The Potential of By-Product Ammonia from Coking as a Low-Carbon Fuel in Power Generation

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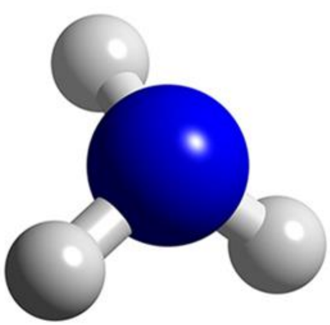

Content

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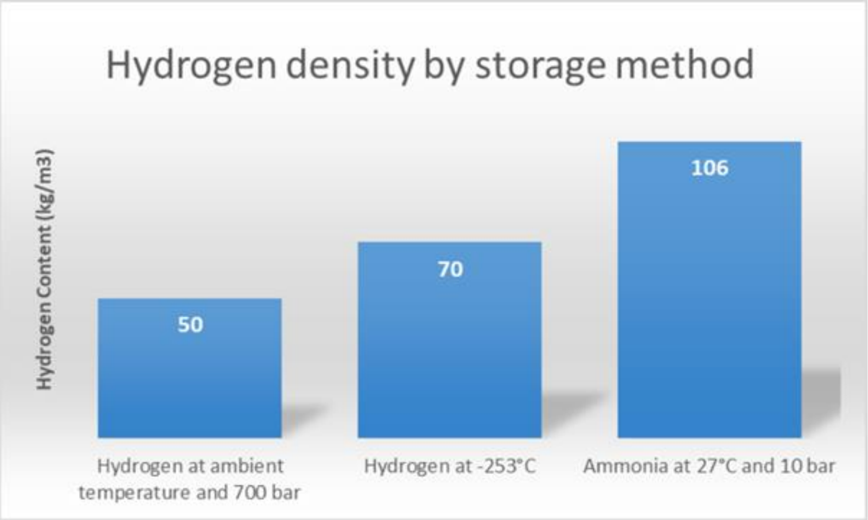
- Why ammonia as a fuel?
- Ammonia statistics and processing
- Main issues in ammonia combustion
- Results of co-firing investigations

Background

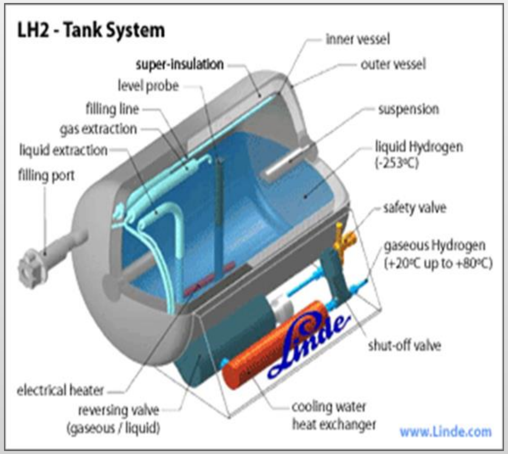
- Large scale production (from natural gas) – around 200 Mtonnes globally each year. Highly developed transport and handling system.
- 'Brown' ammonia – in waste streams of many industries, particularly dairy farming (manure), oil refining, steel manufacture (coking), biomass and sewage.
- 'Green' ammonia – as chemical energy storage for renewable electricity generation.
- Same substance whichever path.

Why the interest in ammonia as a fuel?

- Carbon free
- Cheap and easy to store.
- Established transport and handling networks
- Of sufficient energy density to fulfil 80% of global energy needs (22.5 MJ/kg).
- Potential solution to stranded generation and wind power curtailment due to lack of energy storage (1.5 TWh 2017 costing £100 million).



