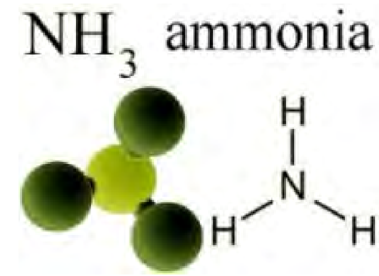
9th Annual NH3 Fuel Association Conference

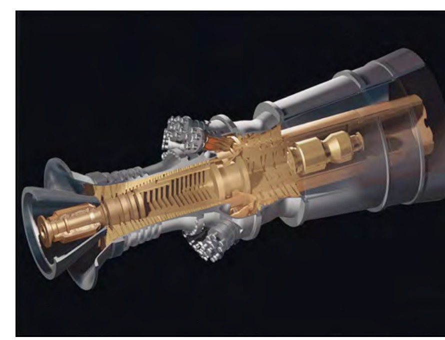
SPG
Advancing Propulsion & Energy



Fuel Conditioning System for Ammonia-Fired Power Plants

Arif Karabeyoglu and Brian Evans

Space Propulsion Group Inc.
Sunnyvale, CA



San Antonio, Texas
October 1, 2012

Statement of the Problem

Energy carrier/storage problem

- Fossil fuels have high energy densities which makes them a perfect medium for carrying and storing energy
- Energy carrying medium must have the properties
  - high in energy density
  - clean
  - safe
  - cost effective

Energy carrier/storage solution

- Hydrogen and batteries are proposed as solutions. Both have major shortcomings
- Solution is mode dependent
  - Transportation systems (automobile, rail, shipping and air travel)
  - Electric power generation
  - Residential/commercial heating

Concentrate on gas turbine power generation mode

Ammonia based fuels

Ammonia as a Fuel

Chemical Storage Media Comparison

	Process	Fuel Production Efficiency, %	CO_2 Emission* lb/mmBTU	Storage Pressure, psi
Ammonia	Haber-Bosch	60-65	0	200
Diesel	Fischer-Tropsch	67	165	14.7
Hydrogen (Gaseous)	Steam Forming	59	0	14.7 (not compressed)
CNG	Compression	88	110	3,000

* Point of use

- Natural gas is the feedstock for all fuels listed in the table
- Production of ammonia using the Haber-Bosch process is almost as efficient as the production of diesel fuel using Fischer-Tropsch process
- Only CO_2 emission free options listed on the table are ammonia and hydrogen. Ammonia is a better energy carrier due to its higher energy density, lower explosion hazard and better conversion efficiency

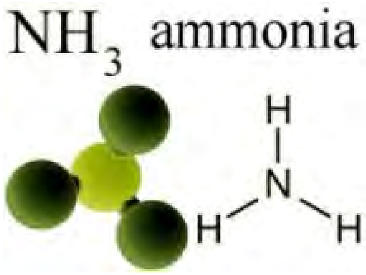
9th NH_3 Fuel Association Conference

Opportunity – NH3 as Energy Carrying/Storing Medium

Green Fuel

As Fuel Source

- NH3 is a fuel source that contains no carbon
- When burned with air no green house gases are generated
- NH3 can also significantly reduce the Nox emissions
- NH3 is not a green house gas itself



NH3 Production

- Production process has to be considered to assess the environmental benefits of NH3
- Energy efficient, carbon free methods are possible in producing NH3

NH3 Transportation/Storage

- NH3 is a widely used commodity
- NH3 can be stored at ambient temperature
- NH3 can be transported effectively using pipelines, railroads, shipping and trucks

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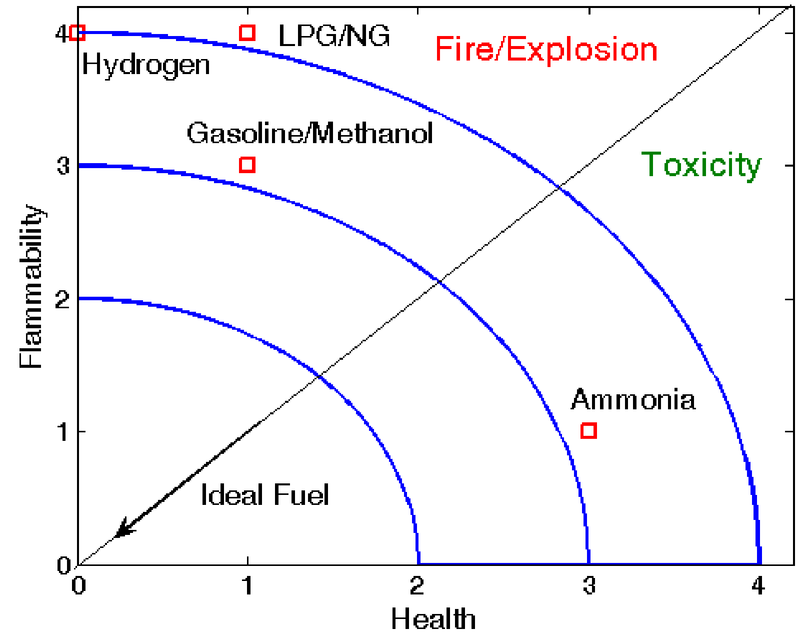
Safety – Experience Base & Safety Record

- Ammonia is a widely used commodity
- Extensive knowledge base exists in
  - Production of ammonia
  - Transportation of ammonia
  - Storage of ammonia
  - Design of ammonia systems (including a comprehensive list of compatible materials)
  - Safe handling
  - Emergency procedures

- Ammonia is regularly handled by farmers in relatively large quantities
- Ammonia related accidents are rare in agriculture
- By following a set of relatively simple rules, ammonia can be handled safely by people with minimal training



NFPA 704 Classification:

Health	Flammability	Reactivity
3	1	0

Excellent data base exists on ammonia related accidents
Ammonia has an excellent safety record
NH3 is overall as safe or safer than any other fuel

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Gas Turbine Power Generation

Gas Turbine Power Generation

Older plants are rapidly being displaced by gas turbine power generators

- Gas turbines supplied 15% of US power generation in 1998.
- Portion will be 39% by 2020.
- Of new demand 81% is for gas turbine power.
- Market is ~ $10 billion. About 700 to 800 new units sold per year.

Engine Types in Use

- Heavy duty gas turbines - centralized power production, 30 to 500 MW.
- Lightweight gas turbines - derived from aircraft engines, generally less than 60 MW.
- Micro gas turbines - distributed power, less than 5 MW

Why Gas Turbines?

- High efficiency - Up to 60% with steam co-generation.
- Low emissions - NOx < 10 ppm.
- Low installed cost - 25,000 hr maintenance interval.
- Multi-fuel capability - Natural gas (methane) is fuel of choice when available. Fuel transition while running

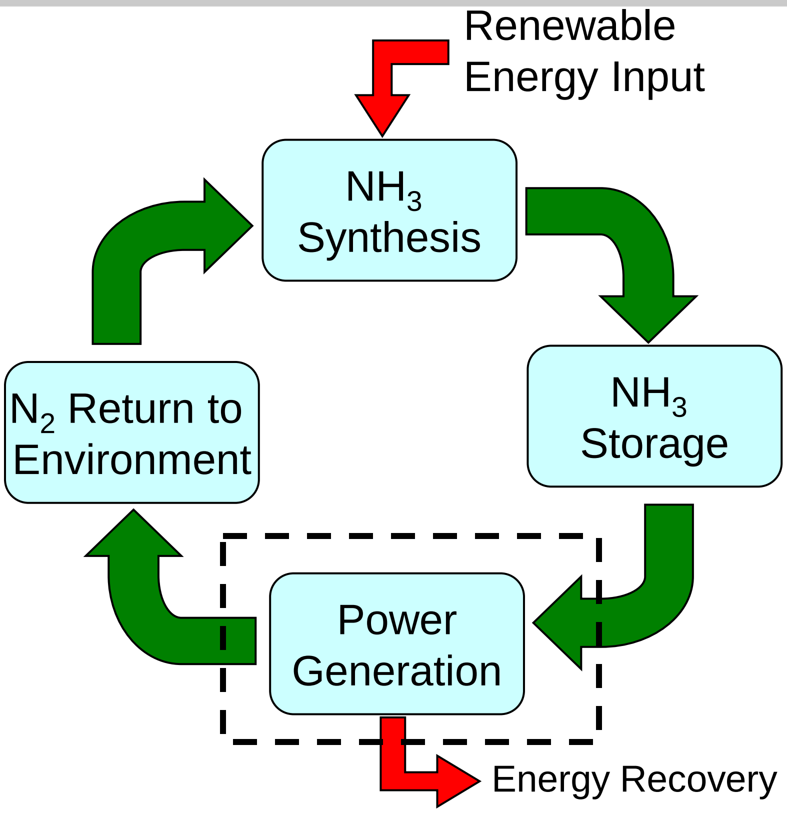
Gas Turbine Power Generation – Role of Ammonia

Transportation Advantages of Ammonia over Natural Gas

- Compression or refrigeration costs of ammonia shipping are far lower than natural gas.
- Liquid natural gas (LNG) is at -163 C, a deep cryogen. Ammonia at the ambient pressure is only at -33 C, a cold liquid.
- Compressed natural gas (CNG) is at 2,900-3,200 psi. Pressure of ammonia is ~200 psi.
- Flammability limits of natural gas is significantly wider.

