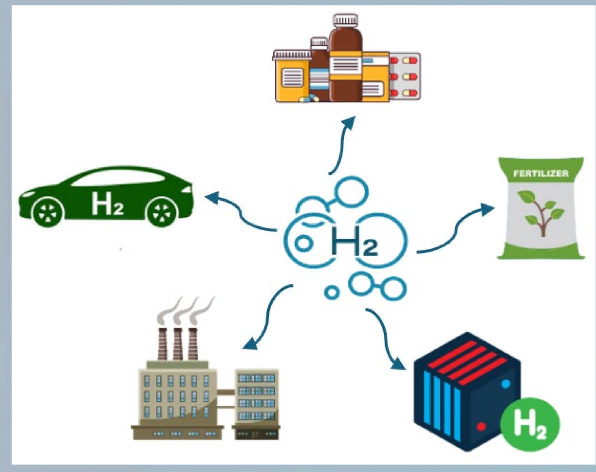
E-Field Enhanced Thermo-Catalytic Decomposition of Methane

J. Heim II, R. Vander Wal, A. van Duin, M. Kowalik

Earth and Mineral Sciences Energy Institute, National Energy Technology Laboratory

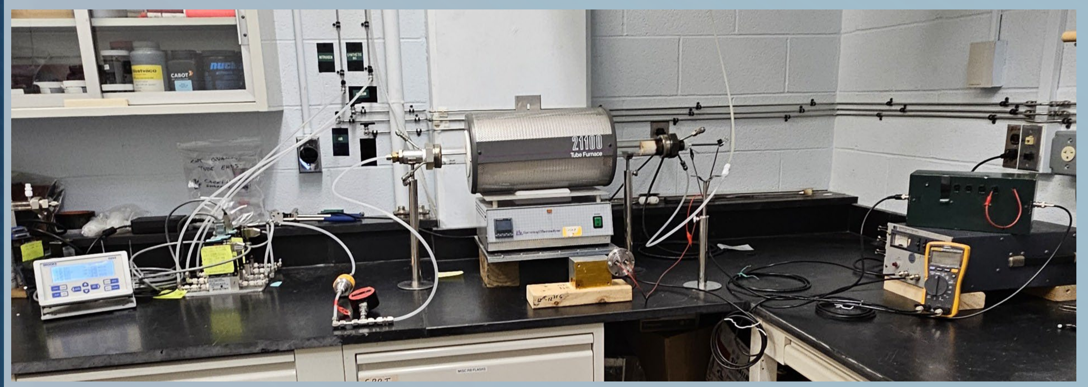
Introduction



Hydrogen is a valuable clean energy carrier. Its potential applications include fuel cells, hydrogen vehicles, pharmaceuticals, fertilizers, jet fuels, synfuels, and petrochemicals. Currently, it is used in oil refining and in producing methanol, ammonia, and green steel. 95% of hydrogen is produced via steam methane reforming (SMR), an environmentally costly and laborious process that has CO/CO2 byproducts, consumes water resources, and requires stock desulfurization, CO2 removal stages and steam generation.

Thermo-catalytic decomposition of methane, an alternative technology that produces turquoise hydrogen by decarbonizing fossil fuels such as natural gas, is an envisioned bridge to the hydrogen economy. However, the carbon deposited in the conventional TCD process covers active sites, decreasing rates and deactivating the catalyst which must then be regenerated via gasification. For both TCD and associated regeneration reactions, applying an electric field offers the potential for maintaining and increasing the reaction rate, either through an increase in the number or type of active sites or a shift in their energy level. Recycling the carbon byproduct for use as a catalyst within the applied E-field has the potential of making TCD autocatalytic.

