SAND2019-10954C

11th Ablation Workshop, September 16-17, 2019
University of Minnesota

Ablation Chemistry Under High-Heat/High Flux Testing

Presented By

Bernadette A. Hernandez-Sanchez

James Nicholas, Jonathan Coleman, James Lassa, Kenneth Armijo

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND#

Understanding Materials Under Extreme Environments

Thermal Protection System (TPS) materials must withstand extreme environments

NASA: “Project Fire Redux: Interplanetary Reentery Test (1966)
https://www.wired.com/2012/07/interplanetary-reentry-tests-1966/

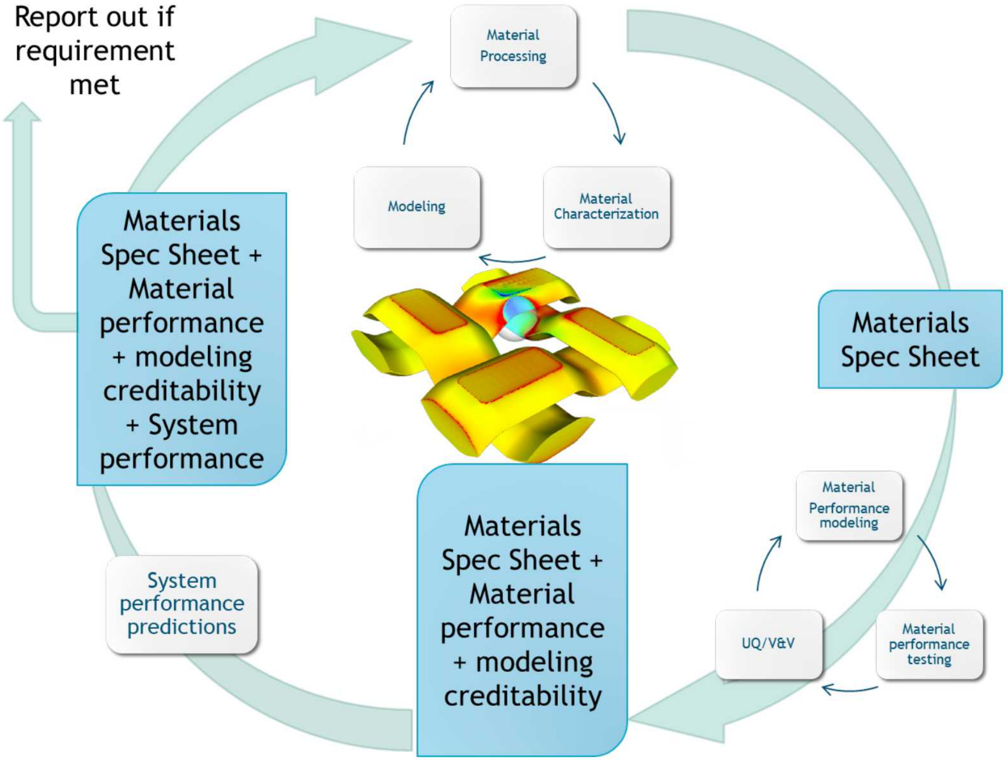
How do we quickly improve our understanding of materials used?

2-fold: computation & performance characterization.

1966 FIRE REUDUX NASA: Complex problem "no substitute for testing specific configurations and materials in the actual environment of interest"

Goal: manufacture materials & improve our understanding of properties under extreme environments through modeling efforts

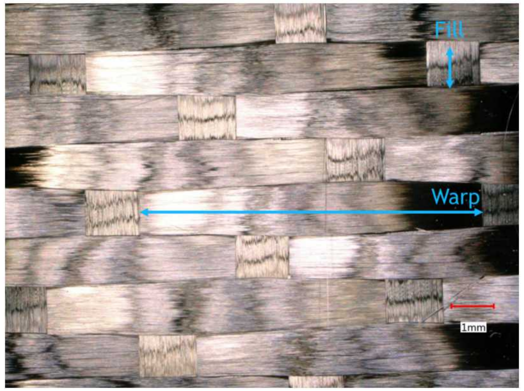
Models are using data from materials science & environmental performance to improve our understanding



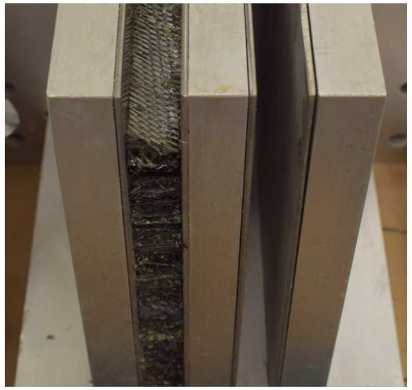
The power of the Sun is used to simulate reentry heating to verify performance behavior

*One of several Sandia testing facilities available to simulate extreme environments

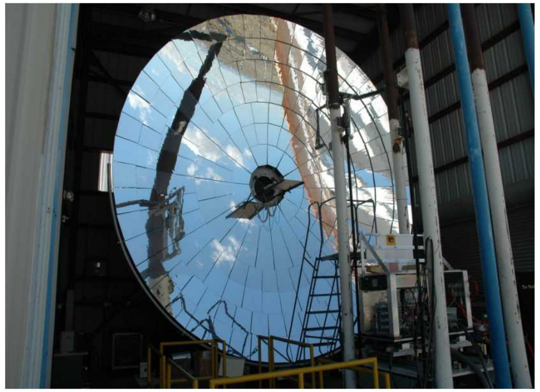
Outline



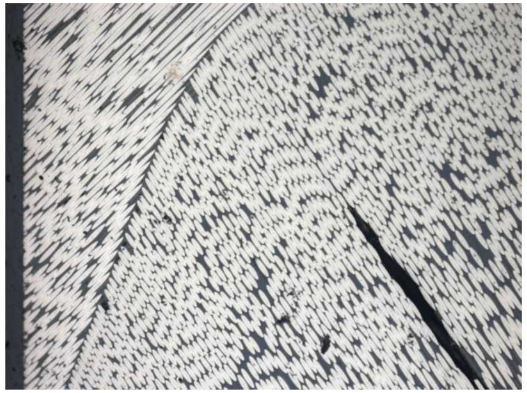
Property measurements



Coupon manufacturing



Solar furnace testing



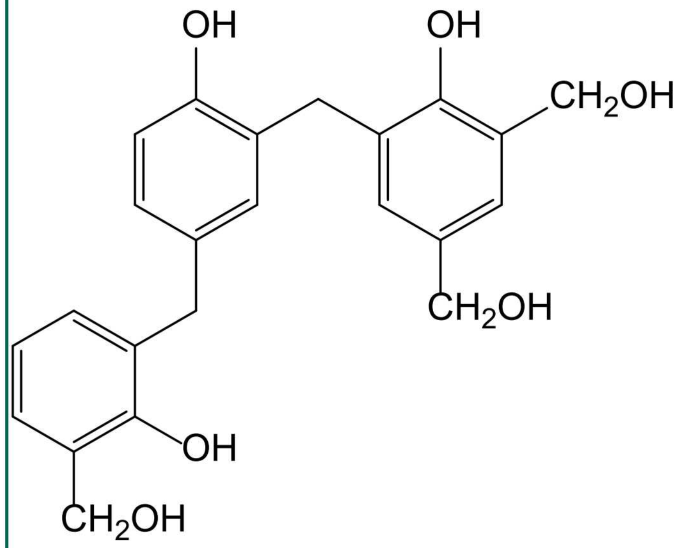
Mesoscale imaging

Goal: What can we learn from Solar Furnace Testing to better understand the ablation process?