Target Market 1 – Distributed Renewable Energy Generation

- Most of the renewable energy sources such a solar or wind have very low capacity factors (10-30%). This requires a backup power system.
- Instead of connecting to the grid (utilities companies would charge for this), use the excess power to make ammonia which can be stored and burned in a micro turbine to generate electricity and heat when needed.
- This requires the development of an efficient synthesis technology for ammonia (from water and air).
- Since ammonia is a widely used fertilizer, its use in electricity generation in rural/agricultural areas makes perfect economical sense.



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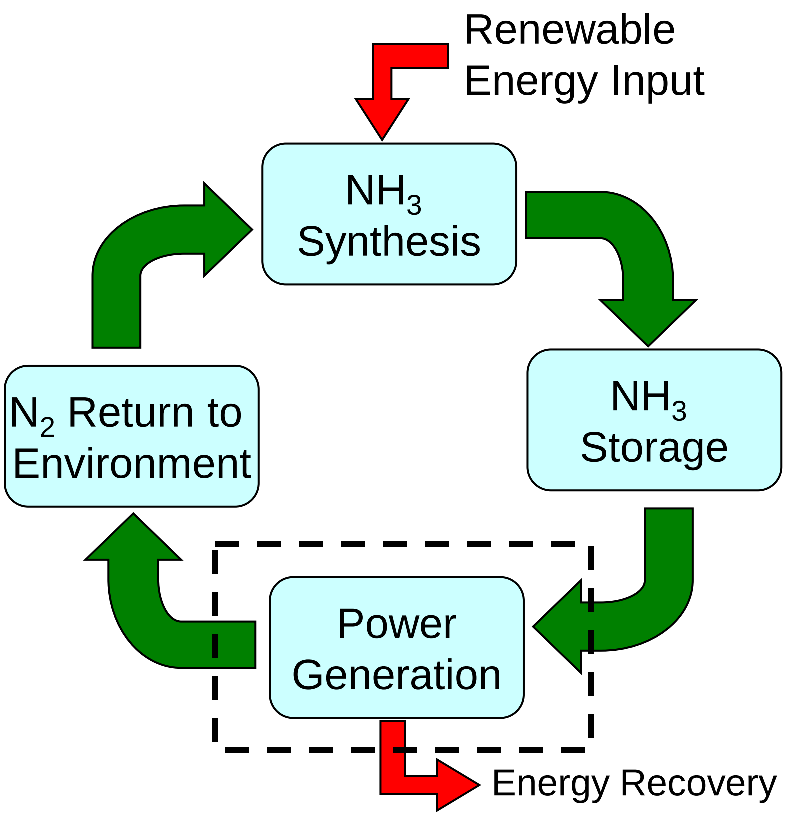
Gas Turbine Power Generation – Role of Ammonia

Target Market 2 – Enabling Technology for Stranded Renewable Energy Source

- Stranded Renewable Energy Sources: Most of the renewable energy sources such as solar, geothermal or wind are not accessible by the existing electric grid system.
- Extending the grid to remote areas is NOT economical. In most cases extension of the grid system is politically difficult (if not impossible).
- Ammonia as energy carrier has the potential to solve the Stranded Renewable Energy problem.
- Using a synthesis method such as SSAS ammonia can be produced at the stranded site from water and air.
- The produced ammonia can be shipped via trucks, railroad or pipelines to the power generation plants to generate electricity.



Ammonia Fired Turbines

Gas Turbine Power Generation – Fuels Comparison

Fuel	Fuel/air ratio*	Tcombuster* K at 20atm	Texhaust K at 1 atm	Enthalpy change (work) kJ/kg
Methane	0.058	2277	1260	1551
JP-4	0.068	2342	1313	1539
Ethanol	0.111	2295	1289	1546
NH3	0.164	2092	1114	1549

* Stoichiometric fuel/air combustion at a pressure ratio of 20:1

- NH_3 requires higher fuel mass flow rate
- NH_3 generates the same work output at lower temperature
- Or NH_3 generates more power at the same temperature

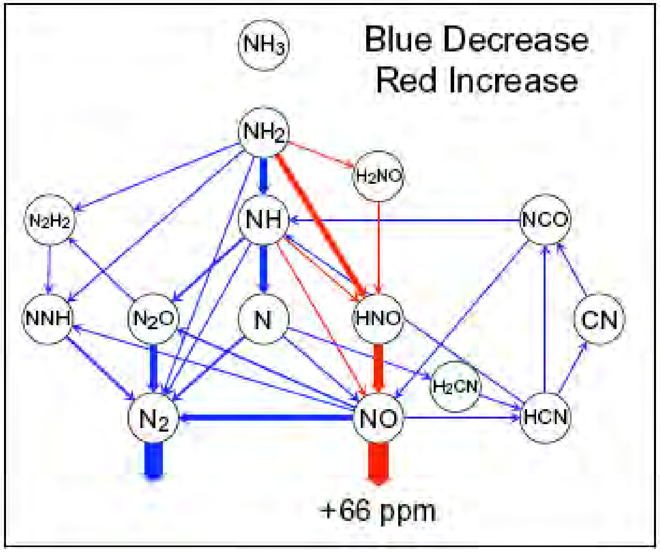
Past Experience with Ammonia Fueled Gas Turbines

History

- Ammonia as a turbojet engine fuel has been tested in 1960's
- At least two DoD programs (reports available)
- Some recent research activity in University of Florida
- No active programs as far as we know

Lessons Learned

- Ammonia is a satisfactory substitute for hydrocarbon fuels in a gas turbine engine
- Complexity and cost of engines using ammonia vapor combustors will NOT be significantly greater than existing hydrocarbon engines
- Use of ammonia would also lead to reduction of NOx emissions



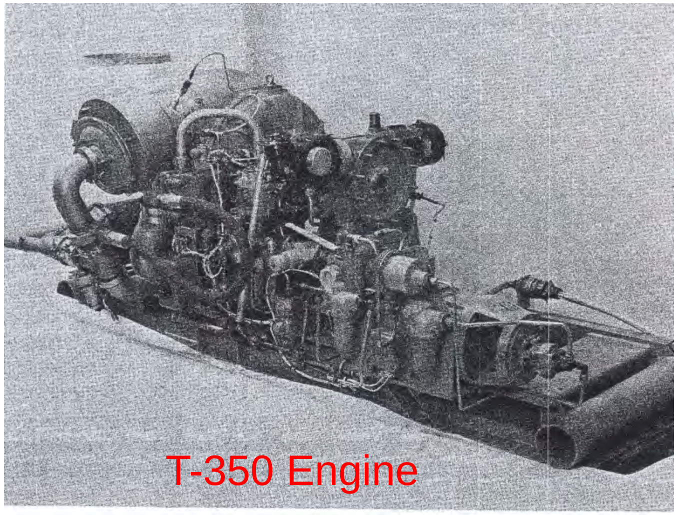
Oxidization chemistry of ammonia is well established

Technical Challenges

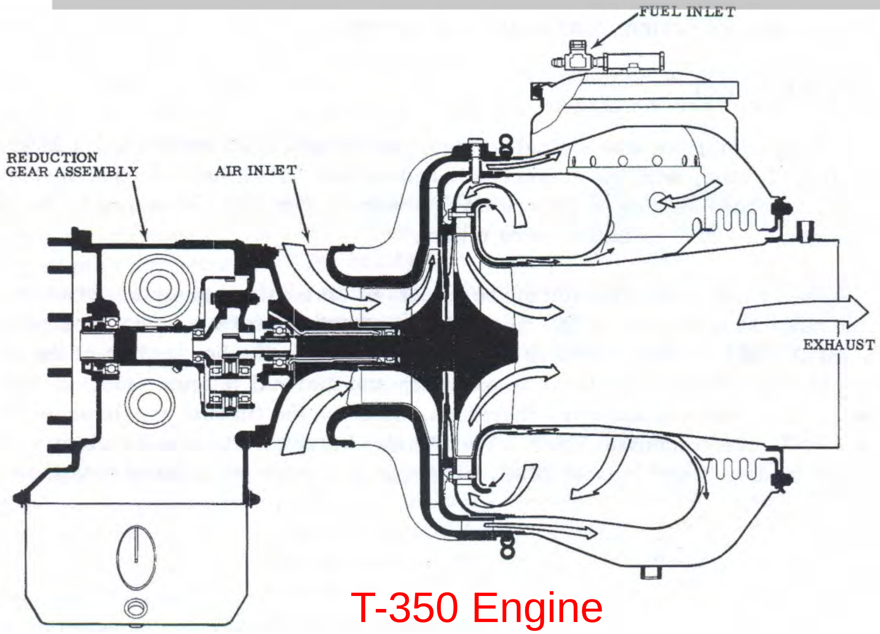
- Low flame temperatures and slow kinetics results in challenges with pure ammonia in a turbojet combustor
- Stable efficient combustion with liquid NH_3 is problematic. Additives would help with this issue
- The DoD programs concluded that ammonia in the vapor phase can be burned in a turbojet combustor. This requires a heat exchanger to vaporize the ammonia
- Cracking helps flame stability

