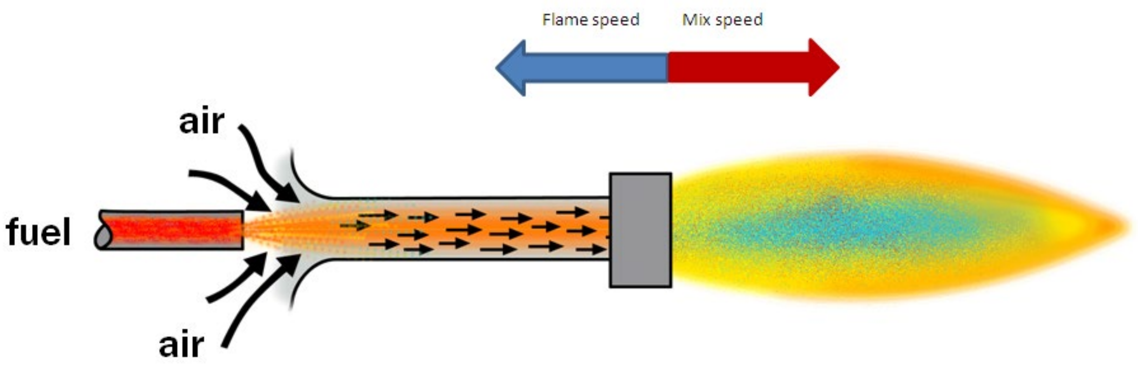
- Even small amounts of ammonia will lead to NO_x emissions in excess of 1000 ppm NO_x. A combination of optimized burner technology plus SCR system is likely required to bring NO_x emissions to acceptable levels.
- During lower temperature operation (start-up, hot steam stand buy and decoking) significant N_2O production as well as ammonia slip need to be considered
- Due to the low flame speed of ammonia, flame stability is a major concern:
  - Most current burner models will not tolerate high percentages of ammonia. However, designs that will tolerate up to 100% ammonia firing are available.
  - As H_2 is available as a byproduct of the cracking process, NH_3/H_2 blends may offer a solution to resolve stability concerns.
- Flame dimensions and consequently heat flux will be changing.
- Fuel gas pressure will increase

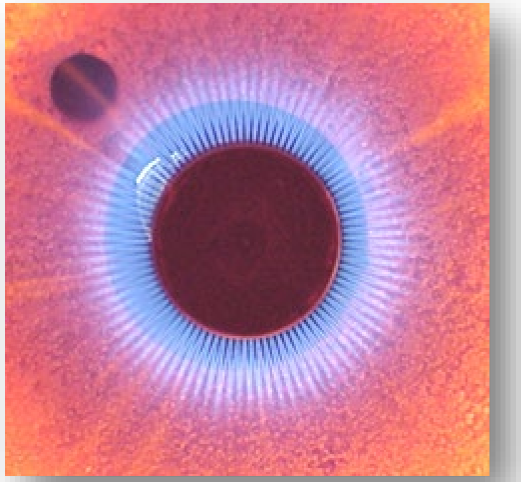
Impact of hydrogen and ammonia on premixed burners (combustion, NO_x)

ZERO-CARBON FUEL IMPACT ON RADIANT WALL - PREMIXED BURNERS

Impact of hydrogen fuel

- The air flow in premixed burners relies on the momentum of the fuel jet and its ‘pumping’ ability