How does the material change from precursor to ablative products with respect to temperature/atmosphere?

Constituent Precursors

Resole Resin



Monomer

Carbon Fiber (Filament)

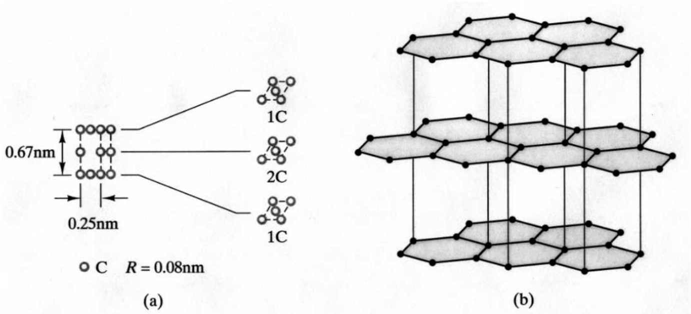
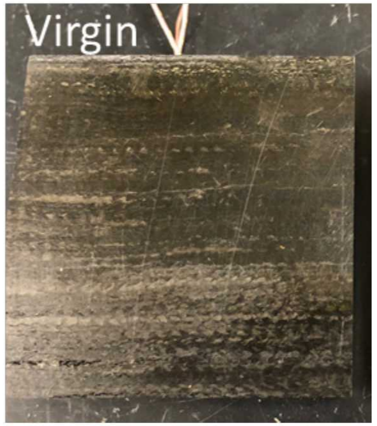


Figure 3-18 *(a) An exploded view of the graphite (C) unit cell. (From F. H. Norton,* Elements of Ceramics, *2nd ed., Addison-Wesley Publishing Co., Inc., Reading, Mass., 1974.) (b) A schematic of the nature of graphite's layered structure. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann,* Introduction to Ceramics, *2nd ed., John Wiley & Sons, Inc., New York, 1976.)*

