Using the full exergetic quality of solid fuels.

DCFC Workshop, NETL DOE Pittsburgh

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Outline

- DOE goals
- Why emphasize solid fuels ?
- Thermodynamics, exergy and entropy production
- Direct Carbon FC
- A fuel cell that produces H₂ and converts heat into power??
- Exergy efficient integrated solar-biomass systems
- Conclusions



DOE goal for the 21st century fuel cell



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Why emphasize solid fuels ?

1. Solid fuels will become more important in the future!

- Coal: abundant and cheap
- Biomass: sustainable
- Waste: negative value
- More efficient CH₄ conversion routes involve solid C

NB: Also liquids are closer to solids than to gases in terms of their exergy value.



Why emphasize solid fuels ? (2)

2. Present conversion of solid fuels is not efficient

- Combustion (Carnot limitation)
- Gasification (Carnot & entropy production)



H₂/O₂ Fuel cell and Carnot efficiency





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Entropy production in conventional gasification

$$C + \frac{1}{2}O_2 = = > CO + Q(heat)$$

 $\frac{1}{2}$: 1

1. Doubling of the # gas molecules 2. Entropy $\Delta S = Q/T$

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Electrochemical gasification :



- (Solar) Heat can be converted into power with an efficiency higher than the Carnot efficiency!
- Self regulating process



The 'holy grail' of electrochemistry : A Fuel Cell that produces hydrogen and converts heat into power !



$\mathbf{CO} + \mathbf{H}_2\mathbf{O} = => \mathbf{H}_2 + \mathbf{CO}_2$

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How to reach or approach this 'holy grail' ?

- Electrochemistry is the key technology because it can approach reversibility = zero entropy production = conservation of exergy.
- Use small driving forces F since $\Delta S \sim (F)^2$
- Solar energy is ideal renewable source to supply the heat, thereby increasing the efficiency of this technology as well.







How to reach or approach this 'holy grail' ? (1)

1. Direct Carbon Fuel Cell:





How to reach or approach this 'holy grail' ? (2)

2. Direct Carbon Fuel Cell at high T: $C + \frac{1}{2}O_2 => CO$



How to reach or approach this 'holy grail' ? (3)

3. In-direct Carbon Fuel Cell/integrated systems :





Explaining the difference between conventional combustion/gasification and electrochemical conversion.



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Energy Research Policy

- Identify solar-biomass regions
- Prevent entrenchment in inefficient technologies by designing a roadmap to develop EXEFF systems
- Electrochemistry and fuel cells are key technologies
- 'First' systems 'then' components
- Demand specification of exergy efficiency
- Promote cooperation between research areas; solar biomass, coal and fuel cells and AI production industry
- Promote cooperation between Europe, USA and Japan



Countries with large potential for Solar and Biomass can become the energy (H₂) producing countries of the future.



How to prevent entrenchment in conventional gasification?





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Conclusions

- Solid fuels will become increasingly important in the future.
- Present conversion systems for solid fuels are inherently inefficient.
- New conversion systems for solid fuels with higher (exergy) efficiency are possible; ultimately a flexible hydrogen & power producing system converting heat into power can be conceived.
- Fuel cell technology is a key-technology.
- The DCFC producing pure CO₂ is one of the very promising options
- A well defined roadmap is necessary to provide a framework for the development of these systems and to prevent entrenchment in inherently inefficient technologies



Identification of R&D needs

- Design of a <u>roadmap</u> towards exergy efficient energy conversion systems with socio-economic analysis of flexible H2/power production
- Design and analysis of exergy efficient energy conversion <u>systems</u> and comparison with conventional systems to show potential benefits
- Integration of solar with gasification and fuel cells
- Steam and CO₂ gasification
- Molten salt (carbonate) gasification and in-situ gas cleaning.
- DCFC design and up-scaling
- Electrochemical oxidation of Carbon including transition from CO₂ to CO production as function of T
- Use of multi-valent ions (V) as catalyst for Carbon oxidation



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Following slides contain additional info for question session.

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Illustration of the reversible and irreversible heat losses in a fuel cell.





• The pyrolysis of $CH_x => C + (x/2)H_2$ consumes 3-8% of fuel value; no ash

JFC:July 03

Concept Direct Carbon Conversion (DCC): electric power from electrochemical reaction of C and O₂





- Total efficiency ~ 80% of ∆H_{std}
- Pure CO₂ product for reuse/sequestration
- Use highly reactive carbons from CH_x pyrolysis
- Inherent simplicity

JFC:July 03

LLNL Carbon/air cells operate at sufficiently high power density for base-load applications



Outline

Table 3 Order of magnitude comparison between the electrochemical conversion efficiencies of C, H₂ and CH₄ (Cooper, J. F. et al 2000)

Fuel	η_{fc}	$\eta_{\text{Nernst loss}}$	η_{irr}	η_{tot}
С	1.0	1.0	0.8	0.8
H ₂	0.7	0.8	0.8	0.45
CH ₄	0.89	0.8	0.8	0.57



Looking for ways to use the full exergetic quality of solid fuel !!

- Solid fuels become increasingly more important (security of supply).
- Coal because it's abundant.
- Biomass because it is CO₂ neutral.
- Waste.
- Also liquids are closer to solids than to gases in terms of their exergy value.







pCO2=0.00033 atm

RT/nF * ln(1/pCO₂) = RT/nF * 8 = 160 mV (T = 650 °C)



Figure 6 Indirect Carbon Fuel Cell concept by Nakagawa and Ishida (Nakagawa, N. and Ishida, M. 88)

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Learning curves of conventional and potentially more efficient technology When to make a transition?

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Indirect Carbon SOFC & gasifier with molten carbonate assistance.





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Combination of Molten Carbonate coal/biomass gasifier and MCFC

- In the syngas (hydrogen) producing integrated system the Fuel Cell can operate at low utilization.
- Hence low Nernst loss and high fuel cell efficiency.



Exergy efficiency of Coal/Biomass conversion





Solar Exergy (approx.)