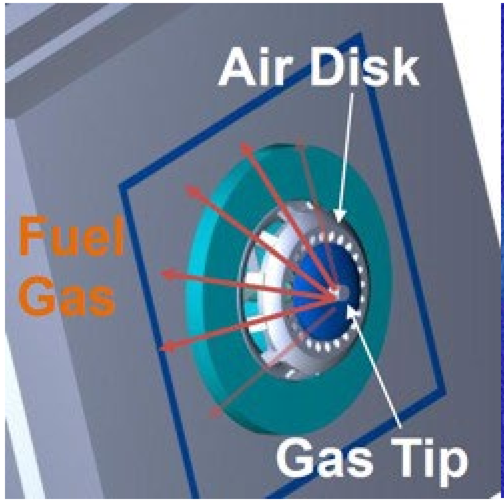


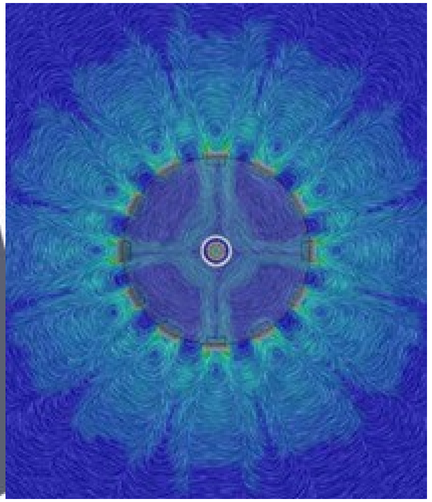
- Standard premixed burners (designed to fire natural gas) will not tolerate 100% H_2 operation due to the high flame speed. The flame will flash back into the burner interior often causing flameout and burner damage
- For low NO_x burners using staged fuel, flashback risk typically becomes a significant concern with H_2 levels above 70 vol%

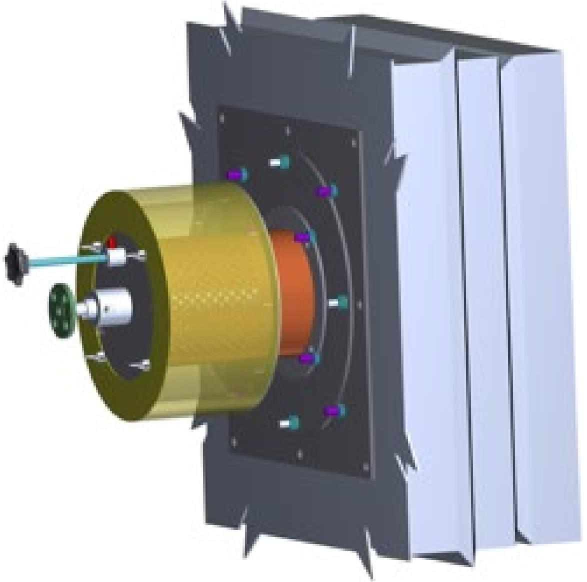
→ **For 80% to 100% H_2 operation, a different technology is required**