Nanocrystalline Graphite

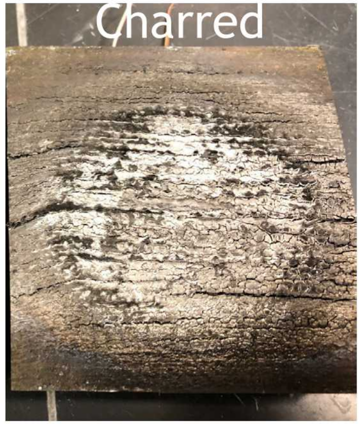
Composite

Virgin Coupon



Cured Resin
+
Nanocrystalline Graphite

Ablation Products



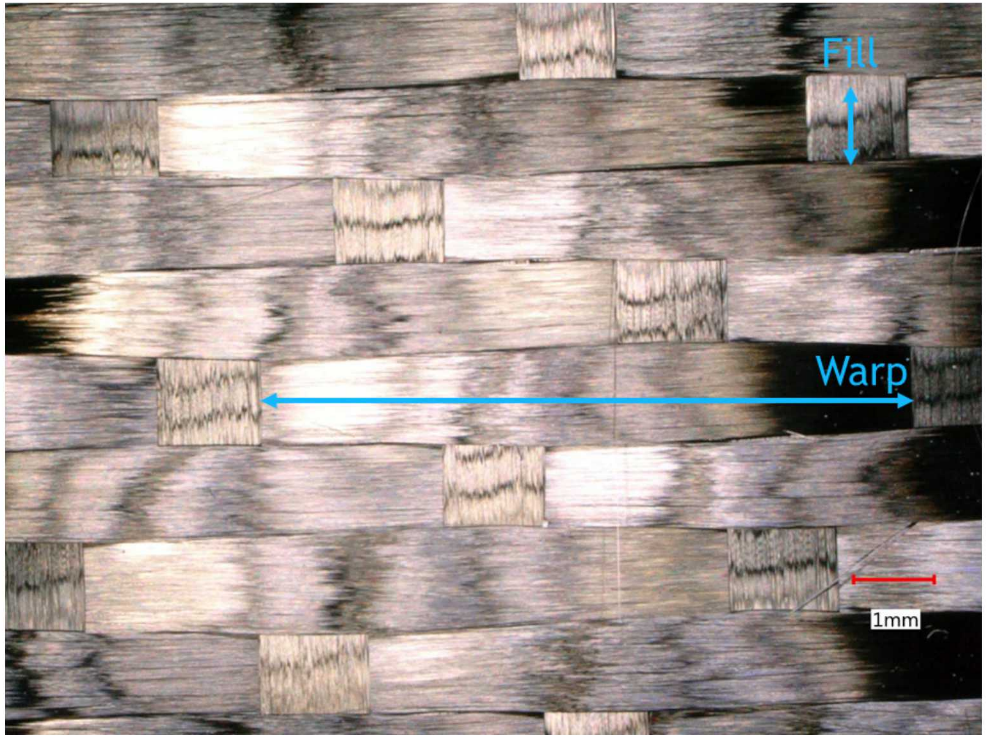
Pyrolysis Gases
+
Graphite

Hexion, Durite SC-1008

Carbon Fiber

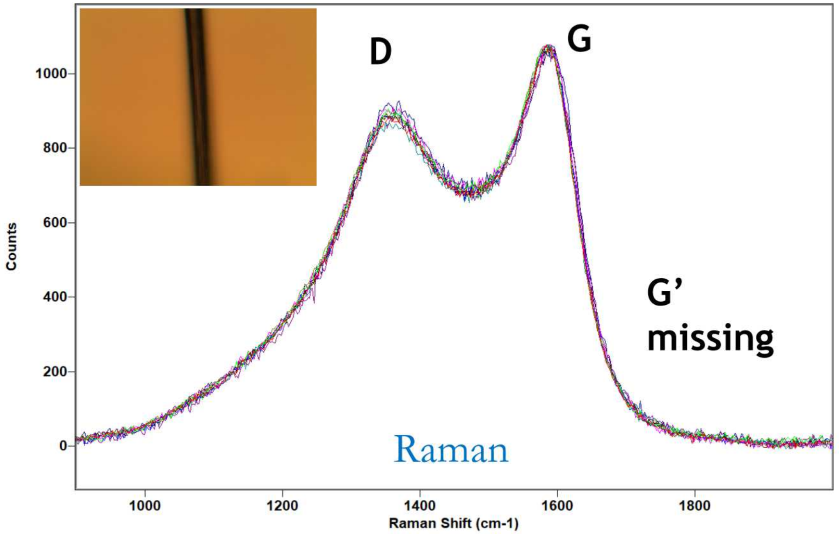
Sandia Coupons

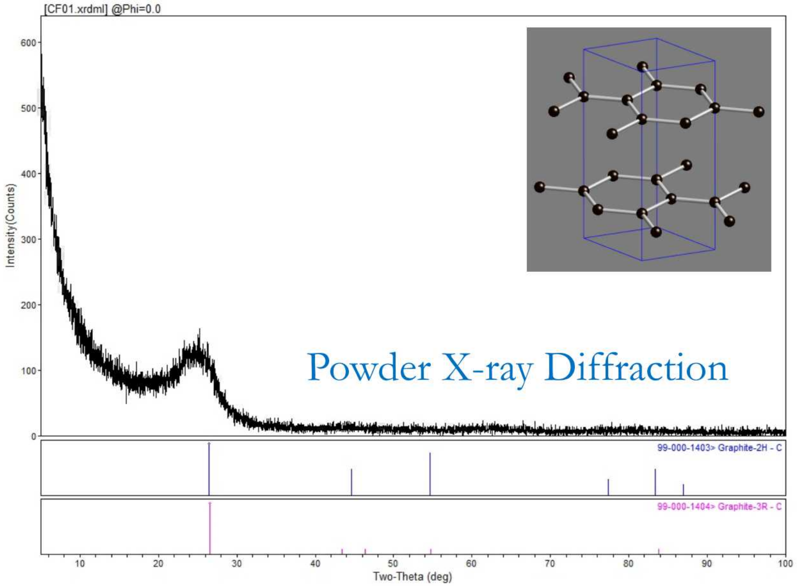
Carbon fibers have nanocrystalline graphite characteristics.



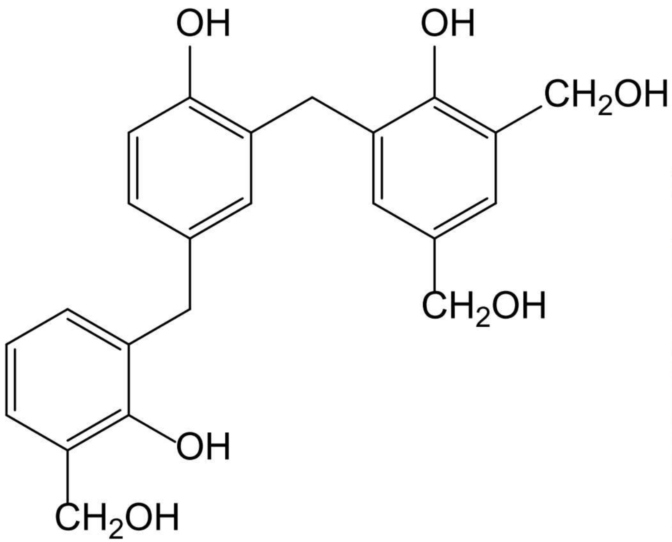
Tow	Dimensions
Warp length & width	~7.7 & 1.2 mm
Fill length & width	~1.0 & 1.5 mm
Filament diameter	~7 µm
Fabric's thickness	0.33 mm
Filaments/tow	3K

- 8-Harness weave fabric
- Filaments are nanocrystalline graphite
- TGA ~3% wt. loss under N_2 to 1200 °C





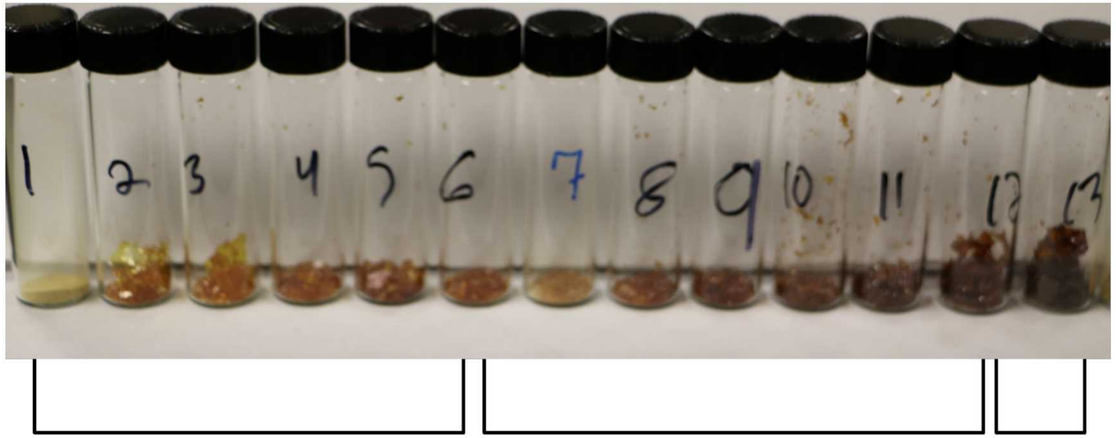
Performed analyses of neat and cured resin to understand crosslinking.



Resole monomer

Hexion, Durite SC-1008

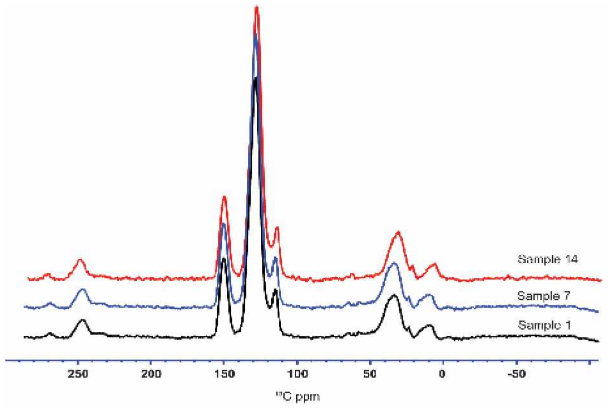
Resin Cure Temporal Study (325°F/163°C)