66 kg more H_2 than 1 m^3 $H_{2(g)}$ at 700 bar



Green ammonia - hydrogen sources

- Electrolysis - renewable electricity:

  $2H^+(aq) + 2e^- \rightarrow H_2(g)$

- From biomass - gasification then water-gas (W-G) shift reaction:

  biomass + limited air + water →

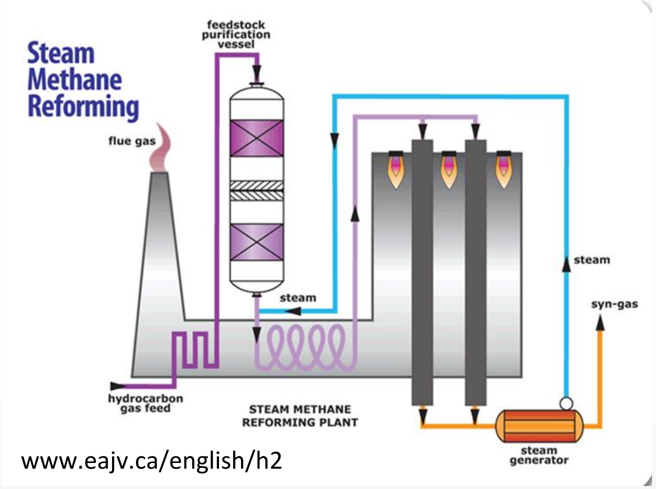
  $CO + CO_2 + H_2$ (+ others)

  Then: $CO + H_2O \rightarrow CO_2$ + *more* H_2

- From biogas – reforming:

  $CH_4 + H_2O \leftrightarrows CO + H_2$ (then W-G)

  (nickel catalyst, 700-1100°C)



With CO_2 capture = carbon negative

Haber-Bosch

Nitrogen + Hydrogen → Ammonia

(atmospheric)