Materials and Methods

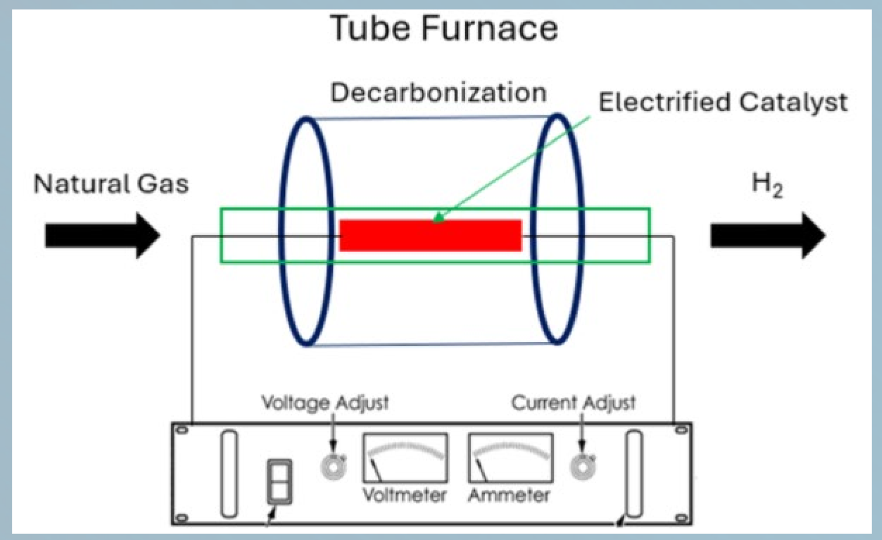


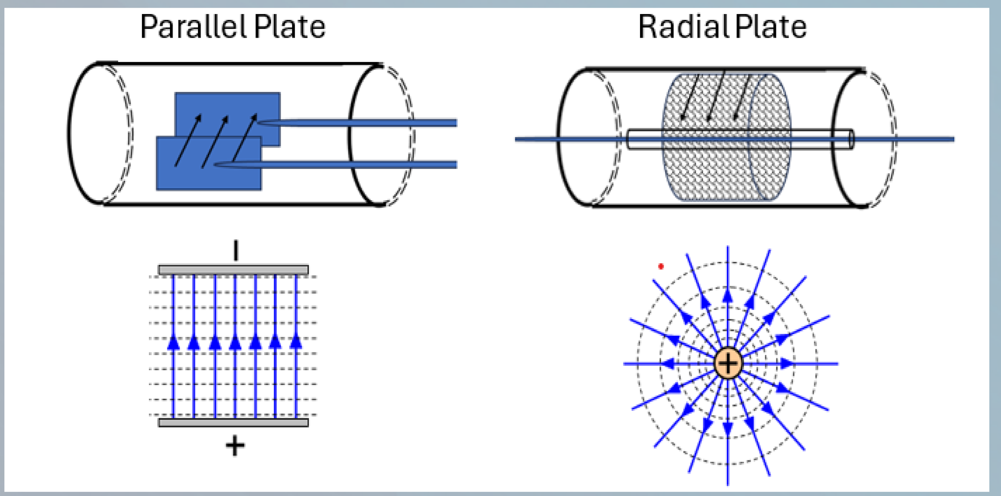
Capacitive Configuration

- high voltage, near-zero current
- strong E-field offers the best potential for mechanistic changes through dipole interactions

Capacitive: Parallel Plate

- employs parallel plates with both electrodes in the reaction tube, allowing for ready testing of carbon deposition with respect to the field direction
- ideal for active site measurements (atomic oxygen % via XPS) on the carbon-covered electrodes

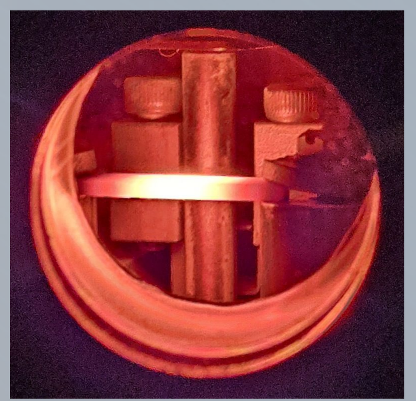




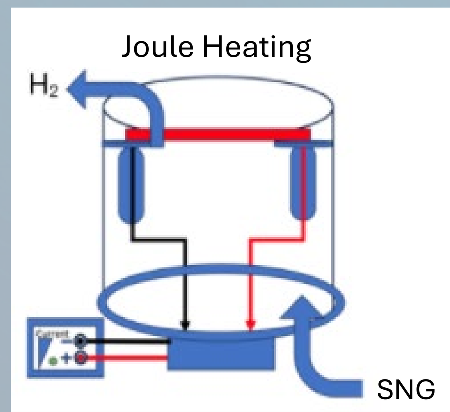
Capacitive: Radial Plate

- higher electrode surface area
- radial geometry naturally forces SNG through the E-field lines
- extended path length (and thus interaction time)
- a quartz tube inserted around the inner electrode prevents shorting due to filamentous carbon growth