10 min

20 min

30 min

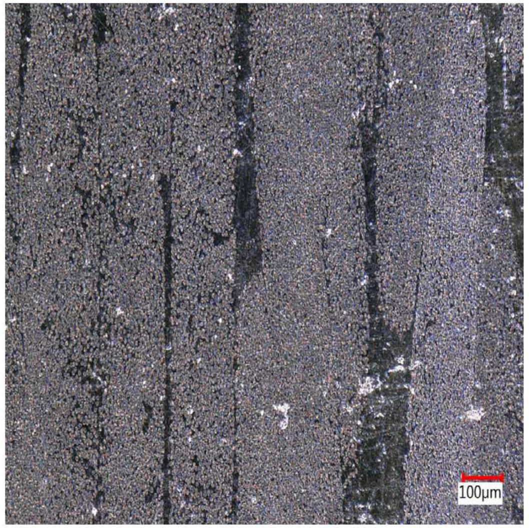


^{13}C CPMAS NMR

- Characterization on neat and cured resin
- Crosslinking examined with NMR & FTIR
- Pyrolysis products determined through TGA/MS

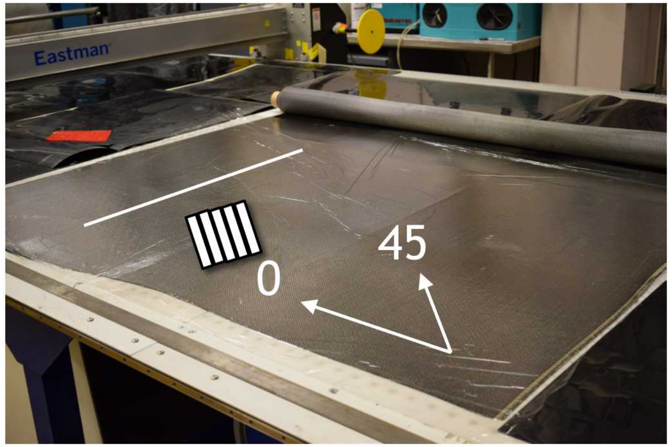
Coupon Fabrication Process

Carbon Phenolic

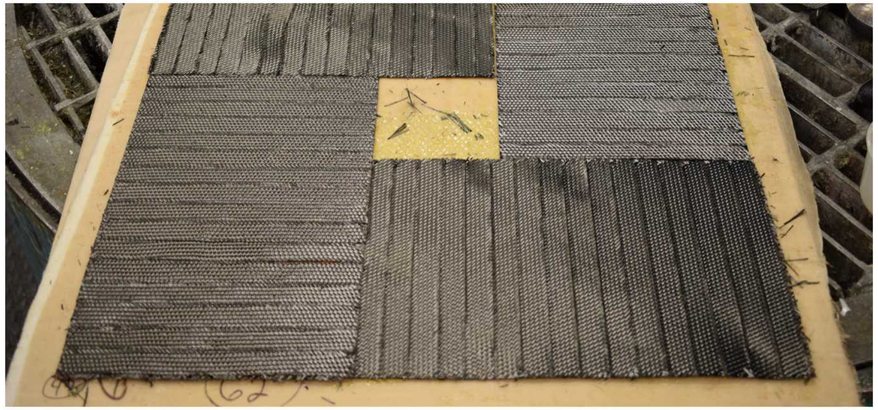


Fabrication Summary

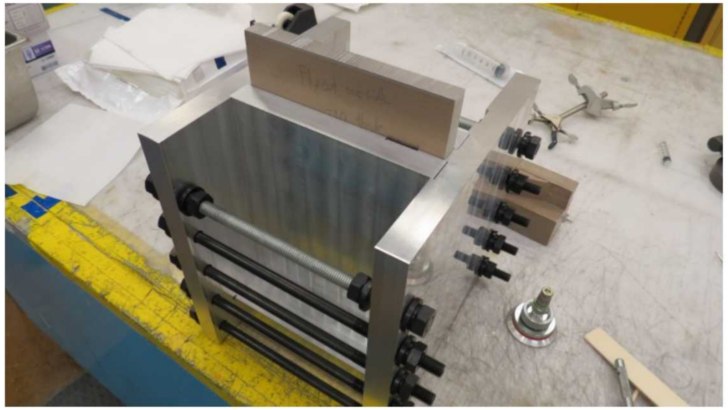
1. Fabric Cutting & Preparation

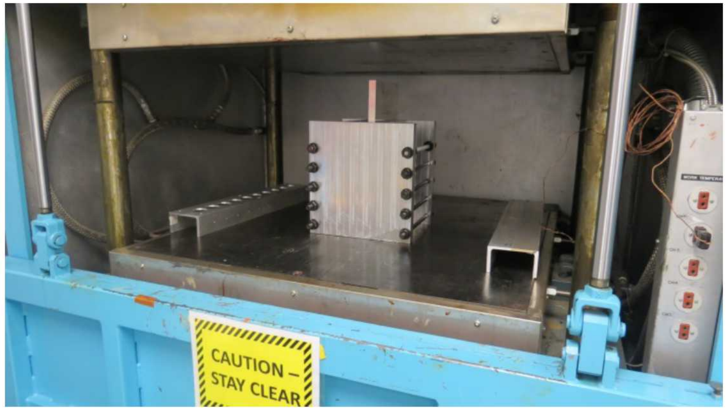


2. Pre-pregnation Preparation



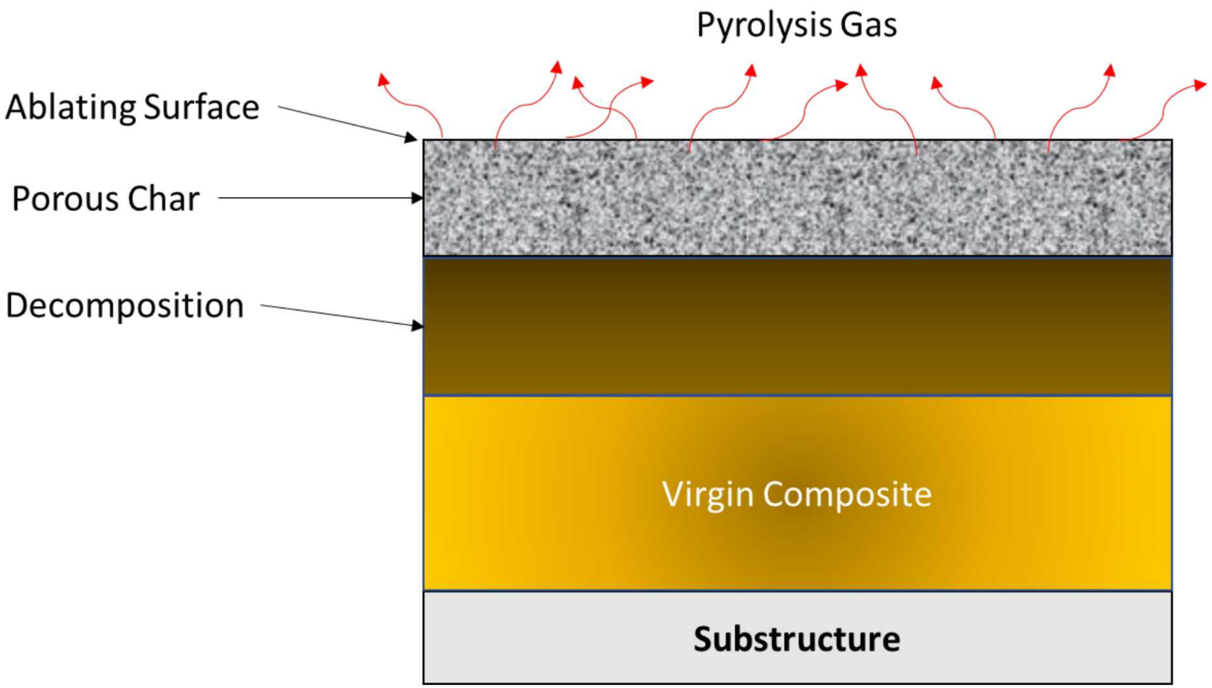
3. Molding Prep & Curing Process (post processing not shown)