Impact of hydrogen fuel: Walfire^{TM} - Non-premixed flame radiant wall burner

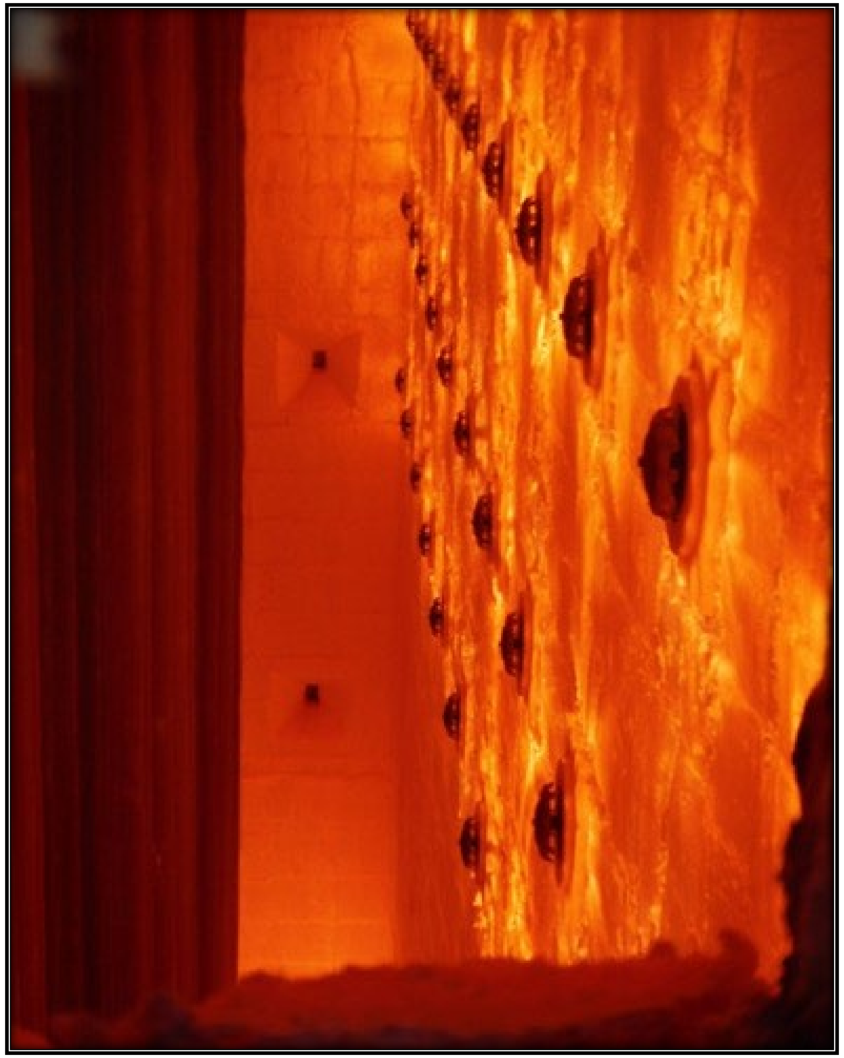
- Pure diffusion burner concept and therefore 100% hydrogen possible without risk of flashback
- Low NO_x due to flue gas entrainment into the flame
- Turndown is greater than a premixed burner
- Low maintenance
- Low noise emissions on high H_2 fuels: 72 dB(A) compared to 92 dB(A) for premixed technology





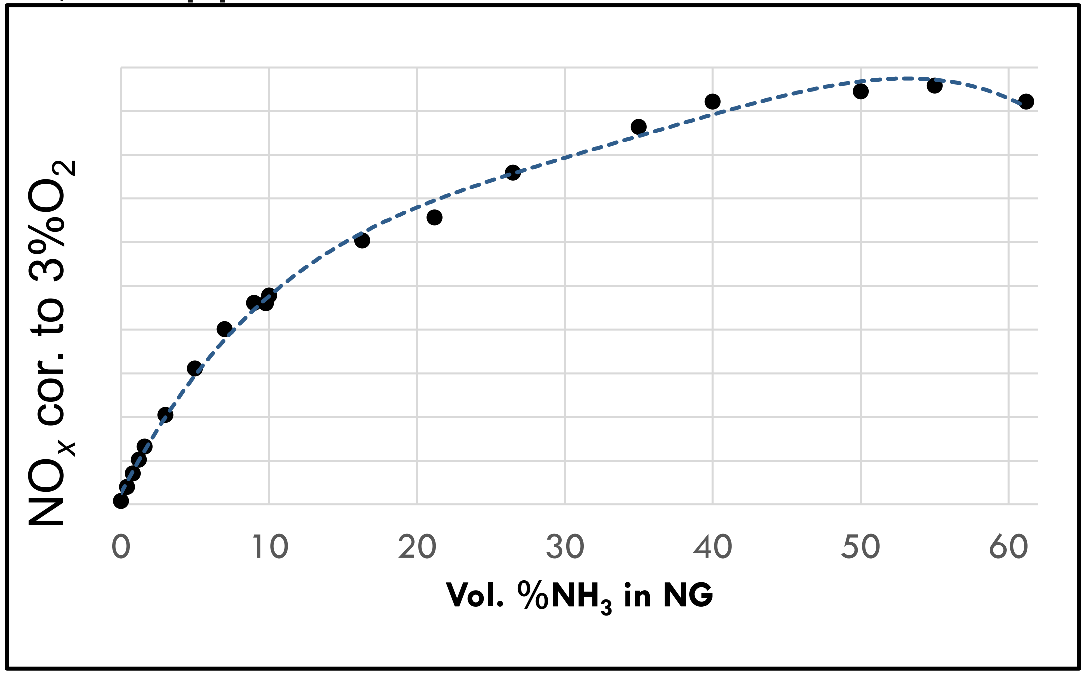


Impact of hydrogen fuel: Walfire™ - Field performance



Impact of ammonia fuel

- Tolerance of ammonia in traditional premixed burners will strongly depend on the design (exit velocity of the mix, air tip design slots,…)
- With the right burner design, it is possible to stabilize mixtures of 60% NH_3/NG or NH_3/H_2. NO_x emission is about 20,000 ppmvd!