Past Experience with Ammonia Fueled Gas Turbines

- Investigations have been conducted by Solar Company and UC Berkeley in the 60's
- Solar used its 250 HP model T-350 single can burner engine.
- UC Berkeley studies were limited to subscale combustors
- Performance of the T-350 engine with ammonia is compared to the performance with JP-4
- Tests were limited to ammonia in vapor phase



T-350 Engine

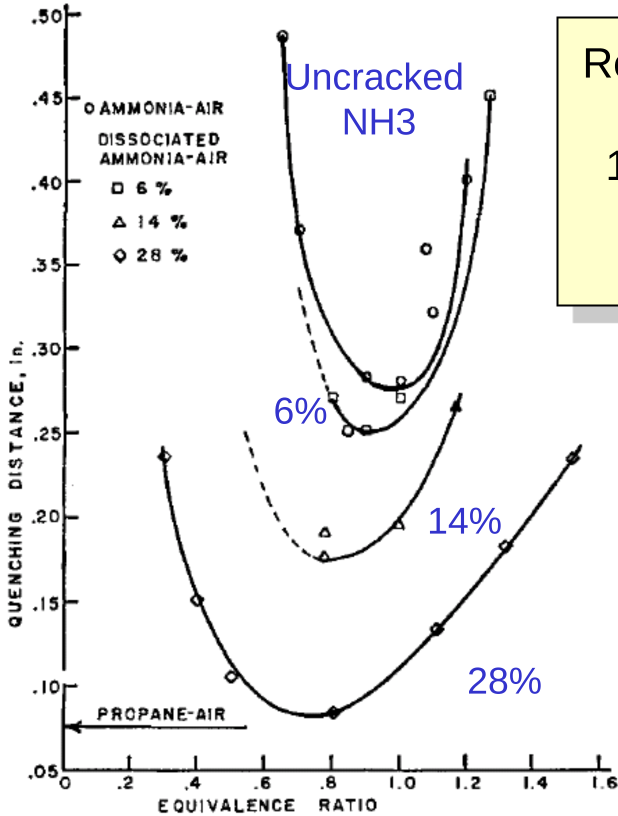


T-350 Engine

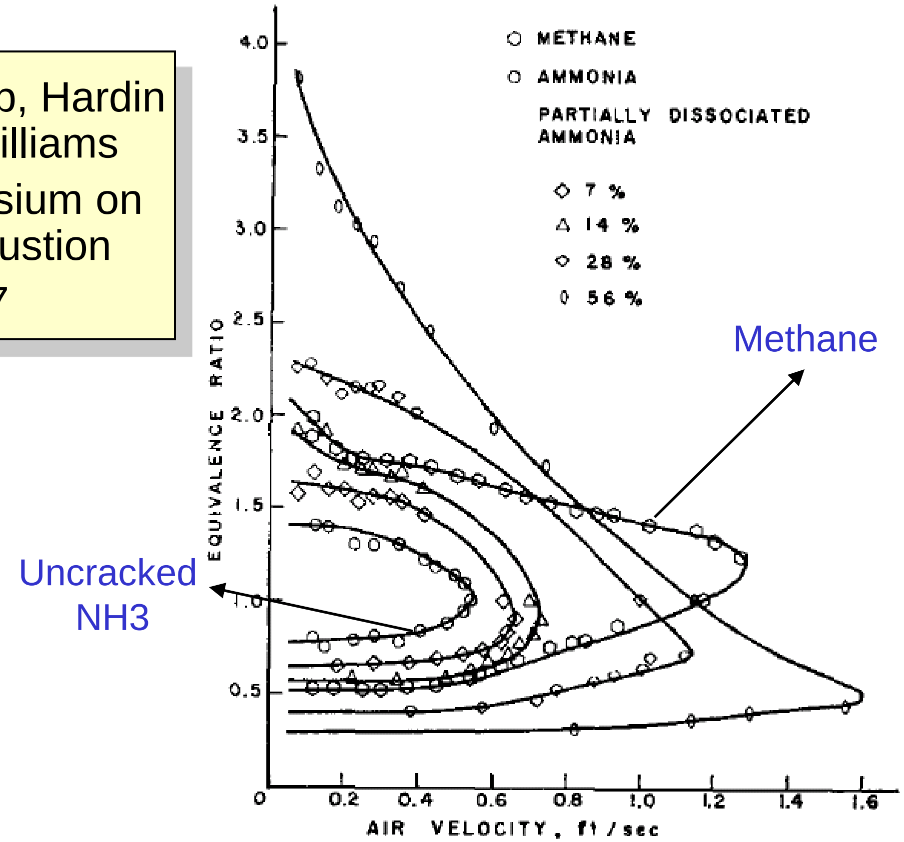
Some Observations

- Both vapor and catalyst combustors have been tested.
- Using ammonia at 2.35 times the HC fuels resulted in cooler turbine inlet temperatures at a given power.
- When the turbine inlet temperatures are matched, the ammonia engine resulted in a power increase of 10-20%.
- Efficiencies were high with the ammonia combustors.

Why Crack?



Ref: Vercamp, Hardin and Williams
11th Symposium on Combustion
1967



- Uncracked NH3: Slow flame speed, large ignition energy, large quenching distance, poor flame stability
- Cracking is needed for 1) stability, 2) efficiency, 3) Low NOx emissions and 4) good power loading

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Ammonia Cracking

Cracking Technology

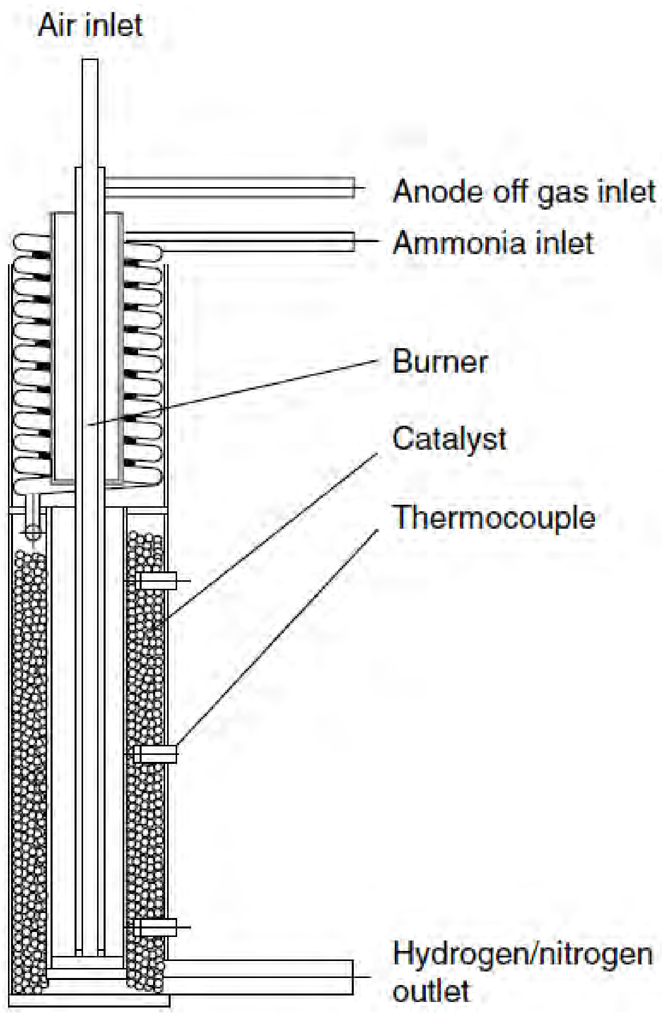
- Most common cracking method is flow over heated catalyst bed
- Electrically heated nickel based catalysts (*e.g.*, Ni-Ru) require high temperatures for efficient cracking
- Thermal decomposition method shortcomings:
    1. Catalysts are expensive and have limited lifetime
    2. Endothermic decomposition requires significant energy input
    3. Significant heat losses are associated with high temperature operation
    4. Long transient periods to reach full operation
- Off-the-shelf units quote an energy requirement of <0.5 kW for 1 Nm^3/hr of gas produced
- That is ~5.2 MJ/kg of NH3 or a 50% cracking efficiency