Resistive Configuration

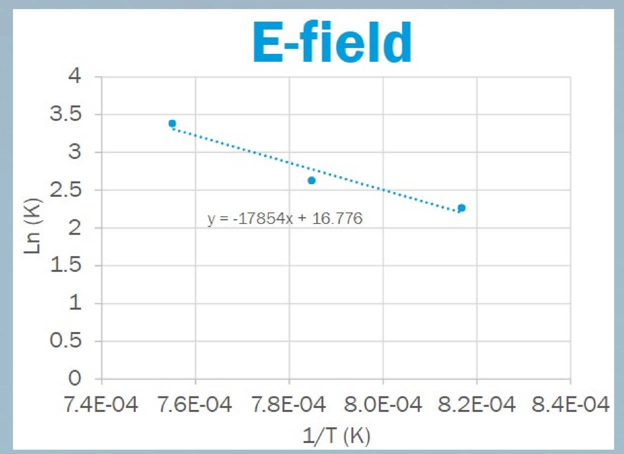


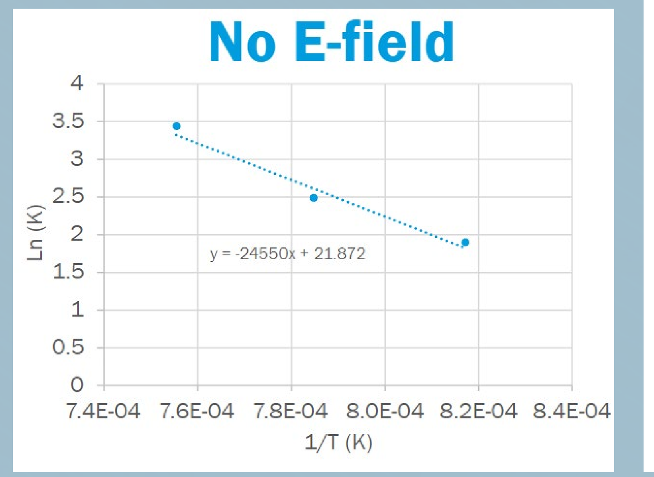
- low voltage, high current
- current flows directly through the carbon catalyst, providing high negative charge and supplemental Joule-based heating (estimated from electrical power; temperature measured by optical pyrometry)
- Possibly more energy-efficient



Results

Kinetics





- E-field TCD has a higher conversion rate than standard TCD at the lower end of the temperature range (950 - 1000 °C), suggesting that the applied E-field lowers the energy barrier for conversion.
- Arrhenius analysis shows that E-field TCD has a 56% lower activation energy (90 vs. 140 kJ/mol) than standard TCD.

Kinetics: E-field vs. Standard TCD

Configuration	Temperature (°C)	% Conversion	Activation Energy (kJ/mol)
E-field TCD	950	19	90
E-field TCD	1000	28	90
E-field TCD	1050	38	90
Standard TCD	950	13	140
Standard TCD	1000	24	140
Standard TCD	1050	38	140

*Notably, at 1050 °C and 75% SNG, the conversion is 65%.

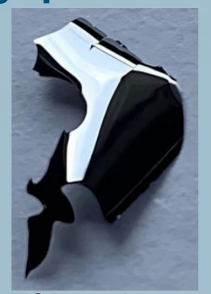
$$\text{Rate} = k\,[CH_4]$$

$$\left[\frac{0.75}{0.50}\right]^x = \left[\frac{0.288}{0.185}\right] = 1.1 = \text{First order reaction}$$

- The E-field facilitates non-planar dendritic carbon growth, maximizing surface area and thereby increasing the number of active sites available for catalyzing reactions, as shown in the images below. This contrasts with standard TCD, in which the carbon deposition is planar, causing catalyst deactivation.