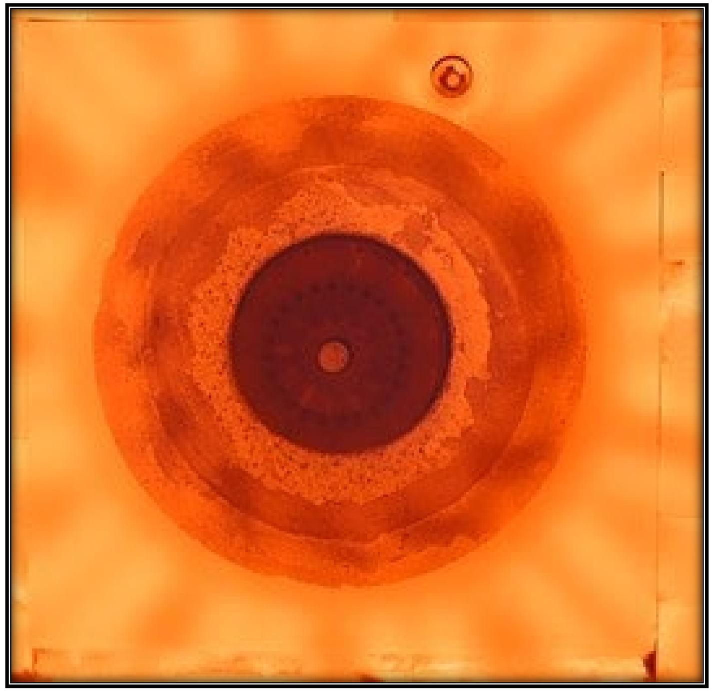


NO_x emissions as function of ammonia percentage in fuel gas for a premixed burner

50% NG+ 50% NH3

Walfire™ - Alternative for ammonia blend operation

- Considering the high NO_x emissions for ammonia/ hydrogen and ammonia/natural gas mixtures, NO_x emission reduction was investigated on existing premixed burners and the **Walfire™**.
- The **Walfire™** non-premixed burner generates much lower base NO_x emissions than premixed venturi type burners.
- A reduction of up to 90% in NO_x emissions has been demonstrated on the **Walfire™** burner compared to premixed burners, This NO_x reduction has been shown for NH_3/H_2 and NH_3/NG.
- In addition, it offers flexibility to increase H_2 content up to 100%



50% NH_3 / 50% NG

- Zero-carbon fuels have different heating value and combustion air requirements
  ➔ Different volume and available duty of flue gas