Improvements on Cracking Methodology

- Rosenblatt, *et al*. (1949) proposed combustion of NH_3 and air over the catalyst bed
- Reduced energy input a benefit to overall cycle
- High temperatures and limited lifetime of catalyst bed operation still a factor

- Goetsch and Schmit (2002) developed an "Autothermal Reformation of Ammonia" system
- H_2/Air combustion over the catalyst bed balances the energy input required for decomposition
- Reduces effective cracking and still requires catalyst bed technology

- Apollo Energy Systems devised cracker using H_2-rich anode off gas of a fuel cell
- Portion of required decomposition energy is offset through combustion enthalpy
- Method is limited to fuel cells and still requires a catalyst bed



Apollo Energy Systems Cracker Design

Relatively low flow rates not suitable for gas turbine application

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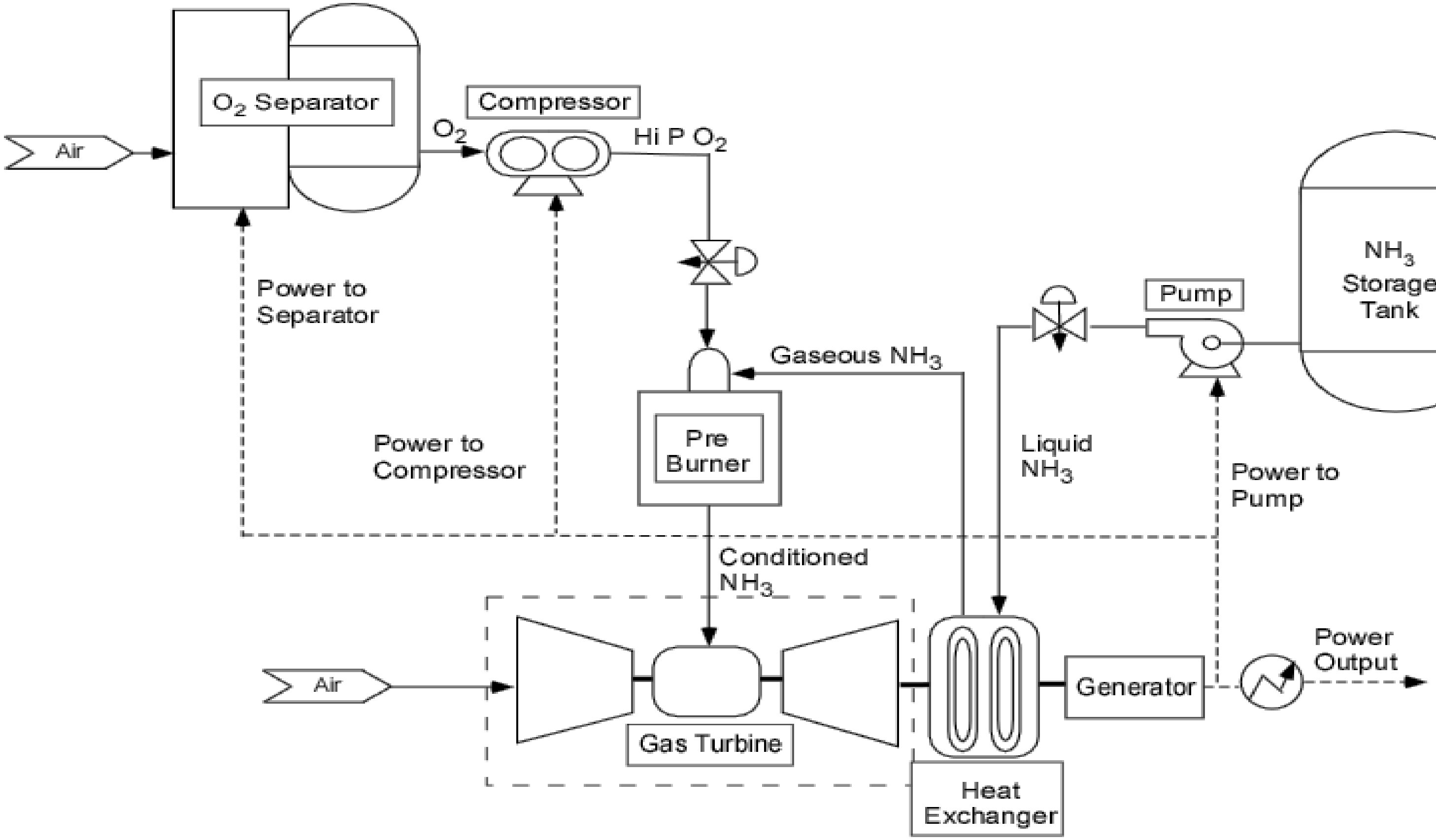
Fuel Conditioning for Gas Turbines

Plant Configuration



- Partially cracked NH_3 is generated using a preburner system
- Oxygen-rich gas reacted at extremely fuel-rich mixture conditions
- Gas could also be supplied from another plant process like NH_3 synthesis

NH_3 Preburner Design Overview

- No catalytic materials required for operation
- Startup transient minimized through combustion process
- Outlet conditions can be varied through reactant flow rate control
- Increased operational lifetime through mixture condition selection
- Preburner can be operated with vapor or liquid phase NH_3
- Design can be easily scaled to large power plants
- High mass flux capability allows significant reduction in system size and weight

No catalytic materials required for operation → **increased lifetime**

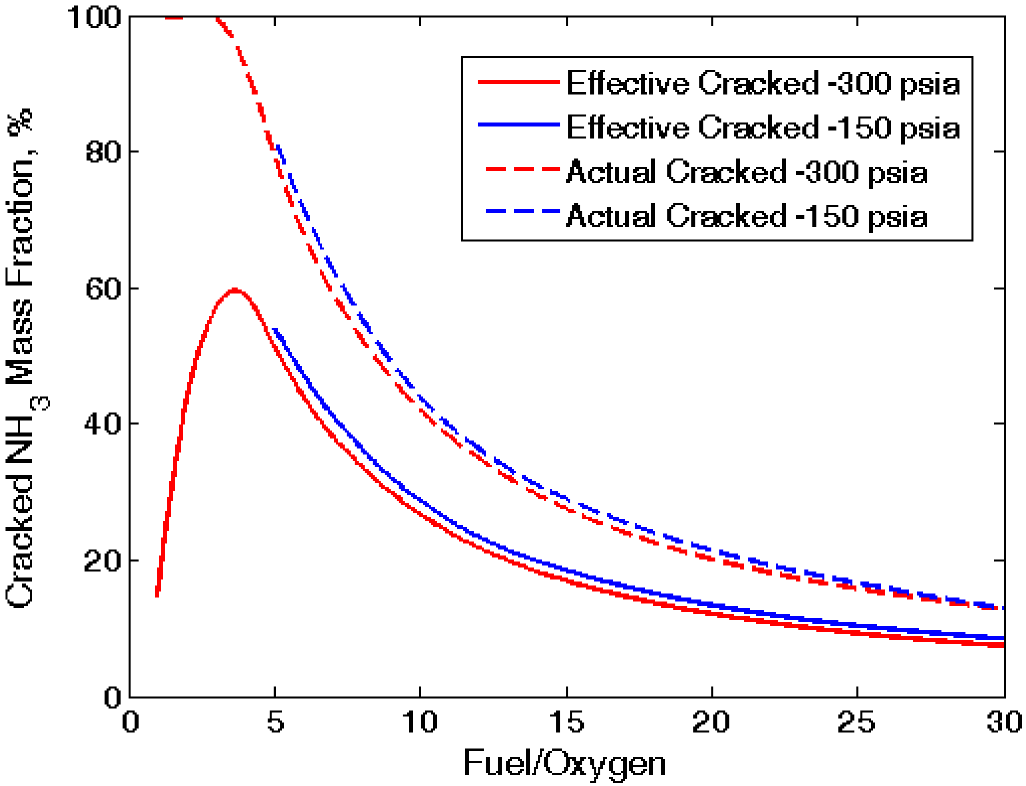
No exotic materials required → **reduced cost**