- Exothermic at 130-170 bar, 400-500°C + iron based catalyst

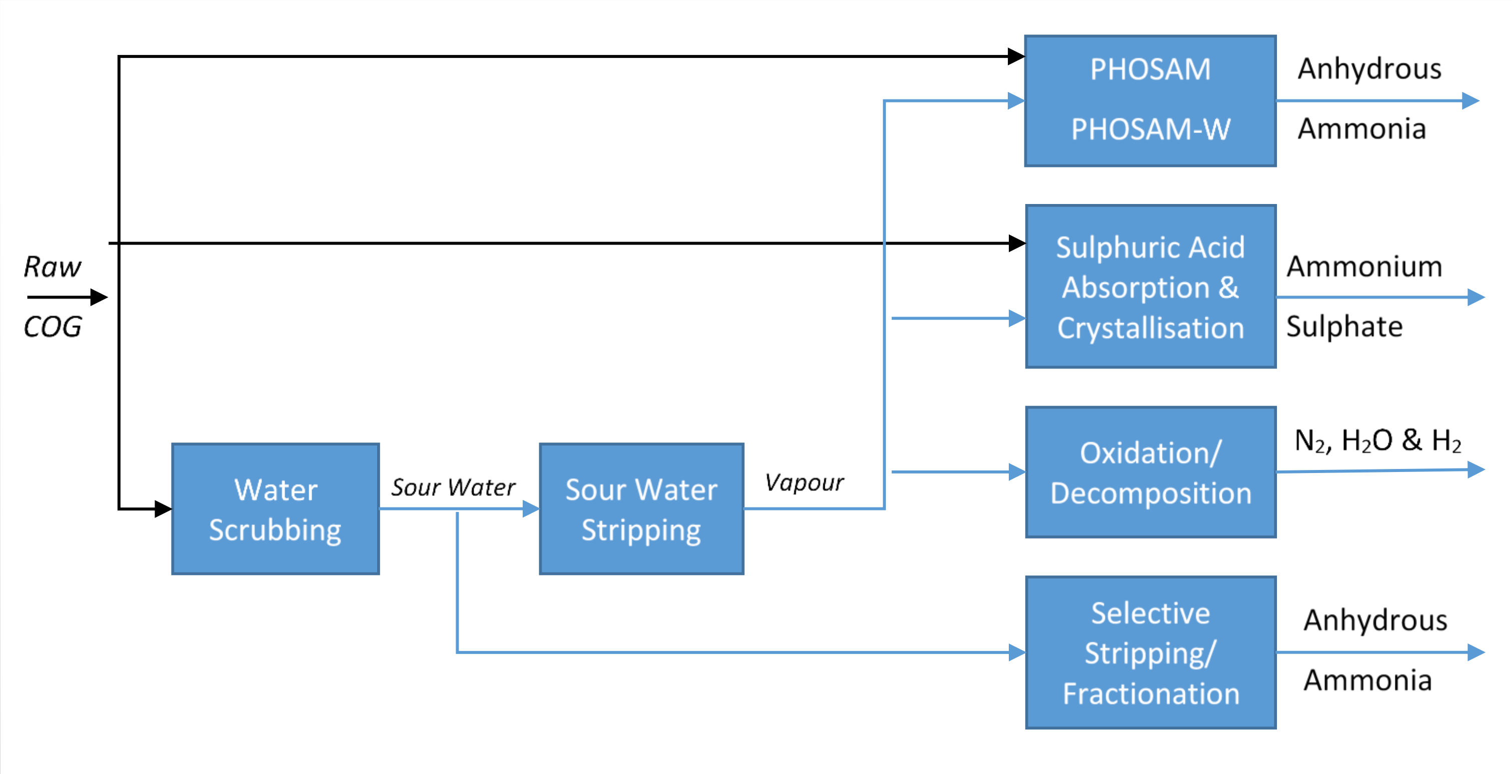
Steel brown ammonia statistics

- BF-BOF process represents 80% of UK (75% global) steel production (20% electric arc furnace)
- Around 400-500 kg coke/tonne steel
- Around 3 kg by-product ammonia/tonne coke - recovered during the cleaning of coke oven gas (COG)
- Up to 1,500 tonnes NH_3 /Mtonne of steel
- For a 4 Mtonnes p.a. steel plant