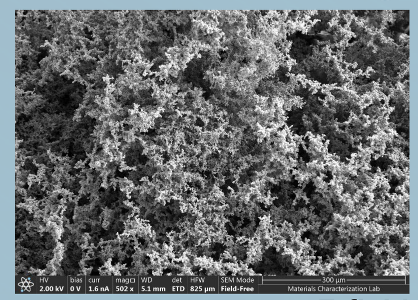
Photographs

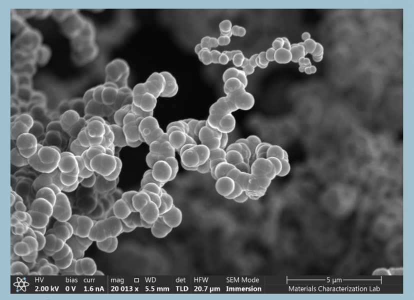
E-field carbon



TCD carbon

SEM

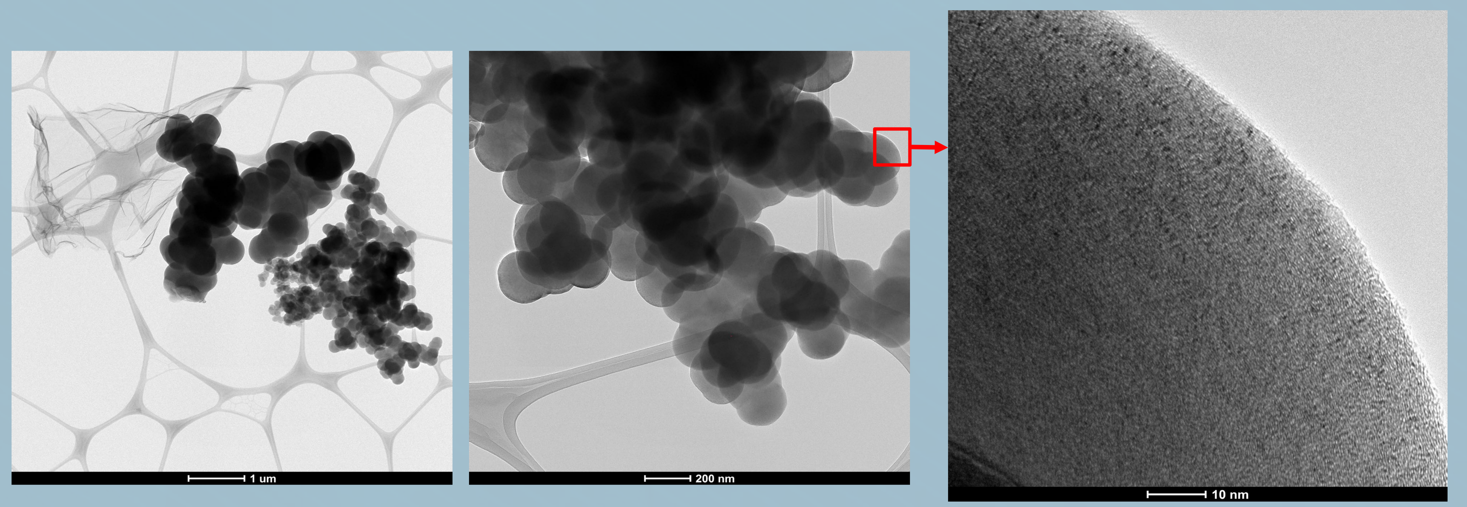




E-field carbon

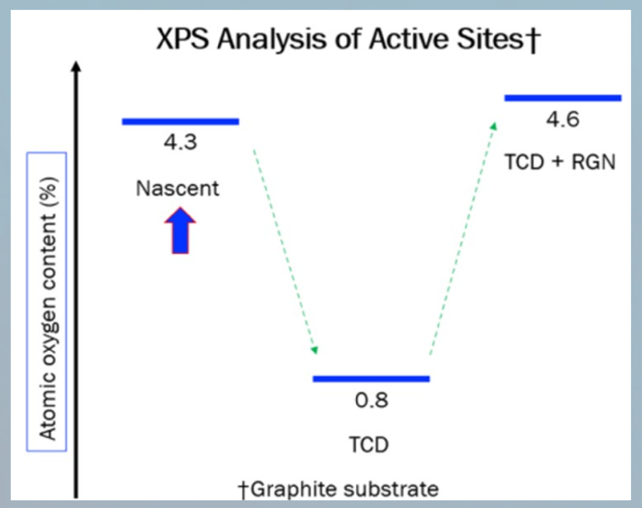
- TEM images show that E-field carbon resembles an aggregation of variously-sized soot particles. (The single-layer graphene sheet in the first image of the sequence was formed by the metal-dusting reaction from the stainless-steel electrodes.)