No external energy for decomposition process → **increased efficiency**

System Performance

Product Species – Effective Cracking Concentrations

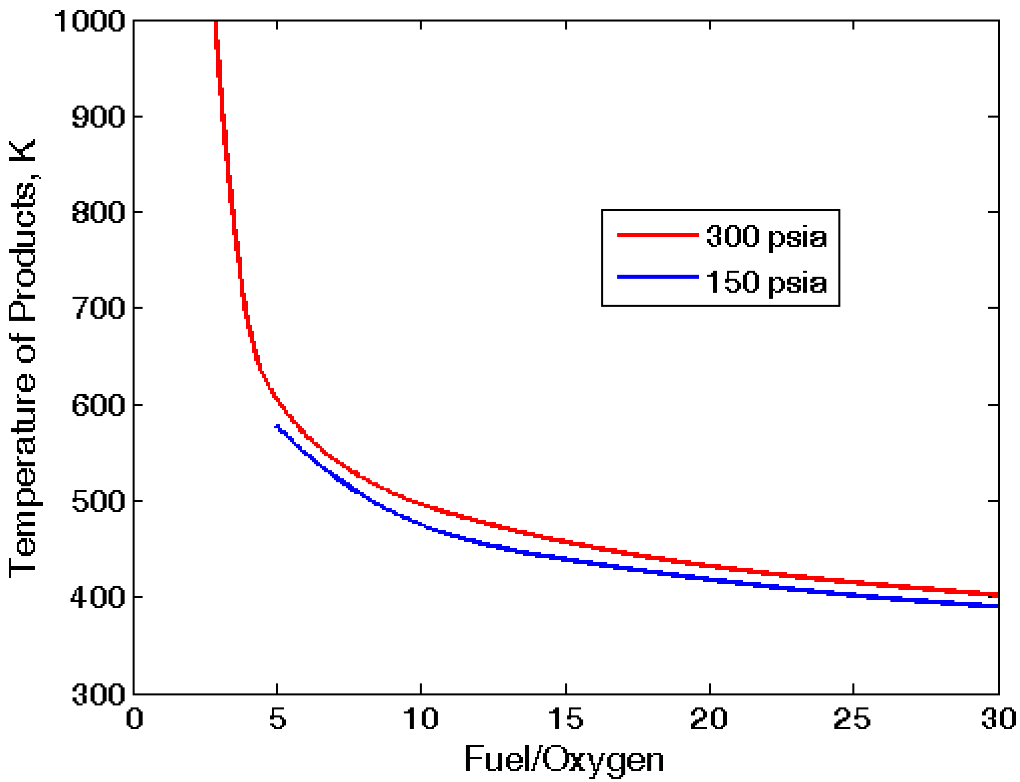
- Effective cracking is matched H_2 concentration in product stream
- F/O mixture between 12-20 supplies 10-25% cracked NH_3
- Operation can be varied during ignition transient of gas turbine
- Significant increase in flame speed from introduction of H_2



Even at very high F/O, significant amounts of hydrogen are generated

Product Species – Temperature Variation

- Operating temperature critical for:
  - Long-life cycle,
  - Low cost production,
  - Reduced heat loss, and
  - Safety
- F/O less than 5 make operation unpractical due to material limitations
- Temperatures less than 500 K for F/O greater than 10



Exotic materials not required under warm gas operating conditions

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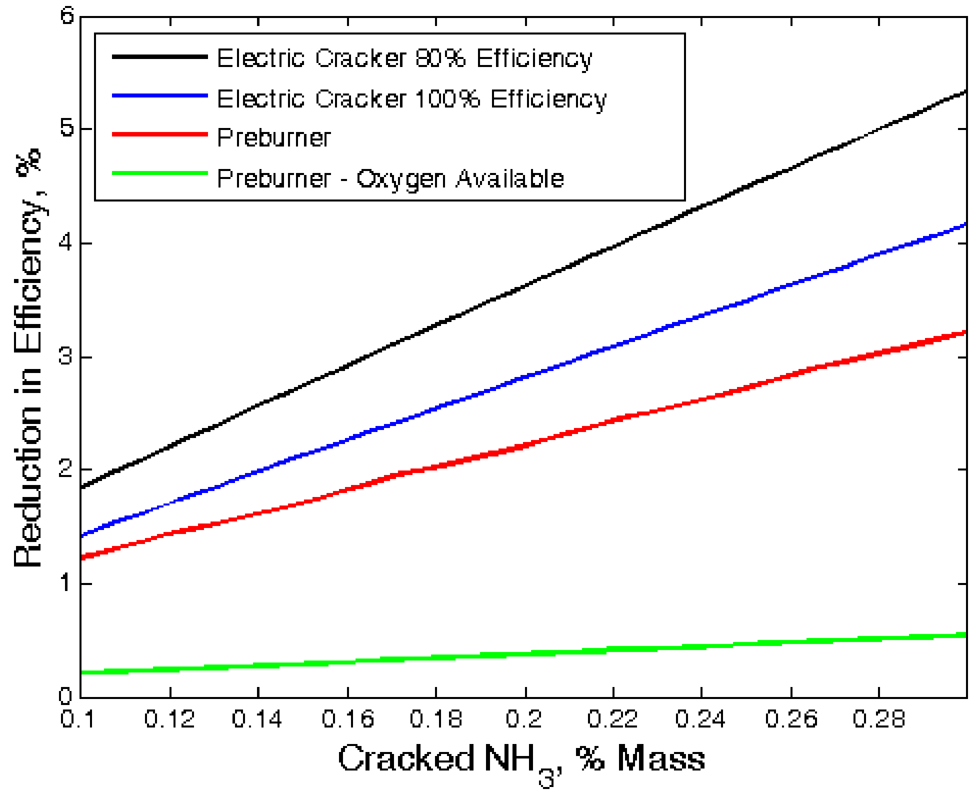
Plant Cycle Efficiency Reduction

- Increased operating efficiency over electric cracking system
- Off-the-shelf electric crackers are significantly more inefficient
- Generation of oxygen-rich gas is the largest energy consumer
- Onsite O_2 through NH_3 synthesis significantly increases efficiency



Preburner design is more efficient than theoretically possible through electrically heated cracker

Development Path

Development - Program Elements

Phase I – Feasibility (Funded by Montana Board of Research and Commercialization Technology)

- Objective: Evaluate the feasibility and economical/technical viability of the concept
- Conduct feasibility studies: Modeling of ammonia combustion, testing in combustors and design of fuel nozzle for J85 and J79 engines

Phase II – Technology Development

- Objective: Develop the necessary technologies to implement the concept
- Work includes: Fuel formulation and laboratory testing, engine cycle analysis, extensive engine testing (using engines such as J85 and J79 – two exist in the AEROTEC facility), development of fuel systems

Phase III – Pilot Plant

- Objective: Implement the concept on a small gas turbine power generation plant
- Work includes: Conversion of the existing facility to an ammonia fired gas turbine, evaluation of the economical viability of the concept
- Partner with an energy company

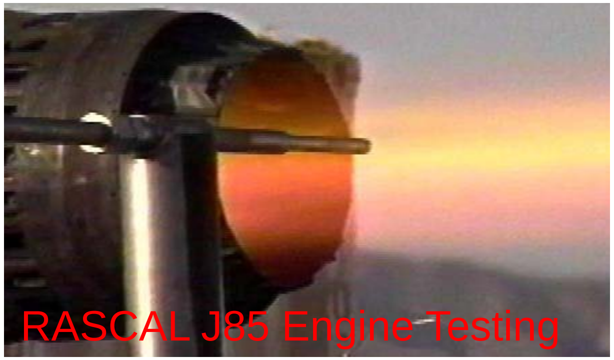
Phase IV – Implementation

- Objective: Convert existing gas turbine power generation facilities to burn ammonia and develop new ammonia-fired gas turbines if necessary
- Partner with a gas turbine producer

SPG's Core Competence

SPG personnel have broad experience in the areas

- Combustion, thermochemistry of fuels, design and analysis of gas turbines
- Testing of gas turbine engines and rocket motor systems



SPG have access to several J79 and J85 engines and all test equipment from the RASCAL program

SPG's capabilities include

- Laboratory testing of fuel properties
- Testing of turbojet engines (AEROTEC test facility in Butte Montana)