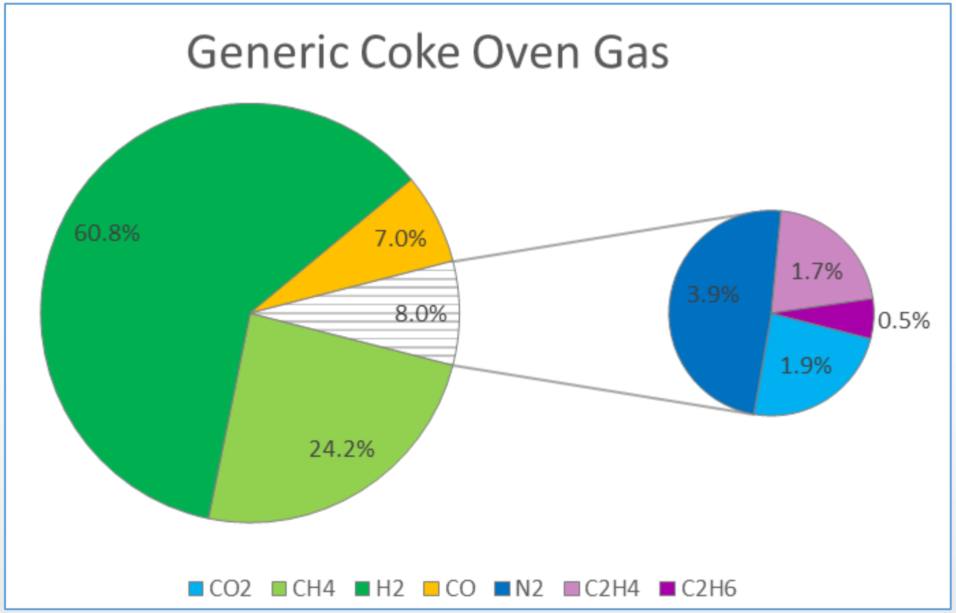
  ≈ 13 to 16.5 tonnes NH_3/day

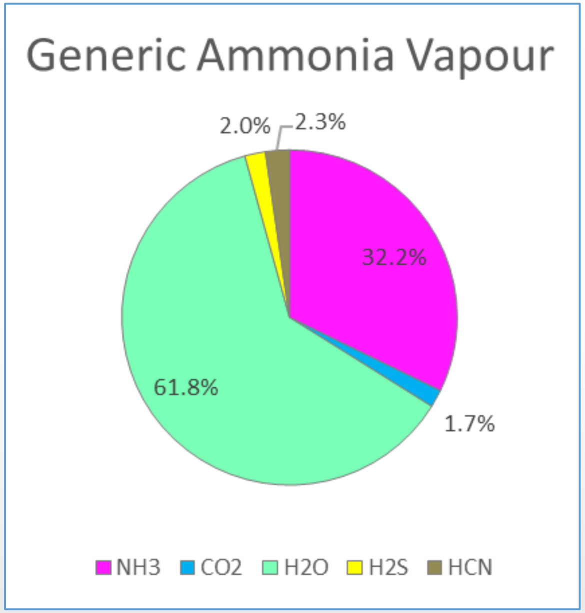
Brown ammonia processing

There are a variety of direct and, more commonly, indirect methods for COG cleaning. Water is cleansing medium for indirect methods and results in an aqueous waste stream termed ‘sour water’.



Coke oven gas and ammonia vapour compositions





- Over 60% of COG is hydrogen, 24% methane.
- Over 60% of the concentrated by-product ammonia stream is water (aqueous ammonia) heated to a vapour.

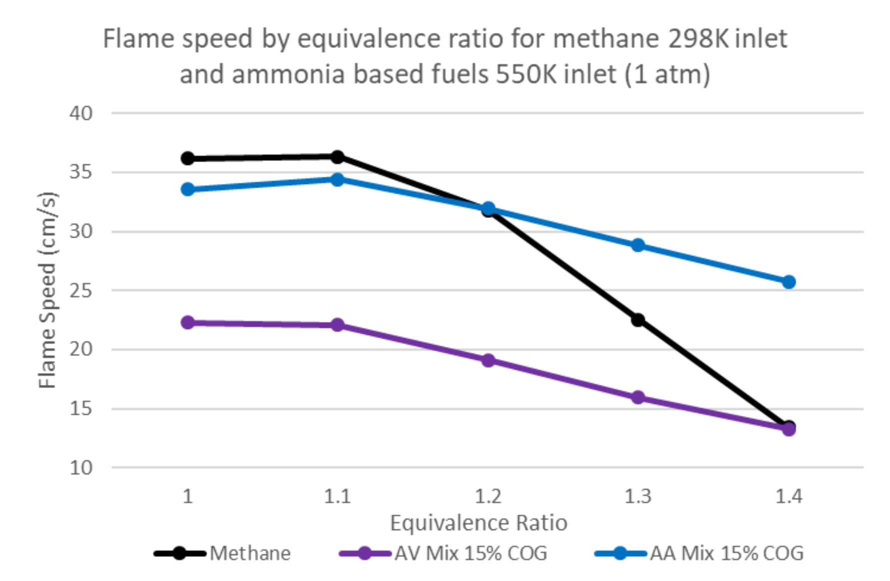
Issues in ammonia combustion (1)

Poor combustion characteristics:

- Low flame speed (6-8 cm/s vs. 35-45cm/s for methane)
- High ignition energy and narrow flammability limit (15-27%) – low reactivity (a positive for safe transport)

Potential solutions:

- Catalytic cracking for H_2 availability
- Fuel mixing
- Pre-heating



Chemkin-Pro – Reaction mechanism by E.C. Okafor *et al.* *Combust. Flame* **187,** 185–198 (2018)