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

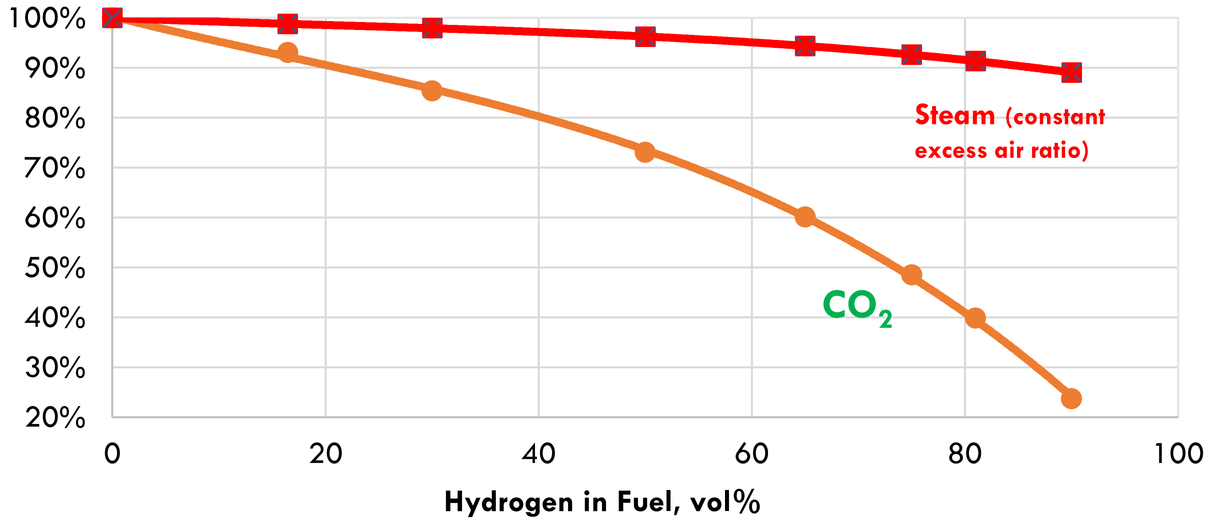
$$NH_3 + \frac{3}{4}O_2 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O$$

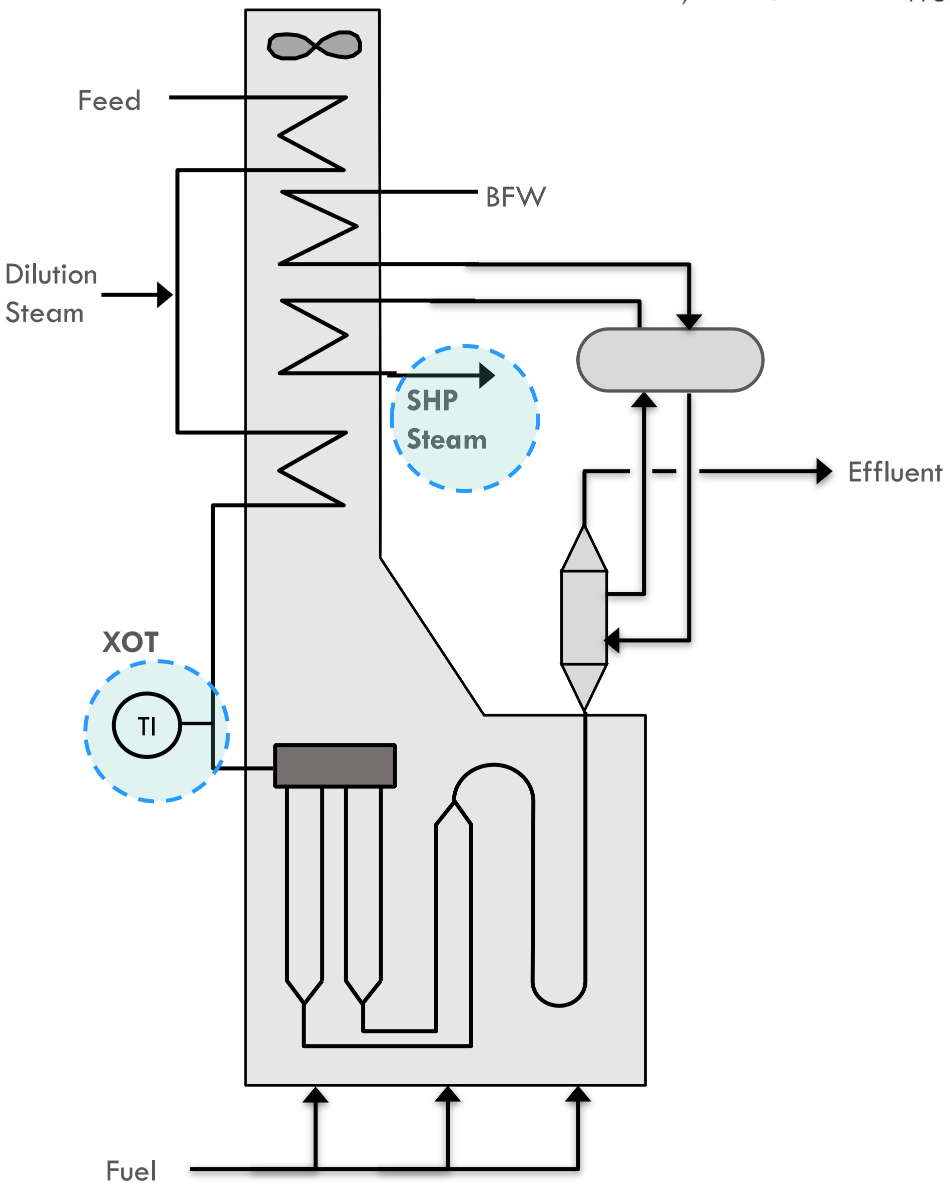
	100% CH_4	100% H_2	100% NH_3
Molar heating value, kcal/Nm^3	8,556	2,581	3,394
Moles of combustion products per mole of fuel	3	1	2
Moles of O_2 per mole of fuel	2	0.5	0.75
Flue gas per fired duty, kg/MMkcal **(normalized)**	1660 **(1.0)**	1342 **(0.81)**	1722 **(1.04)**
Flue gas composition, mol%			
O_2	1.7%	1.6%	1.4%
N_2	72.1%	66.3%	69.6%
CO_2	8.7%	0%	0%
H_2O	17.4%	**32.1%**	**29.0%**