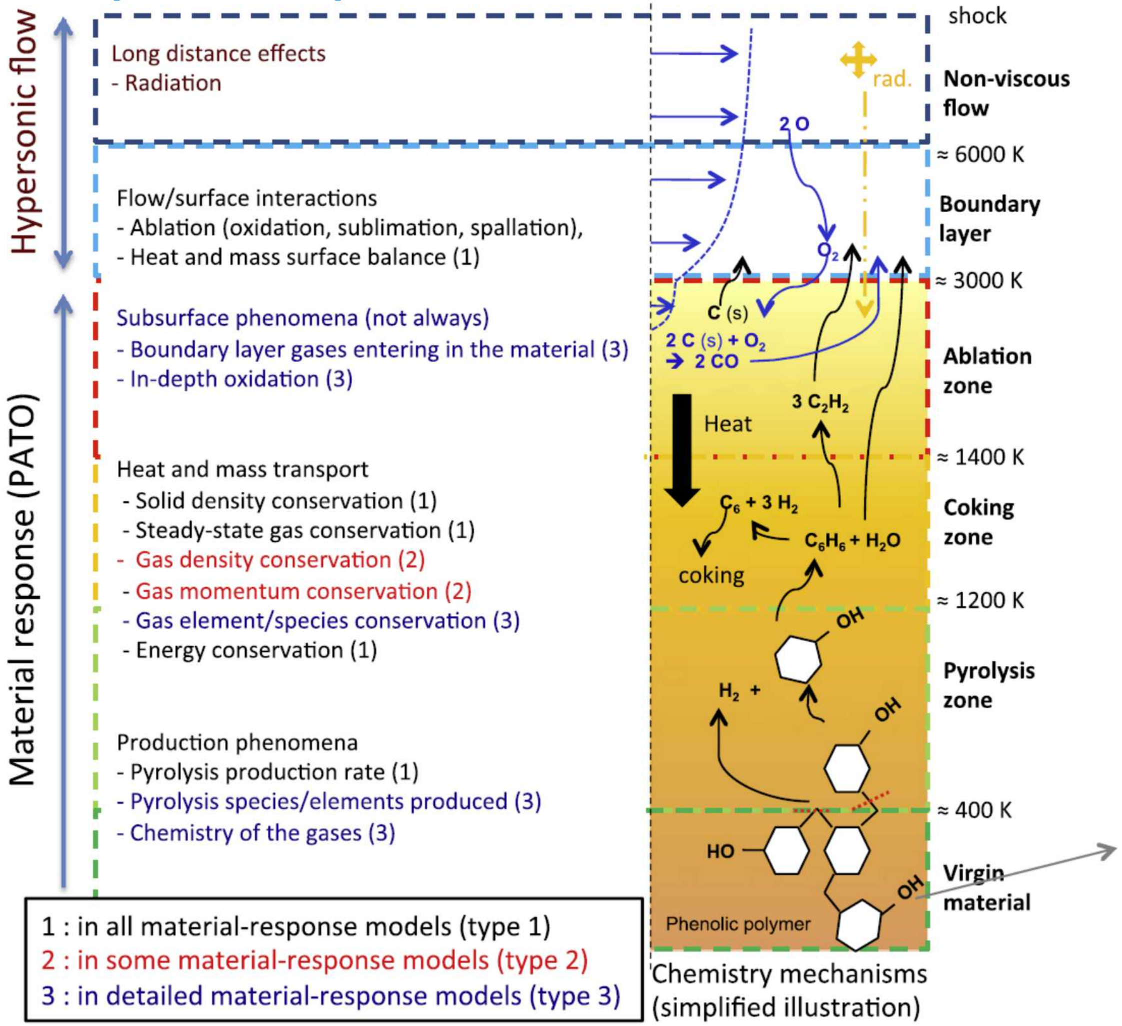


Predicting TPS performance requires an understanding of ablation behavior.

Ablation of a Reinforced Phenolic Material



Example of Response Models Used for Ablation



J. Lachaud et al. International Journal of Heat & Mass Transfer 90 (2015) 1034–1045

Pyrolysis Mechanisms based on Phenolic Resin (Literature)

Phenol Release

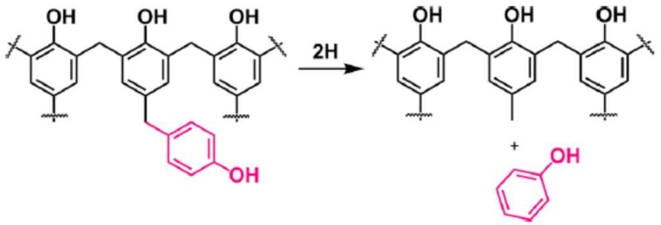


Figure 12. Liberation of a pendant group in the form of a phenol molecule. Based on the proposal by Parker and Winkler[21] that phenol (and presumably its substituted derivatives) can only be produced from pendant groups on the polymer backbone.

