Diesel Reforming For
Solid Oxide Power Generation

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Outline of Presentation

- Diesel fuel sources and characteristics
- Diesel fuel reforming: approaches, challenges, implications
- Examples of diesel reforming for Naval Ship Service Program
  - Fuel Cell Energy
  - McDermott Technology
- Effect of sulfur on nickel catalyst activity
- Sulfur removal alternatives to hydroprocessing
- Off-stack vs. on-stack reforming
- On-stack hydrocarbon electrochemical oxidation
- Conclusions

Diesel Fuel: Production and Supply

- Diesel derives from several crude oil distillation cuts
  - Distillate—straight run or with hydrotreating
  - Vacuum gas oil—hydrocracking or catalytic cracking plus hydrotreating
  - Resid—coking plus catalytic cracking plus hydrotreating
- Crude fraction and extent of upgrading determines quality
  - Sulfur content
  - Aromatics and polynuclear aromatics (PNA) content
- Synthetic diesel (Fischer Tropsch) is produced from syngas
  - No sulfur
  - No aromatics

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Diesel Quality Varies With End Use

	California	US Other Than California			
	CARB	LSD	Off Road	Heating Oil	Marine
Volume, MM barrels	16.0	196.4	53.4	32.3	2.5
API Gravity	36.5	34.4	34.4	32.6	33.9
Sulfur, ppmw	140.0	350.0	2950.0	1720.0	4790.0
Cetane Number	50.1	44.1	47.4	Not regulated	Not regulated
T10, F.	440.0	431.0	432.0	430.0	442.0
T90, F.	623.0	606.0	610.0	616.0	613.0
Aromatics, vol%	18.2	32.3	31.3	Not regulated	Not regulated
Polynuclear aromatics, vol%	2.8	5.2	2.6	Not regulated	Not regulated

Source: M. Kulakowski; CARB Fuels Subcommittee Meeting; April 29, 1999

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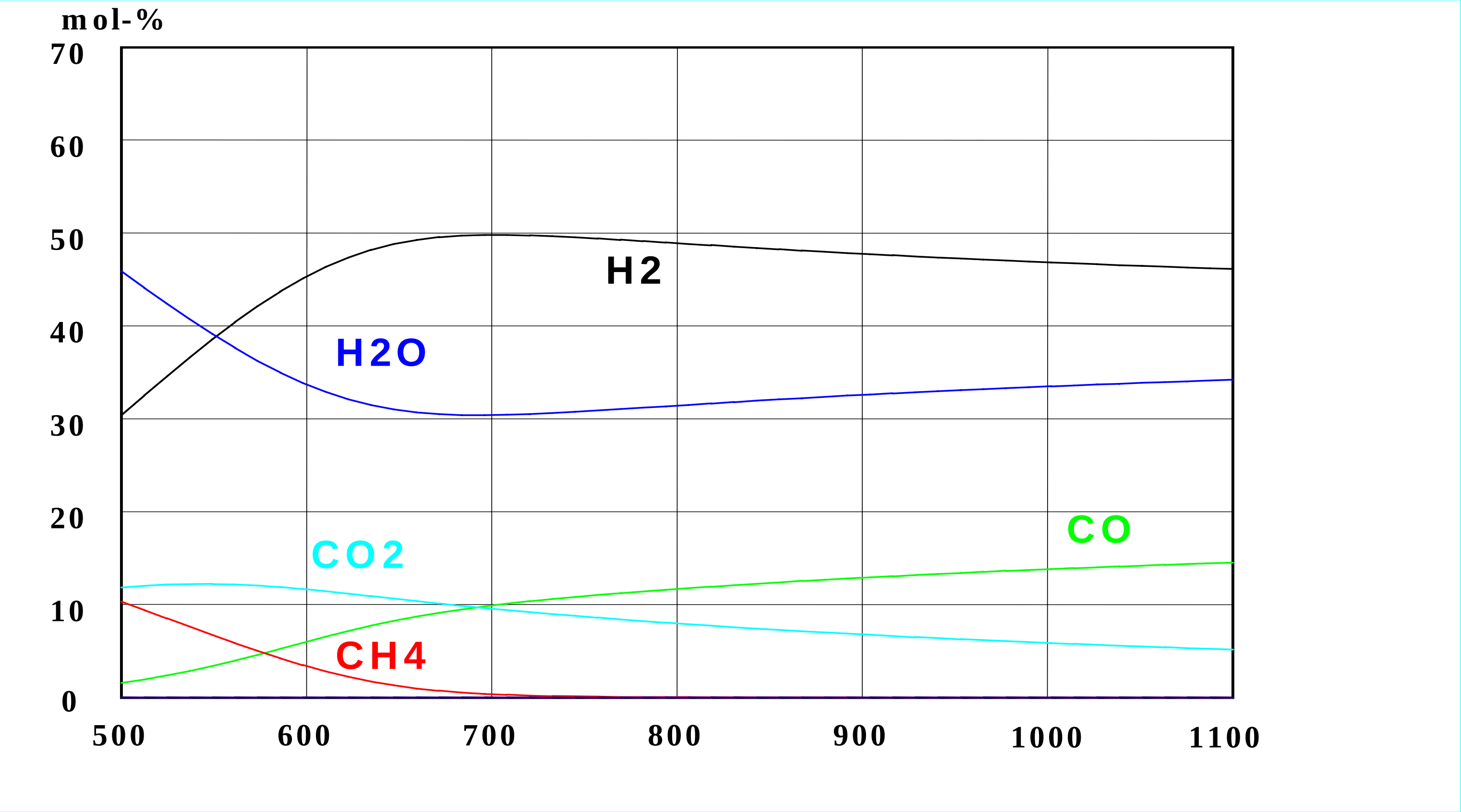
Steam Reforming of Dodecane