- Increasing water content of flue gas affects heat capacity
- Net result:
  - **Decrease** in convection section duty by adding hydrogen
  - **Increase** in convection section duty by adding ammonia

CONVECTION SECTION PERFORMANCE

- Designed for maximum heat recovery:
  - Feed preheat, BFW preheat, SHP steam superheat, DS superheat
- Changing flue gas will impact various convection banks, most importantly:
  - ➢ **Crossover temperature** (XOT) – selected for given feedstock to maximize heat absorption without initiating cracking reactions
    - Lower XOT means higher radiant heat flux, decreased run length
  - ➢ **SHP steam production** – critical to drive recovery section compressors





CASE STUDY 1: ETHANE CRACKING WITH H_2 FUEL (200 KTA SRT-III, 0.3 S/O, 2.1 BARA COP)

	Base normal plant fuel	**100% H_2,** normal excess air	**100% H_2,** increased excess air	**100% H_2, modified convection surface**
	Base Heater Design			**Modified Heater**
HC feed rate, kg/hr	46,902	46,902	46,902	46,902
Fuel composition, mol%				
H_2	**82.7**	**100**	**100**	**100**
CH_4	16.8	0	0	0
Other	0.5	0	0	0
% Excess air	**10**	**10**	**17**	**10**
Fired duty, MMkcal/hr	86.8	83.5	86.8	82.2
Fuel flow rate, kg/hr	4,847	2,909	3,022	2,868
Imported H_2, kg/hr	0	1,111	1,224	1,071
Overall thermal efficiency, %	93.9	94.3	93.9	94.3
Crossover temperature, °C	**Base**	**-12**	**-1**	**-3**
Run length	Base	< Base	~Base	~Base
SHP steam production, % of base	**100**	**94**	**99.6**	**91**
Flue gas rate, kg/hr	131,756	115,384	127,250	113,711
CO_2 emission, % of base	100	0	0	0

- Without modifications and keeping 10% excess air, XOT (run length) and SHP steam production drop
- Base performance can be maintained by increasing 10→17% excess air
- With modifications and keeping 10% excess air, process performance can be maintained with 9% drop in steam

Approx. 5.4 t/h H_2 import required for 1000 KTA plant to achieve zero CO_2 emissions

CASE STUDY 2: ETHANE CRACKING WITH NH_3 FUEL (200 KTA SRT-III, 0.3 S/O, 2.1 BARA COP)