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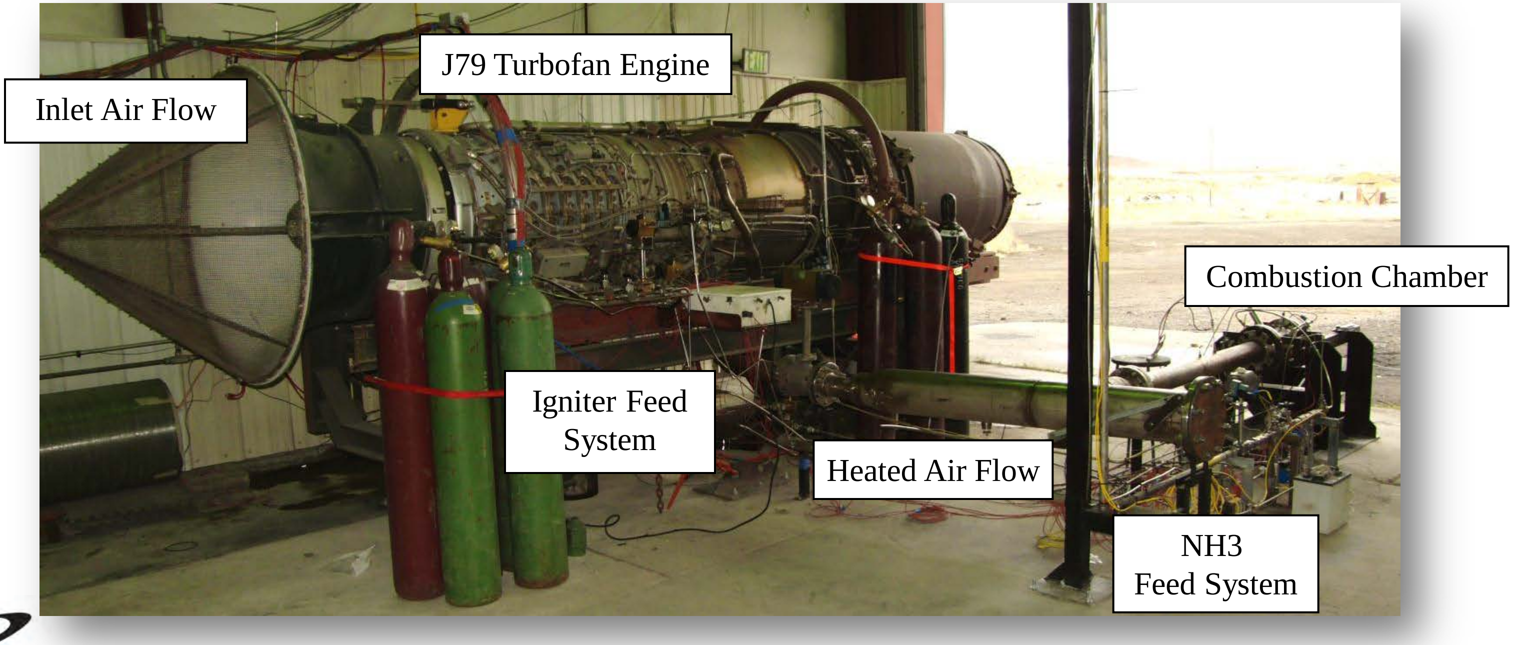
Phase I Progress – Developement of Test Setup

- Test rig designed to simulate gas turbine combustor conditions
- Bleed air from a J-79 turbofan engine supplies high pressure, hot air for combustion
  - Air flow rates of >8.0 kg/s can be achieved
- At full thrust, an NH_3 mass flow rate of 0.690 kg/s required for stoichiometric mixture
- NH3 vapor is pulled from the run tank and mixed with N_2/H_2 to simulate cracking
- Extent of simulated cracking is precisely controlled



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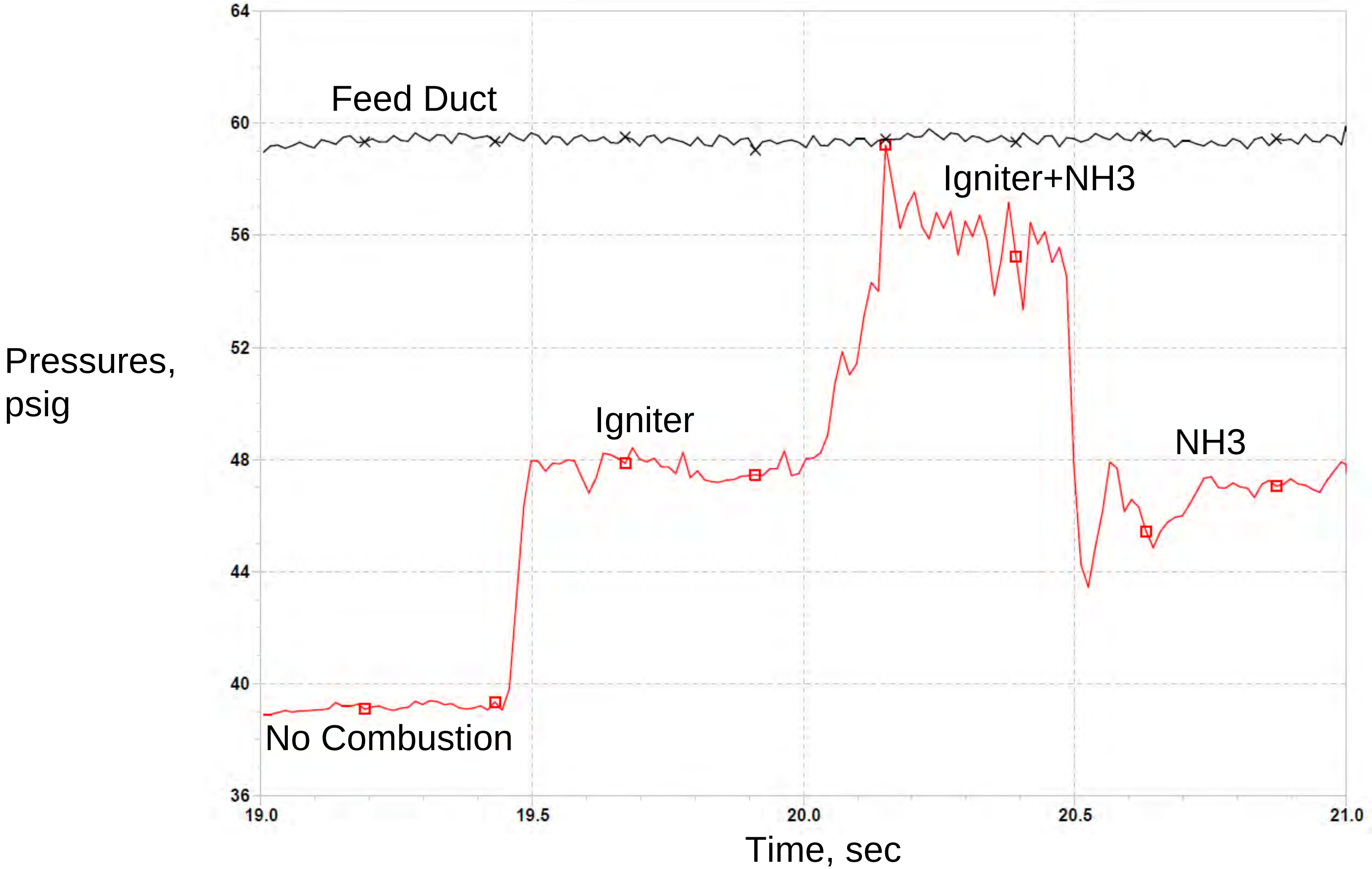
Phase I Progress – SPG's NH3 Test Setup

- Primary Measurements
  - Flow rates
  - Pressures
  - Temperatures
  - NOx
- 3 kHz sampling rate

Phase I- NH3 Combustion



Self Sustained NH3 Combustion @ 10% Cracking

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Summary

- Ammonia is a very promising environmentally friendly energy storage/carrier
  - No CO_2 emission when oxidized
  - High hydrogen density
  - Easy to transport and store
  - Widely produced and used commodity
  - Triple use as fertilizer/industrial/fuel
- Existing oil or gas fired gas turbine plants can be easily converted to burn ammonia
- Some limited experience on using ammonia in gas turbines exist
- Conditioning of ammonia for stable & efficient gas turbine combustion is required
- Preburner design is advantageous in that it:
  - Does not require catalysts
  - Can be easily scaled to large power plants
  - Operates at low temperatures
  - Has a short operational transient
  - Can handle significantly higher throughput
  - Operates at higher efficiency levels
- Oxygen rich preburner concept is not limited to power generation, can also be applied to any stationary or mobile ammonia combustor
  - Provisional Patent Application filed on concept

Thank You!

Transportation vs Electricity Generation

Due to its high hydrogen density, ammonia has been studied as transportation system fuel extensively

"DOE does not plan to fund R&D to improve ammonia fuel processing technologies for on-board use on **light weight vehicles** at the present time"
Ref: *Potential Roles of Ammonia in Hydrogen Economy*, *DOE Report, Feb 2006*.