TEM



- A comparison of gasification kinetics done by TGA in the case of Joule heating and by Arrhenius analysis in the case of furnace heating suggests that activation energy is significantly lower in Joule heating.
- Application of an E-field has the advantage of free-space conversion without a packed bed; the reactor does not clog from carbon buildup, and can be readily cleaned by mechanical means, and/or by gasification. Carbon in a packed bed can be cleaned only through gasification.

XPS

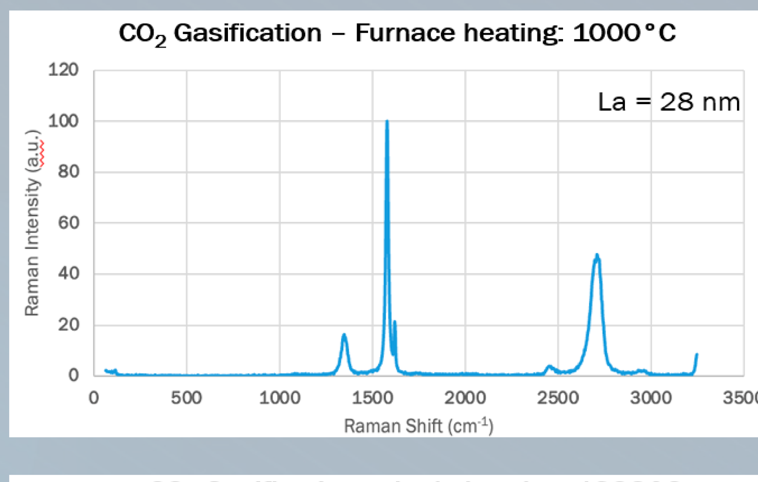


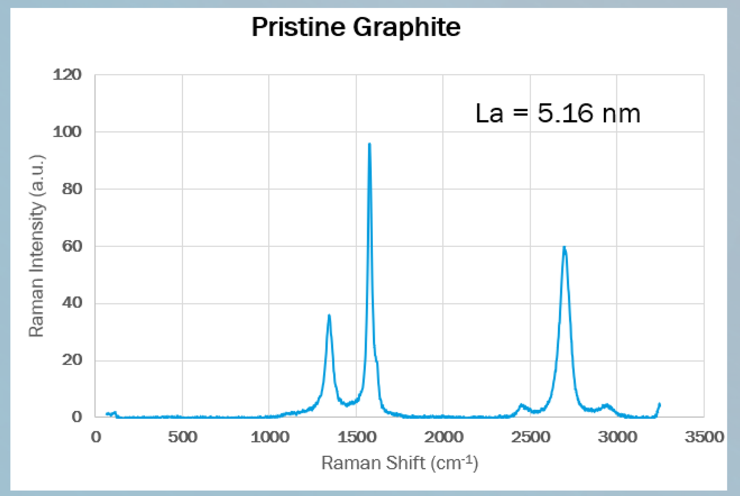
- XPS reveals a decline in atomic oxygen content of the initial carbon catalyst (from 4.3% to 0.8%) due to TCD carbon deposition blocking active sites; however, after regeneration, the number of active sites (i.e., atomic oxygen content) is greater than in the nascent catalyst.

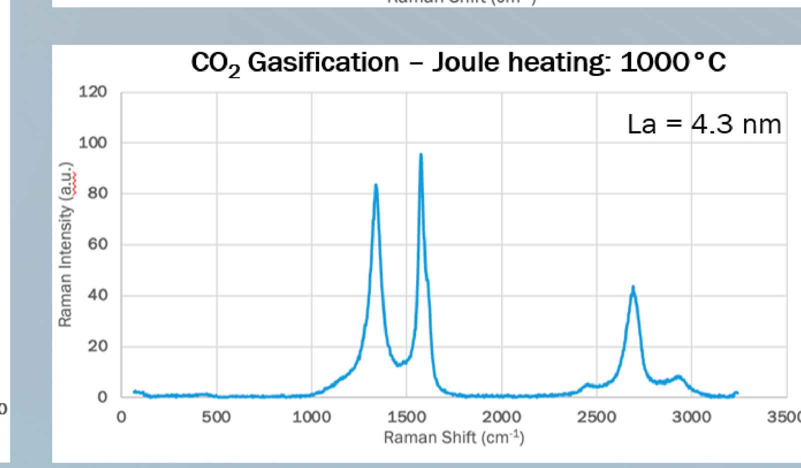
Results

Raman

- Raman analysis of CO_2 gasified graphite samples showed that Joule-based heating made the graphite sample more amorphous than furnace heating at 1000 °C. This suggests that Joule-based heating is more effective at producing active sites.