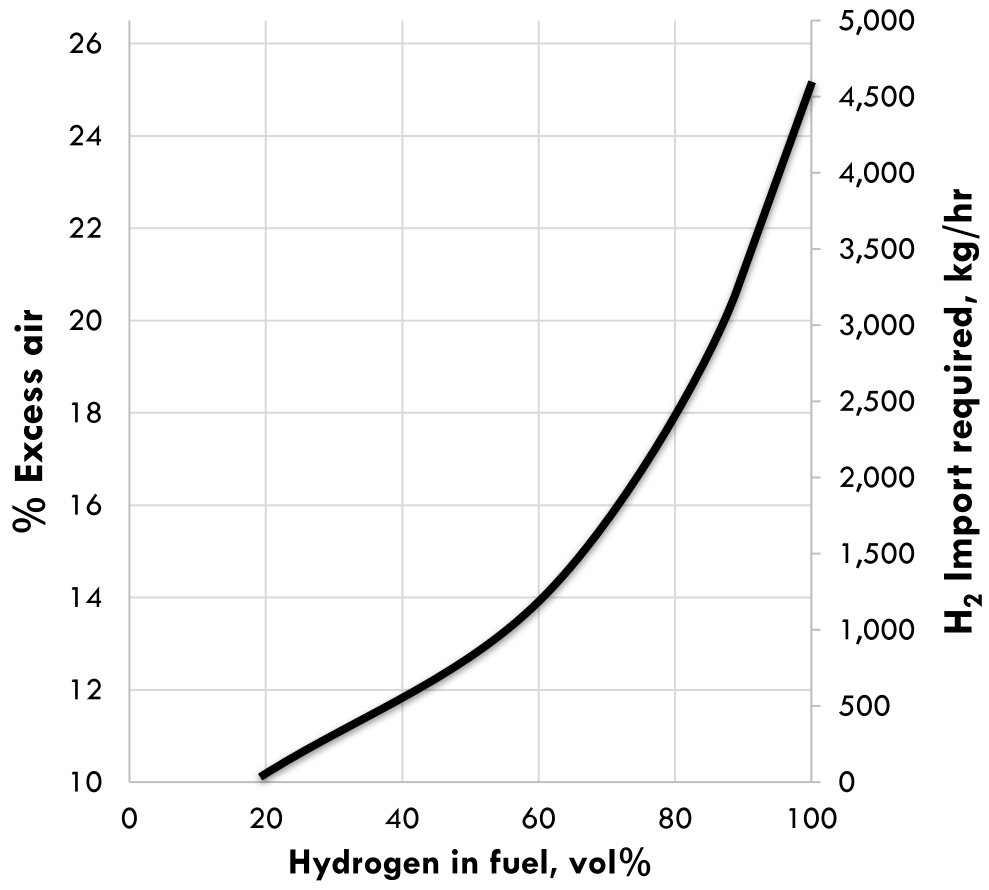
	Base normal plant fuel	Partial NH_3 firing
	Base Heater Design	
HC feed rate, kg/hr	46,902	46,902
Fuel composition, mol%		
H_2	82.7	59.5
CH_4	16.8	0
NH_3	**0**	**40**
Other	0.5	0.5
% Excess air	10	10
Fired duty, MMkcal/hr	86.8	91.2
Fuel flow rate, kg/hr	4,847	11,266
Imported NH_3, kg/hr	0	9,420
Overall thermal efficiency, %	93.9	93.3
Crossover temperature, °C	**Base**	**+13**
Run length	Base	> Base
SHP steam production, % of base	**100**	**103**
Flue gas rate, kg/hr	131,756	**142,546**
CO_2 emission, % of base	100	~0

- ~40% NH_3 / 60% H_2 to achieve fuel balance
- Almost identical performance, except slight increase in XOT and steam
- ID fan to be evaluated for higher flue gas rate