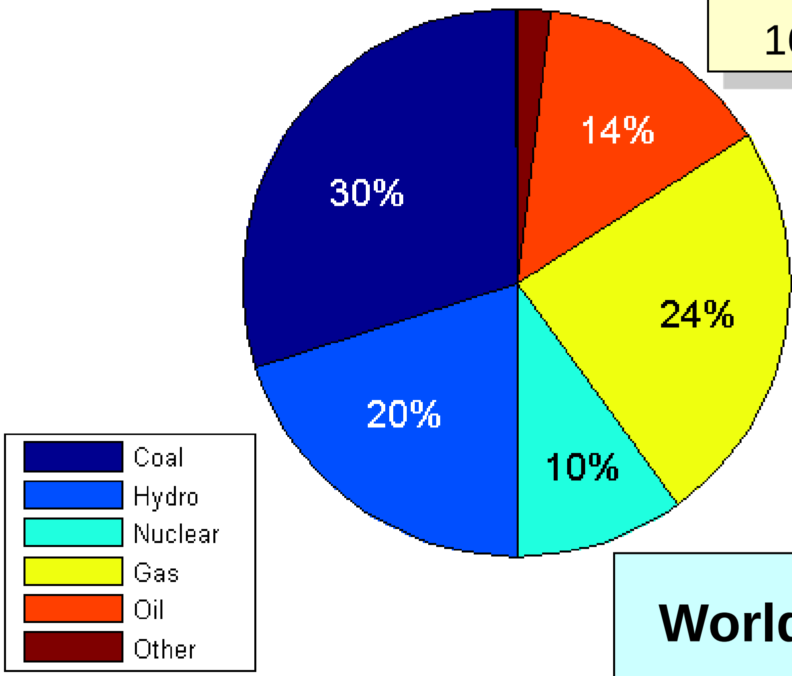
The following are quoted as the main reasons
- Safety – toxicity
- Ammonia cracking issues: start up, efficiency, conversion rate
- Storage: Lack of light, compact and robust storage tanks

	Transportation	Electricity Generation
Safety	Very critical	Not as critical
Cracking	Cracking reactors heavy/expensive	Easily done
Storage tank weight	Critical	Not an issue
Storage tank robustness	Need to be "Indestructible"	Existing storage tanks are suitable
Distribution	Complicated	Relatively simple
Start up	Problematic	Not many start ups
Operational	Pumps operated by unprofessionals	Delivered/handled by professionals

Major shortcomings of ammonia for transportation systems are NOT relevant to electricity generation

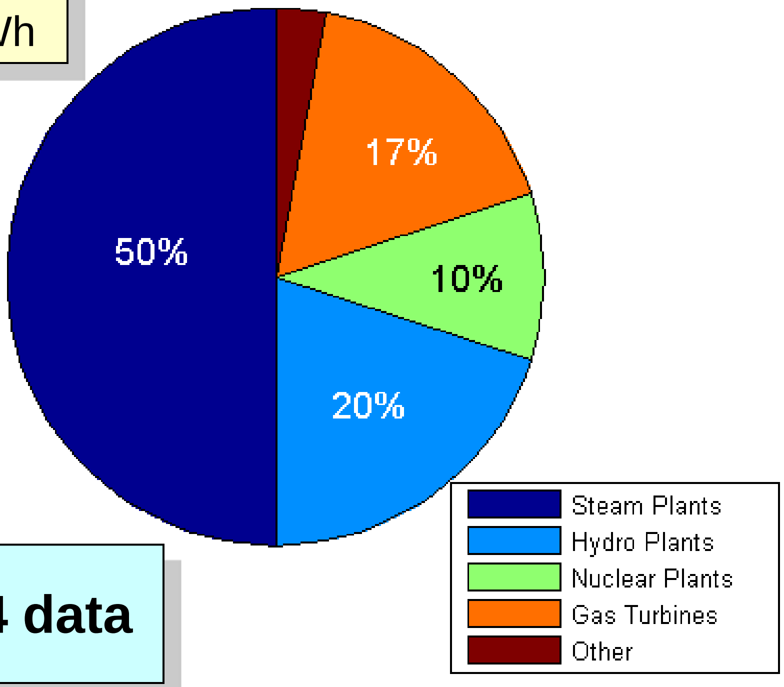
Electricity Generation Market

Fuels



Total Capacity
16,668 billion kWh

Technology



World Wide 2004 data

- Coal fired conventional steam plants still dominate energy generation market
- Energy generation by the gas fired gas turbines has been growing rapidly
- Oil fired plants can be converted to clean burning ammonia gas turbines

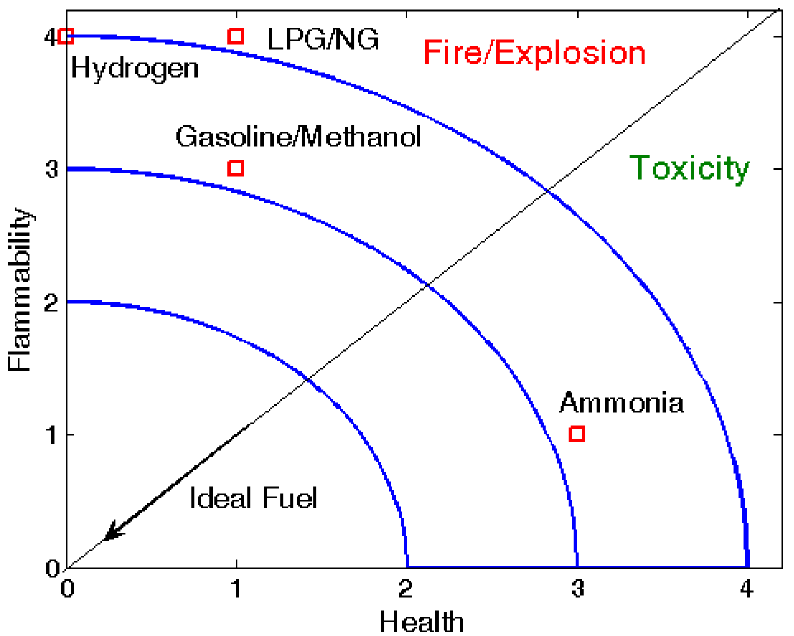
Safety Overview

Safety – Overview

NFPA no. 704 classification is a good starting point to assess the safety of fuels

Substance	Health	Flammability	Reactivity
Ammonia	3	1	0
Hydrogen	0	4	0
Gasoline	1	3	0
LPG	1	4	0
Natural Gas	1	4	0
Methanol	1	3	0

0=No hazard, 4=Severe hazards

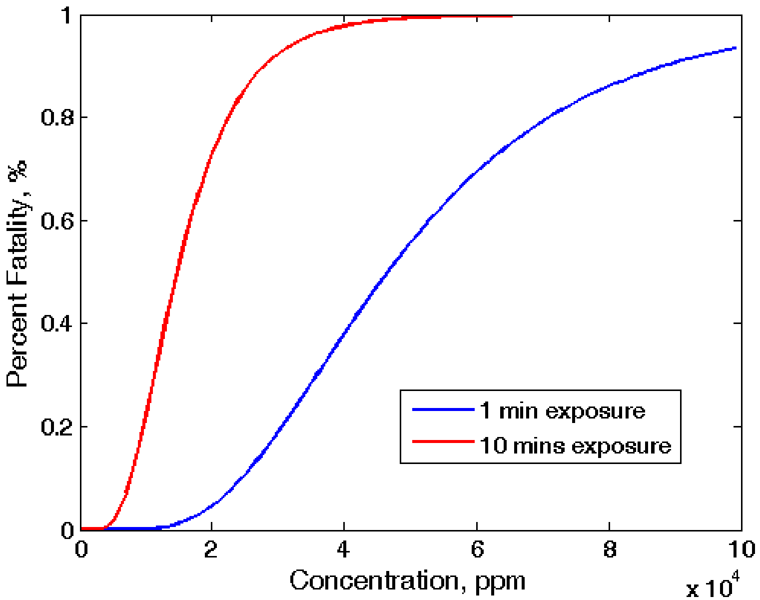


- There are serious hazards associated with all fuels
- With the exception of gasoline and methanol health related hazards of fuels other than ammonia are low
- Hazards associated with flammability are low in the case of ammonia
- Ammonia is rated as a toxic substance but NOT as a poison (NFPA Health: 3)
- With ammonia Fire/Explosion hazards of the other fuels are traded with the Toxicity hazard

Safety – Toxicity Hazard

- Ammonia is a toxic substance with the exposure limit of
  TWA: 25 ppm 8 hours
- LC50 level for 20 min. exposure is
  29,000 ppm

Effect	Ammonia Concentration in Air (by volume)
Readily detectable odor	20-50 ppm
No impairment of health for prolonged exposure	50-100 ppm
Severe irritation of eyes, ears, nose and throat, No lasting effect on short exposure	400-700 ppm
Dangerous, less than ½ hours of exposure may be fatal	2,000-3,000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5,000-10,000 ppm



The following are the mitigating factors
- Ammonia is lighter than air – plume moves up quickly, reducing the exposure times
- Perceptible odor at safe concentrations
- The “self-alarming” feature of ammonia is particularly useful since readily detectable odor concentration is well below the fatal level
- Ammonia is NOT a carcinogenic substance