- $C_{12}H_{26} + 12H_2O = 12CO + 27H_2$
- At S/C ratio ≅ 3, H_2O is significant diluent fed to stack



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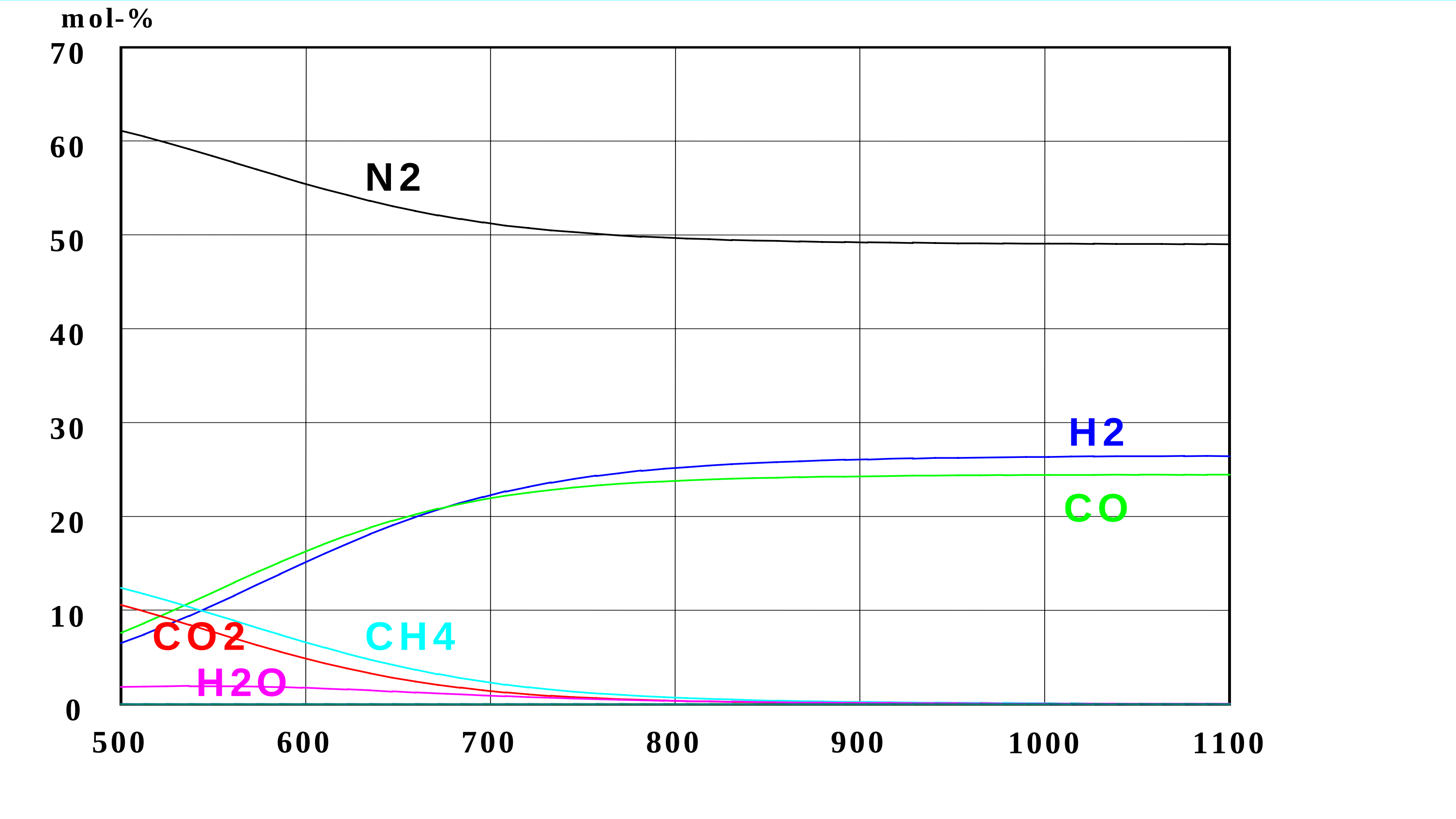
Partial Oxidation of Dodecane