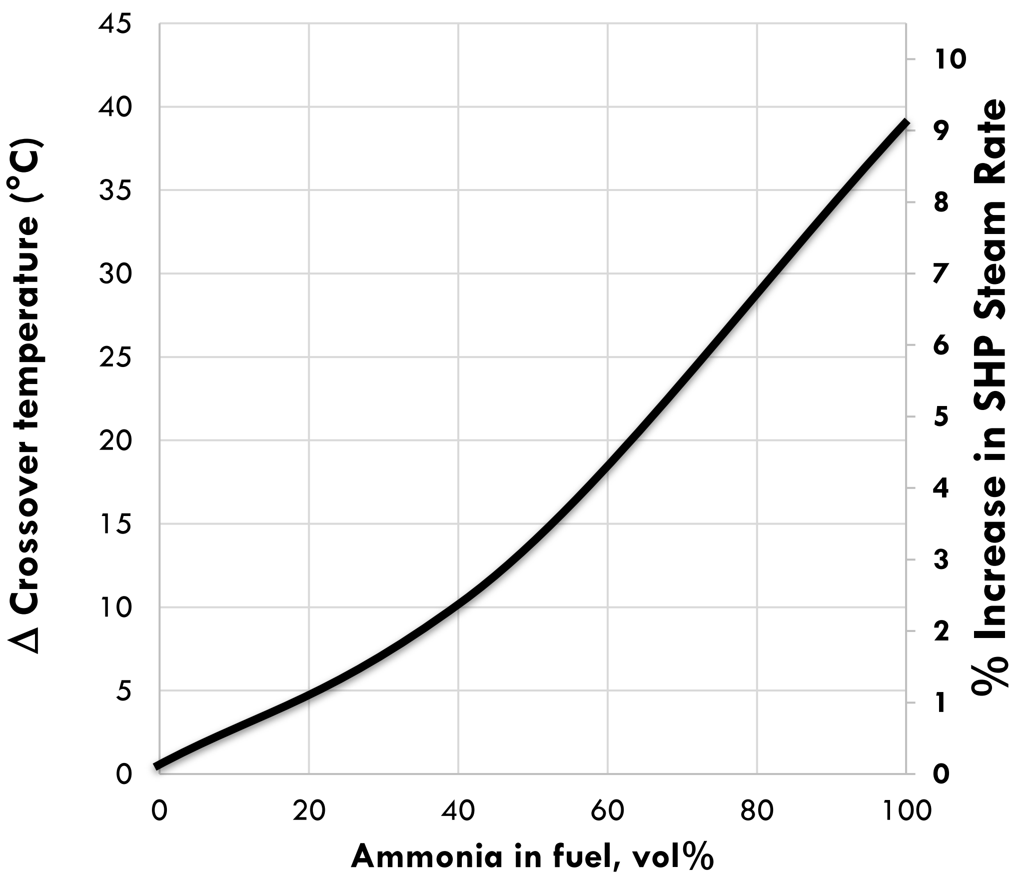
Approx. 47 t/h NH_3 import required for 1000 KTA plant to achieve zero CO_2 emissions

NAPHTHA CRACKING WITH ZERO-CARBON FUEL (200 KTA SRT-VII, 0.5 S/O, P/E = 0.5)

Increasing **hydrogen**
- with same XOT & SHP steam production



Increasing **ammonia**
- with fixed 10% excess air



Complementary Technologies

Oxidative Coupling of Methane (OCM)

- If plant methane offgas is replaced with H_2 or NH_3, then another outlet is required for methane
- OCM can produce valuable ethylene + propylene

Combustion Air Preheating

- Can be applied to minimize H_2 or NH_3 import
- Up to ~30% reduction in firing and associated drop in SHP steam production

Conclusions

Zero-carbon fuels provide a “drop in” opportunity to reduce CO_2 emissions without major equipment changes or electrical infrastructure

While pure hydrogen firing has not been commercialized in steam crackers, broad knowledge exists for hydrogen-rich (85 vol%) fuel gas

For hydrogen firing, most floor burners can be adapted through modifications unless specific constraints like NO_x emissions will dictate a full replacement. Proven technologies are available.

Premixed type wall burners will not cope with pure hydrogen firing, but proven alternative designs such as the Walfire™ are available.

Ammonia combustion is still in its infancy. In particular, flame stability, high NO_x emissions and NH_3 slip need to be addressed. Operation on fuel blends is possible today.

Impact on convection section performance can be mitigated by increasing excess air or modifying the heating surface to achieve desired performance

Thank You