CO_2 Release

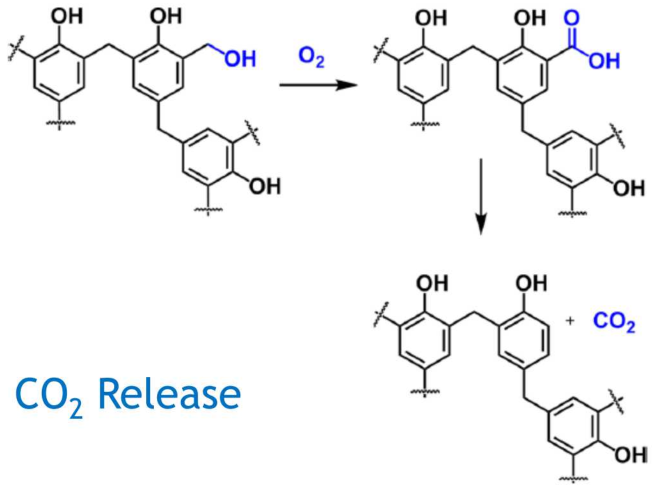


Figure 13. Oxidation of a methylol group leads to formation of a carboxylic acid group that subsequently decomposes and releases a CO_2 molecule. Based on a mechanism proposed by Jackson and Conley.[18]

CO Release

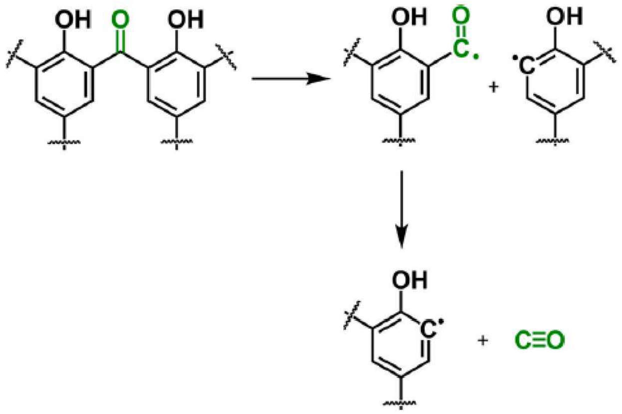


Figure 14. Two-step decomposition of a carbonyl cross-link to produce CO. The carbonyl cross-link may be the result of the oxidation of a methyl cross-link during the postcure of the phenolic resin in air. Based on similar mechanisms proposed by Jackson and Conley[18] and by Ouchi.[23]

Pyrolysis of Phenolic Impregnated Carbon Ablator (PICA)

ACS Appl. Mater. Interfaces 2015, 7, 1383–1395

CH_4 Release

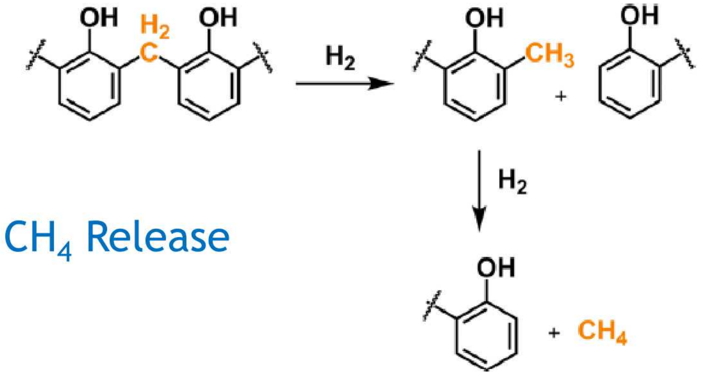


Figure 15. Two-step decomposition of a methylene bridge to produce CH_4. Based on a mechanism proposed by Ouchi.[23]

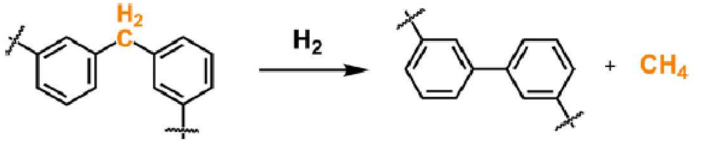


Figure 16. One-step decomposition of methylene bridge to produce CH_4. Based on a mechanism proposed by Trick and Saliba.[22]

presumably come from the fusing of aromatic rings (Figure 17), although one could imagine similar mechanisms to those

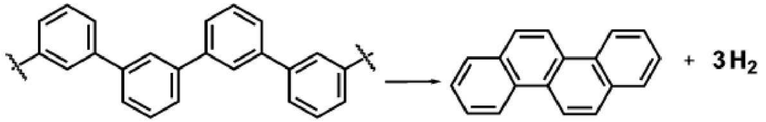


Figure 17. An unstable char coalesces to a stable char and H_2 is evolved. Based on a mechanism proposed by Trick and Saliba[22]

Char Production (Onset of Graphite/ H_2 Release

Table 2. List of Compounds Selected As Potential Pyrolysis Products and Their Respective Electron-Impact Ionization Cross-Sections[a]

Table derived from literature for potential products.

Species boldly highlighted in color were those observed experimentally from Minton's group.

Product Species	Ionization Cross Section / Å^2	Product Species	Ionization Cross Section / Å^2
CH_4	3.52	o-cresol	17.19
H_2O	2.28	p-cresol	18.94
CO	2.52	mesitylene	18.18
CH_2CH_2	5.12	2,6-dimethyl phenol	19.82
CH_3CH_3	6.42	2,4-dimethyl phenol	21.58
CH_3OH	5.11	3,4-dimethyl phenol	23.82
Ar	2.99	2,4,6-trimethyl phenol	24.22
CO_2	3.52	hexamethylenetetramine	-
$CH_3CH_2CH_3$	8.62	2-methylnapthalene	22.12
$(CH_3)_2CHOH$	10.94	2-methyl-1,1'-biphenyl	25.58
benzene	15.03	dibenzofuran	33.05
hexane	16.58	diphenyl methane	34.18
2,2-dimethyl-propanol-1-ol	-	diphenyl ether	34.18
toluene	16.62	anthracene	33.05
phenol	14.55	benzophenone	29.54
o-xylene	15.81	xanthene	33.05
p-xylene	17.04	(4-methylphenyl)-phenyl-methanone	32.56

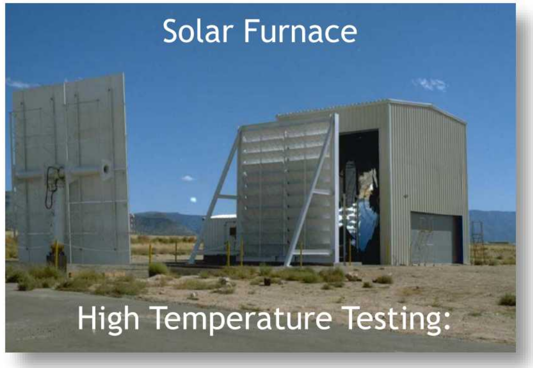
[a]Of the 34 compounds listed, only 14 (shown in color and larger font) made a significant contribution to the fit of the experimental mass spectra. The total EI ionization cross-sections were taken from several sources[35−37] and scaled to give a set of cross-sections that were consistent with those reported in the NIST database.[38] Electron-impact ionization cross sections for 2,2-dimethyl-propanol-1-ol and hexamethylenetetramine were not found in the literature, so the relative molar yields for these species were not corrected for ionization cross section. The lack of correction for ionization cross section would lead to an overestimate of the relative molar yield, but even without correction, the yields of these two species were negligible.