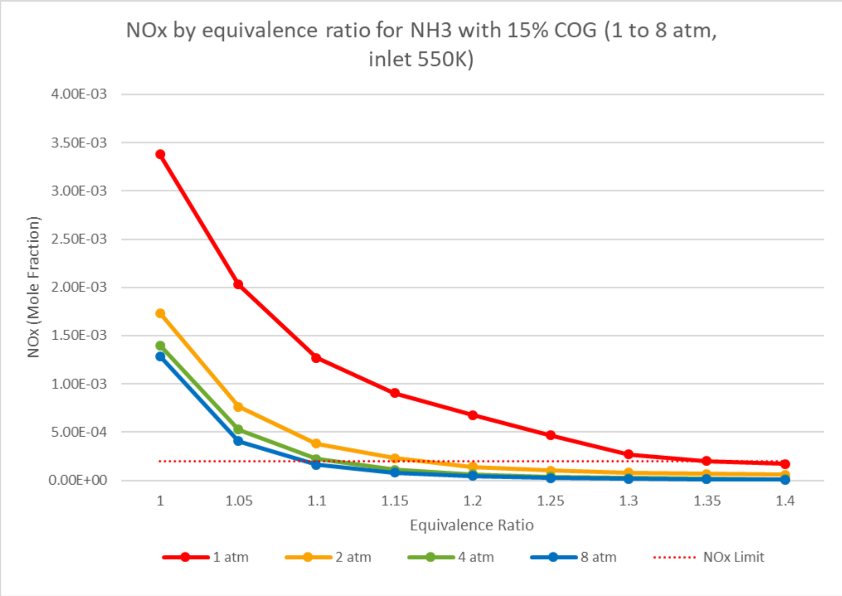
Issues in ammonia combustion (2)

Emissions:

- Potential for high NOx emissions – super equilibrium amounts as NO destruction is comparatively slow
- Ammonia slip in fuel rich combustion (toxic)

Reducing NOx:

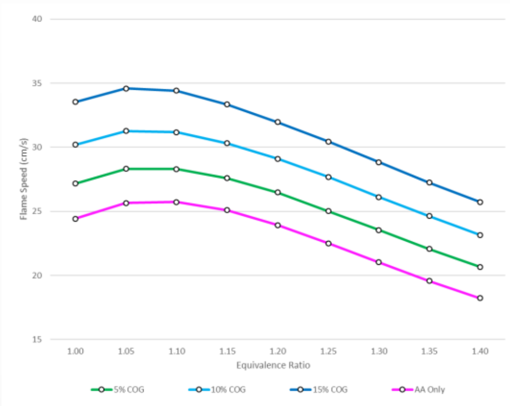
- Fuel rich
- Increasing pressure
- Adding water
- NH_3 used to reduce NOx in conventional systems



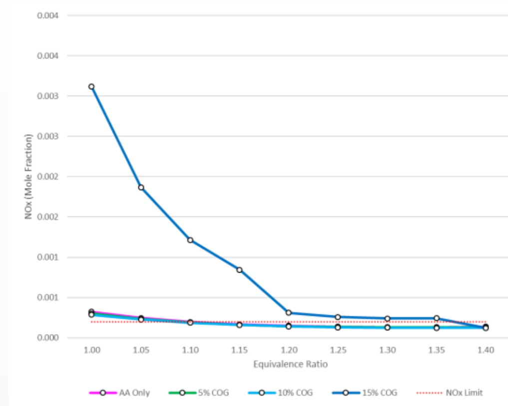
Chemkin-Pro – Reaction mechanism by Tian *et al. Combust. Flame* **156,** 1413–1426 (2009)

Choosing a mix ratio - Anhydrous Ammonia with COG (inlet 550K)