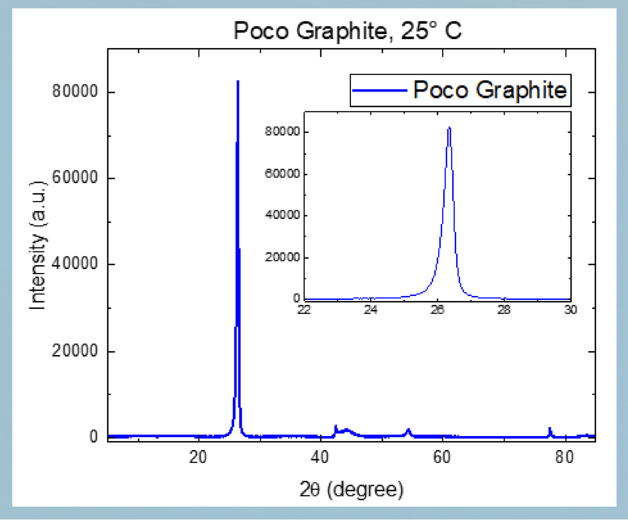


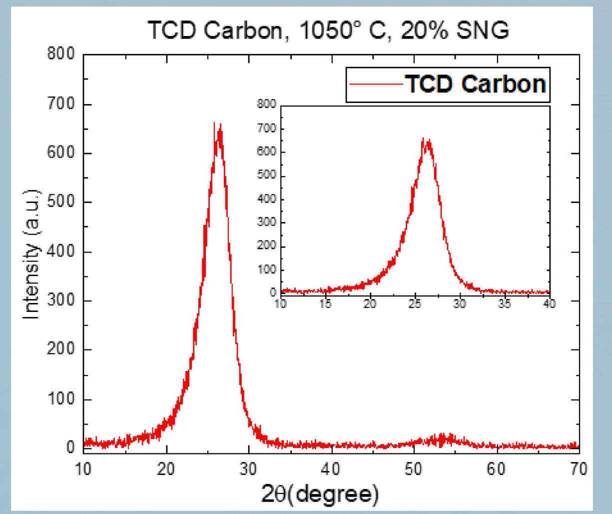




XRD

- XRD and Raman analysis indicate that E-field carbon and TCD carbon are both highly amorphous.





Poco Graphite, 25° C

Planes	d (Å)	Angle (2ϴ)	La (Å)	Lc (Å)
002	3.378	26.36		218.6
100	2.130	42.40	967.4	
110	1.230	77.55	741.1	

TCD Carbon (no EF), 1050° C, 20% SNG

Planes	d (Å)	Angle (2ϴ)	La (Å)	Lc (Å)
002	3.3701	26.43		20.7

Future Research

- Continue investigating different E-field TCD and regeneration configurations and/or varying experimental parameters to optimize hydrogen and, by extension, carbon production
- Evaluate reaction kinetics for TCD and regeneration (gasification - H_2O and reverse Boudouard - CO_2) as a function of applied E-field strength and polarity
- Map active site and kinetic dependence with reactive gases (SNG, CH_4, CO_2, and H_2O)
- Evaluate the nano- and micro-structure of E-field and TCD carbons for similarities and differences as a function of process parameters and/or E-field differences
- Investigate possible uses of E-field and TCD carbon in composites after modifying the carbon through functionalization and/or graphitization

Acknowledgements & Contact

- Jeffrey Shallenberger - XPS Analysis at the MCL
- Nichole Wonderling - XRD Analysis at the MCL

Contact Information:

- Penn State – Prof. R. Vander Wal; Email: ruv12@psu.edu
- Penn State – PhD Student J. Heim; Email: jwh44@psu.edu

PennState College of Earth and Mineral Sciences

John and Willie Leone Family Department of Energy and Mineral Engineering

Funding: This material is based on work supported by the Department of Energy, Office of Fossil Energy, under cooperative agreement DE-FE-0032070.