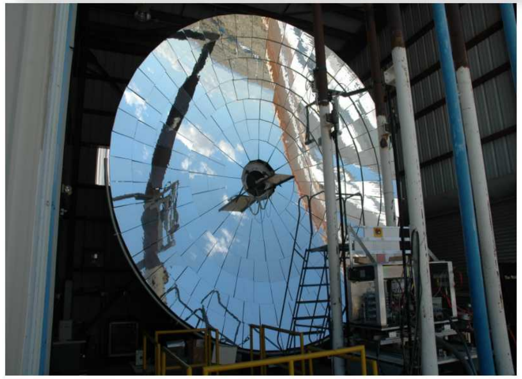
Pyrolysis of Phenolic Impregnated Carbon Ablator (PICA)

ACS Appl. Mater. Interfaces 2015, 7, 1383–1395

National Solar Thermal Test Facility (NSTTF)

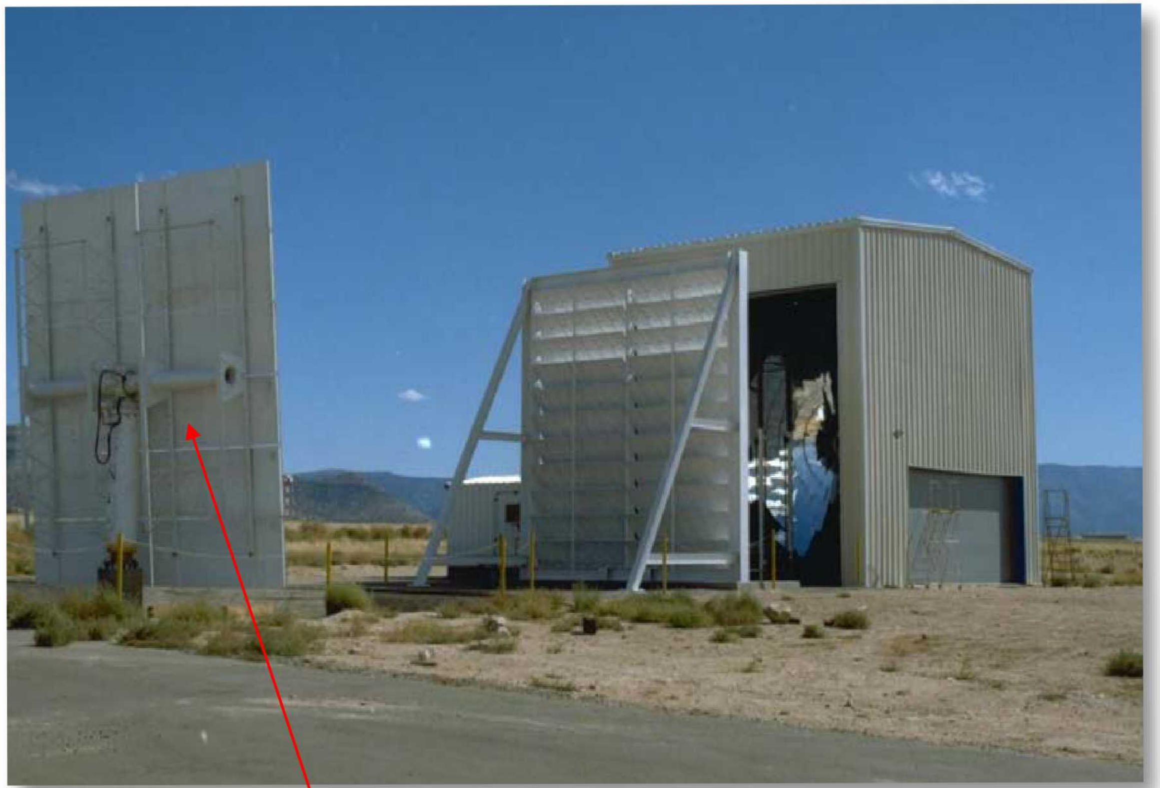
The power of the Sun is used to simulate reentry heating to verify performance behavior



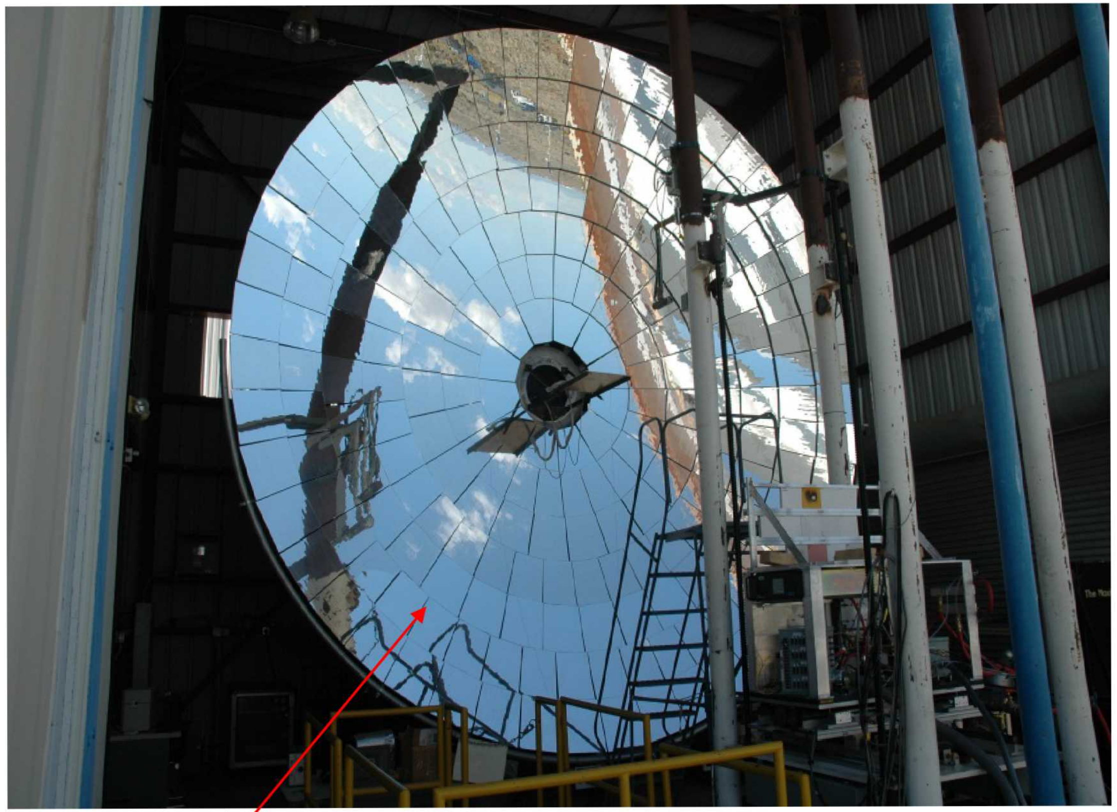


*One of several Sandia testing facilities available to simulate extreme environments