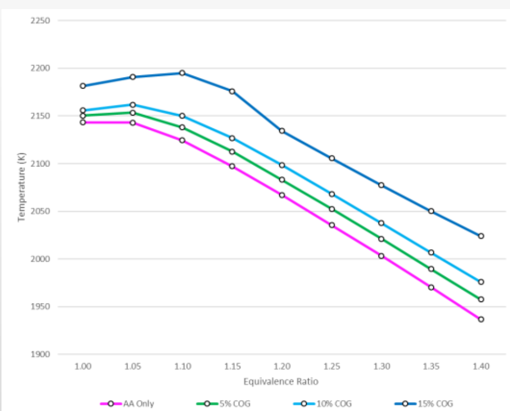
Flame Speed by Equivalence Ratio 1 bar



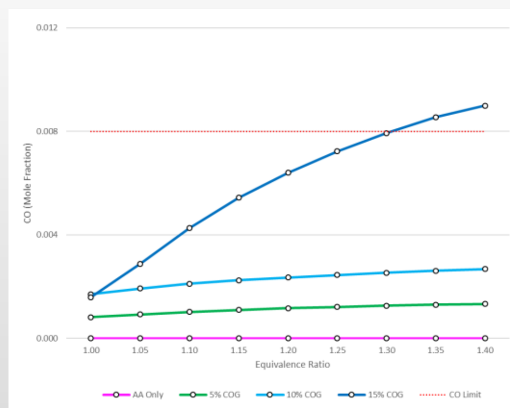
NOx by Equivalence Ratio 1 atm



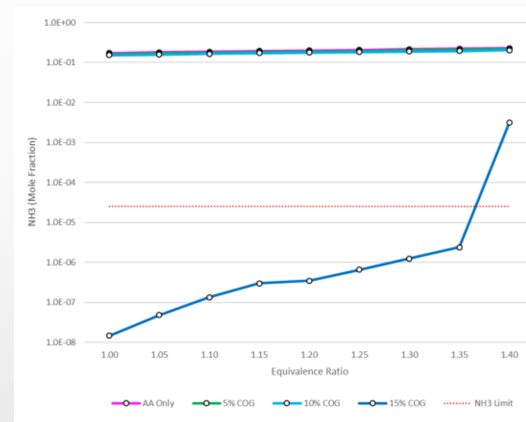
Temperature by Equivalence Ratio 1 atm



CO by Equivalence Ratio 1 atm



NH_3 by Equivalence Ratio 1 atm



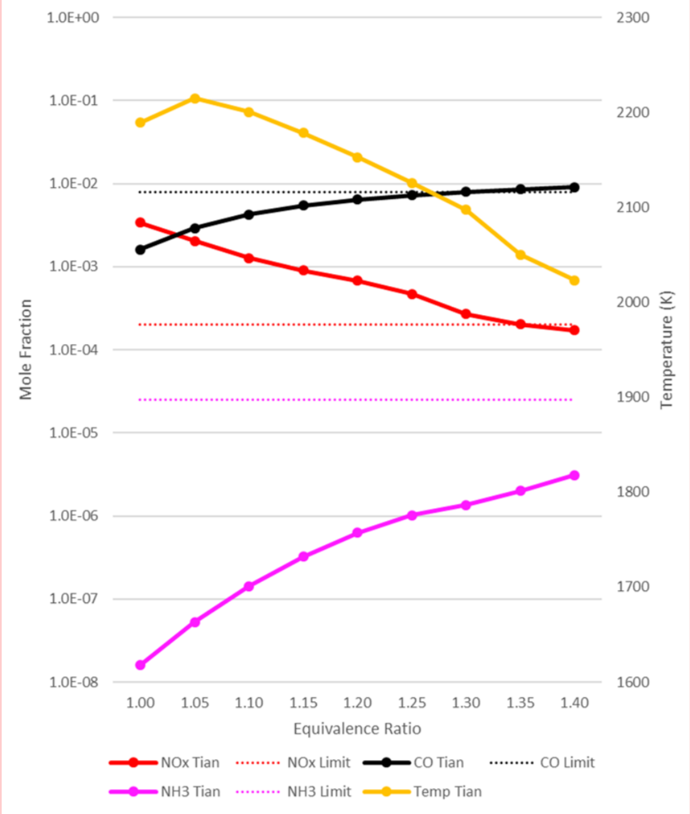
Chemkin-Pro – Reaction mechanism by E.C. Okafor *et al.*
Combust. Flame **187,** 185–198 (2018)

Best mix temperature & emissions results

Anhydrous NH3 Result

85%NH_3:15%COG (1 atm & 550K inlet)

Reactor model in Chemkin Pro, Tian *et al.* reaction mechanism



Ammonia Vapour Result

85%AV:15%COG (1 atm & 550K inlet)

Reactor model in Chemkin Pro, Tian *et al.* reaction mechanism