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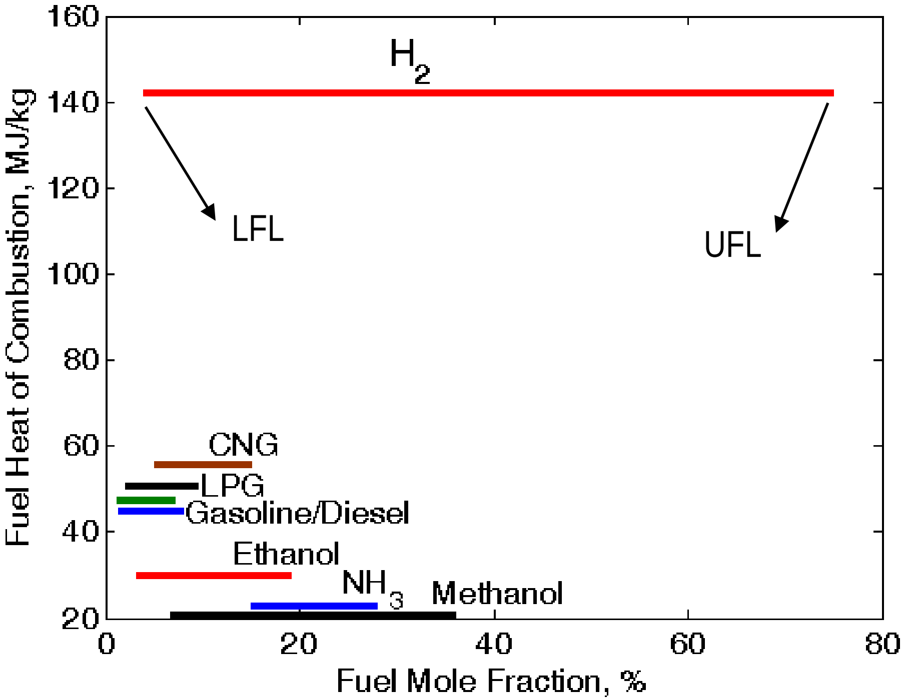
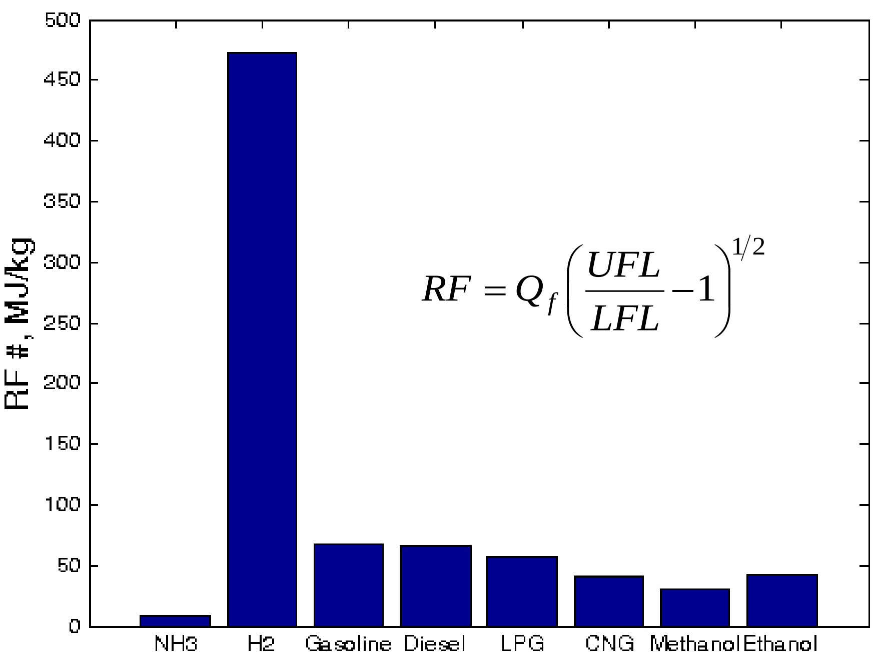
Safety – Fire/Explosion Hazard

- Ammonia has
  - Low heat of combustion
  - Narrow flammability limits
- Fire/explosion hazard for ammonia is very low





$$RF = Q_f \left(\frac{UFL}{LFL} - 1 \right)^{1/2}$$

- RF index is used to assess the fire/explosion hazard of a flammable substance
- Higher RF # indicates more fire/explosion hazard
- RF number for ammonia is much smaller than the other fuels
- RF # of H2 is almost 100 times larger

Safety – Tank Rupture Hazard

PV Driven Explosions

- Energy associated with high pressure gases
- H2 and CNG are stored at extremely high pressures resulting in substantial PV energies in the storage vessel

BLEVE's

- Explosive boiling of a saturated liquid
- Both ammonia and LPG are subject to BLEVE events
- Fatal BLEVE events have been reported with both substances

Fuel	TNT equivalent for 1 kg of fuel	Relative Mass Basis	TNT equivalent for 1 MJ of fuel	Relative Energy Basis
Hydrogen @ 10,000 psi	570 g	50	4.1 g	7
Ammonia @ 298 K	11 g	1	0.6 g	1

- No combustion energy is used in the calculations
- Reported ammonia BLEVE's are limited to large industrial systems
- BLEVE's are unlikely in the small tanks of transportation systems
- Melting liners can be used to prevent fire induced BLEVE's

Blast wave and fragment hazards associated with the rupture of a small ammonia tank is negligible
The rupture of GH2 and CNG vessels present a significant risk

Safety – Experience Base & Safety Record

- Ammonia is a widely used commodity
- Extensive knowledge base exists in
  - Production of ammonia
  - Transportation of ammonia
  - Storage of ammonia
  - Design of ammonia systems (including a comprehensive list of compatible materials)
  - Safe handling
  - Emergency procedures

- Ammonia is regularly handled by farmers in relatively large quantities
- Ammonia related accidents are rare in agriculture
- By following a set of relatively simple rules, ammonia can be handled safely by people with minimal training

Excellent data base exists on ammonia related accidents

Ammonia has an excellent safety record

NH3 is overall as safe or safer than any other fuel

Safety – Ammonia Vehicle Safety Studies

Two comprehensive studies on the safety of ammonia as a transportation fuel exist

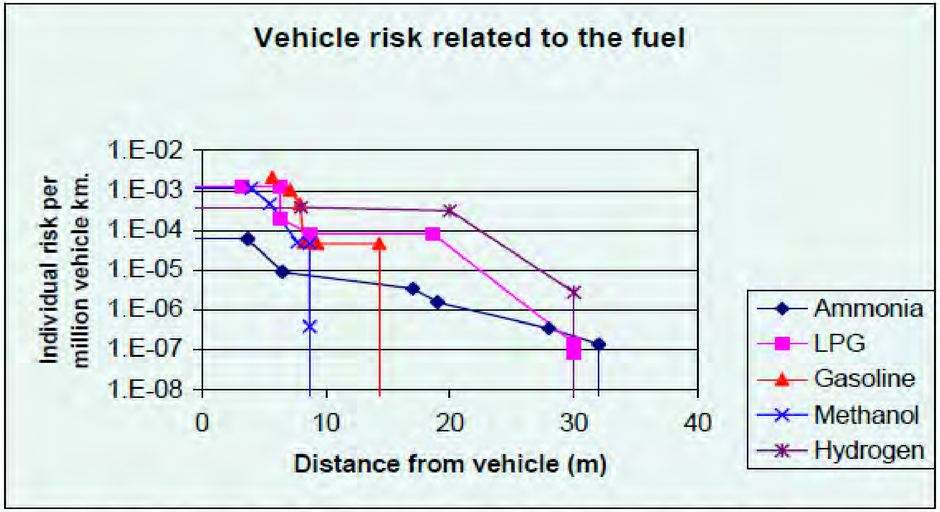


Figure 10 Comparison of individual risk as function of distance to a vehicle

Risk (per million km) is plotted against the distance from the vehicle for various fuels. Flash fire, heat radiation, explosion and toxicity damage modes are included in the calculations

Ref.: "Safety Assessment of Ammonia as a Transport Fuel", RISO National Laboratory, Denmark, 2005

The other study, by Quest Consultants of Norman, OK, came to a similar conclusion: the safety issue is NOT a show stopper for ammonia as a transportation fuel

Gas Turbine Power Generation – Role of Ammonia

Target Market 3 – Lightweight and Micro Gas Turbines

- Even with the current production technologies and excluding the CO_2 emission related issues ammonia is an economically viable option for
  - Oil fired light weight gas turbine systems
  - Oil fired micro gas turbines used for distributed power generation
- Note that since CO_2 sequestration is NOT feasible for these relatively small power generation units, ammonia has huge environmental advantages over fossil fuels.
- This market opportunity exists currently and does not require the development of new production/distribution/storage technologies for ammonia.

Target Market 4 – Heavy Duty Gas Cycles

- Most of these plants utilize natural gas. Thus within the current paradigm switching to ammonia is not economically viable.
- However since ammonia is a commodity that can be shipped cost effectively compared to natural gas, the production of ammonia in large production facilities at the natural gas source (where the natural gas is as low as the 1/10th the market value in the US*) using CO_2 sequestration would make ammonia a viable alternative to natural gas even for the heavy duty combined cycle power generation plants.

* Ref: *Feibelman and Stumpf, Sandia National Laboratories*

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