- $C_{12}H_{26} + 6O_2 = 12CO + 13H_2$
- Feed to stack is rich in CO, N_2



Issues and Implications of Current Reforming Approaches

- Steam reforming
  - Response time of system
  - Water management (self-sufficiency, freezing, reformate dilution)
  - Effective waste anode gas utilization
  - Partial on-stack steam reforming could reduce diluent water fed to stack and overall water inventory
- Partial oxidation/autothermal reforming
  - Nitrogen dilution of reformate
  - Less effective waste anode gas utilization
  - On-stack partial oxidation could reduce diluent nitrogen fed to stack
- Effective heat integration between processor and stack essential for high efficiency operation

Specific Issues With Diesel Fuel Reforming

- Diesel fuel is difficult to reform
  - Fuel vaporization
    - Energy intensive
    - Slows system response
    - Tendency toward cracking, carbon deposition in preheat zones
  - Fuel reforming
    - Sulfur in fuel deactivates catalysts
    - More refractory compounds -- higher severity operation
    - Carbon deposition more favorable
    - More severe operating conditions
      - Higher temperatures
      - Higher S/C ratios
      - Potential for catalyst deterioration
- Diesel fuel has lower H/C ratio than other hydrocarbon fuels

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Specific Issues With Diesel Fuel Reforming

- Benchmark data on diesel reforming generally unavailable
  - Catalyst activity
  - Catalyst durability
  - Catalyst cost
- Pre-reforming to C_1 species is frequently implemented in commercial scale reactors
  - Allows separate optimization of C_n and C_1 reformer
  - But, pre-reforming catalysts are prone to deactivation by sulfur

Sulfur Irreversibly Poisons Nickel Steam Reforming Catalysts

Temperature, ºC.	Sulfur, ppmw
600	0.06
700	0.60
800	3.7

- Carbon deposition increases effect of poisoning
- Similar effect anticipated for nickel anode

Source: Catalyst Handbook, 2nd Ed.; M. Twigg, ed.; Chapter 4

Fuel Cell Energy's Approach to Diesel Fuel Processing (Molten Carbonate)

- Hydrotreat fuel
- Remove H_2S by ZnO adsorbent bed
- Pre-reform fuel to provide C_1 feed for second stage (primary) reforming
- Complete C_1 reforming adjacent to stack (indirect internal reforming)

Source: P. Patel, private communication

McDermott's Approach to Diesel Fuel Processing (PEM)

- Autothermal reforming using sulfur tolerant catalyst (no pre-removal of sulfur)
- High temperature shift
- H_2S removal with regenerable zinc titanate adsorbent plus ZnO polishing
- Low temperature shift
- Prox

Source: Scoles et. al., 2000 Fuel Cell Seminar, Abstracts, p. 252; R. Ryan, Jr, private communication

Fuel Cell Energy, McDermott Approaches to Diesel Fuel Processing

- Both approaches are feasible at large scale of Ship Service Program, but less so for compact fuel processors
- Sulfur removal is more difficult in compact fuel processors for solid oxide fuel cells
  - 1^{st} step hydrotreating requires
    - High P H_2
    - Available hydrogen at startup
    - Relatively large reactors
  - Sulfur tolerant ATR with subsequent H_2S trapping requires
    - Cooling reformate for compatibility with ZnO-type adsorbents
    - More difficult heat integration with solid oxide

Fuel Cell Energy, McDermott Approaches to Diesel Fuel Processing

- Effective path forward for solid oxides could borrow from both approaches
  - Sulfur-tolerant (pre)reforming at moderate temperatures
  - H_2S removal via adsorption
  - Partial on-stack reforming for better heat integration

Alternative Desulfurization Approaches : Are They Applicable to Compact Reformers?

- Adsorption/reaction
  - Weak physical adsorption—ineffective for diesel sulfur
  - Reactive adsorption based on metal-loaded zeolites (JPL)--moderately effective for diesel fuel
    - 50% desulfurization of high sulfur feeds
    - Adsorbents regenerable
- Selective oxidation of sulfur organics (Petrostar)
  - Two liquid phase peroxide oxidation
  - Two liquid phase solvent extraction
  - Effective in removal of hds-resistant molecules
- Biodesulfurization (Energy Biosystems Corporation)
- Conclusion: large unmet need for high efficiency, compact diesel desulfurization

Off-Stack or Partial Off-Stack Reforming of Heavy Fuels is Necessary

- Complete on-stack reforming of heavy fuels unfeasible
  - Sulfur poisoning
  - Carbon deposition
- Compact low pressure sulfur removal technology would eliminate requirement for post-reformer H_2S cleanup
- Partial reforming or pre-reforming coupled with H_2S removal should also be investigated
  - Allows different catalysts for C_n vs. C_1 reforming
  - Facilitates better heat integration of unit operations
  - But, sulfur tolerant pre-reforming catalyst currently unknown

Partial On-Stack Steam Reforming Deserves Consideration

- C_1 is best candidate fuel
- Overall heats of reaction support on-stack steam reforming of fuel
  - $CH_4 + H_2O = CO + 3H_2$ $\Delta H_{800} = +54.0$ kcal/mole CH_4
  - $CO + 3H_2 + 2O_2 = CO_2 + 3H_2O$ $\Delta H_{800} = -245.5$ kcal/mole CH_4
- Water generated on stack can support steam reforming
  - Lower input water duty
- Challenges:
  - Moderate reforming activity to avoid endothermic cold spots
  - Minimize excess H_2O from upstream pre-reformer
  - Tolerate to ppb-to-ppm levels of sulfur

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Partial On-Stack Hydrocarbon Oxidation Also Deserves Consideration

- Nitrogen diluent avoided
- Produces H_2O and CO_2 directly, no localized endotherm
- Couple with on-stack steam reforming for heat management
- But …. electrocatalytic oxidation is at early stages of development

Conclusions

- Diesel fuel has end use-dependent composition and properties
  - Mandated improvements continue for transportation application
  - Sulfur in fuel remains issue for foreseeable future
- Diesel is challenge to reform
  - Vaporization
  - Sulfur, aromatics, carbon deposition
  - Additional challenges emerge with compact reformers
- Various reforming options are possible
  - All have apparent limitations
  - Some require breakthrough developments

Conclusions

- Sulfur handling may dictate ultimate approach to diesel fuel processing
  - Conventional sulfur removal (hds) not an option
  - Catalytic pre-reforming attractive, but sulfur sensitive
  - High temperature sulfur tolerant ATR or steam reforming possible
    - H_2S removal not well heat integrated
    - Catalyst activity and longevity needs to be established
  - Nickel anode also sulfur sensitive
  - Challenge and opportunity for new technology breakthroughs
- Combination off-stack and on-stack reforming is longer term goal
  - Off-stack pre-reforming for carbon control
  - On-stack C_1 steam reforming or electrocatalytic oxidation for increased efficiency