Solar Furnace



A heliostat that is 95 m^2



A dish that is 6.7 meters in diameter

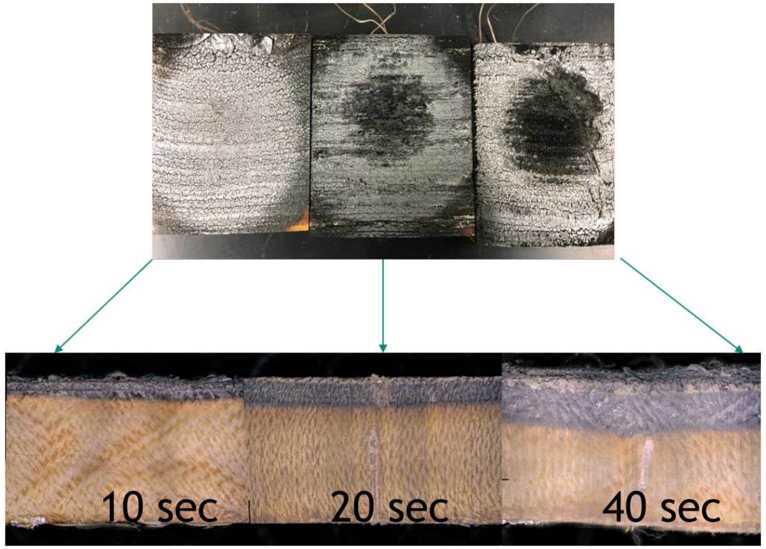
- 16 kW total thermal power
- Peak flux up to 600 W/cm^2
- The furnace has a power control to simulate nuclear and other thermal transients

Solar furnace chamber is used for high heat flux testing under controlled atmospheres.

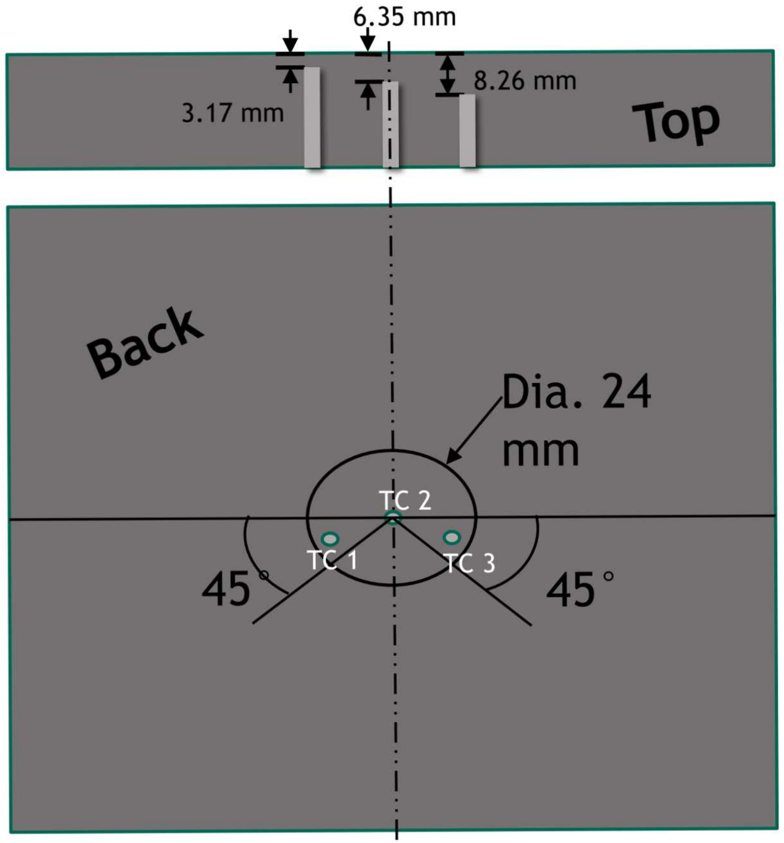
- Accommodates pressures up to 10 ATM (150 PSI) with different flow rates of nitrogen, air or a mixture of both
- Window to allow solar flux to pass through
- Equipped with a gas collection system
- Equipped with video capabilities

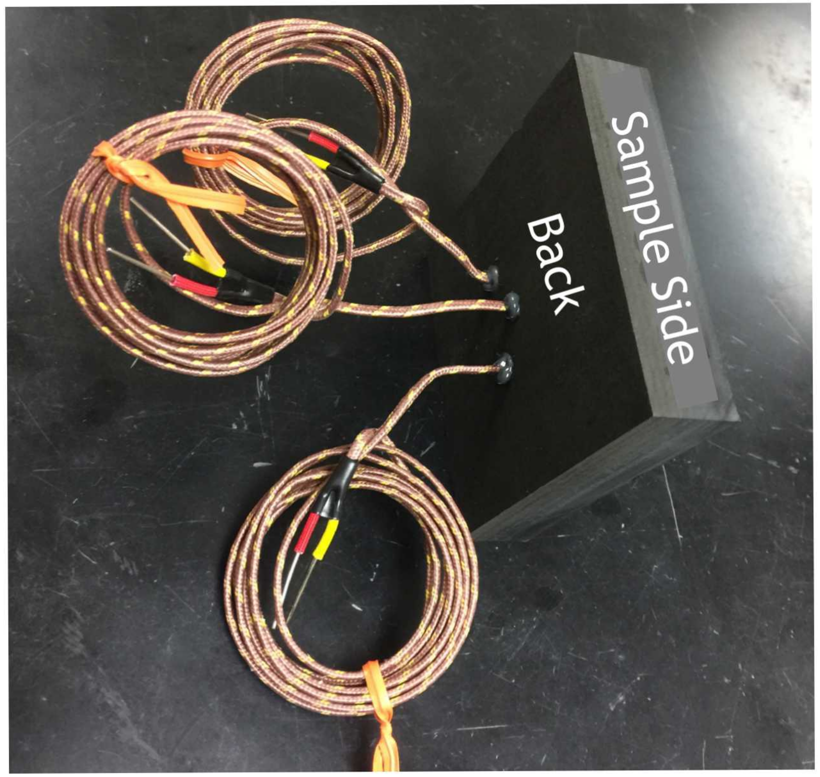
We can learn the following:

- Thermocouple/Pyrometer temperatures
- Pyrolysis/decomposition Gas identification
- Mass loss
- Effects of atmosphere (N_2/Air)
- Char results
- Ablation performance



Thermocouple Placement

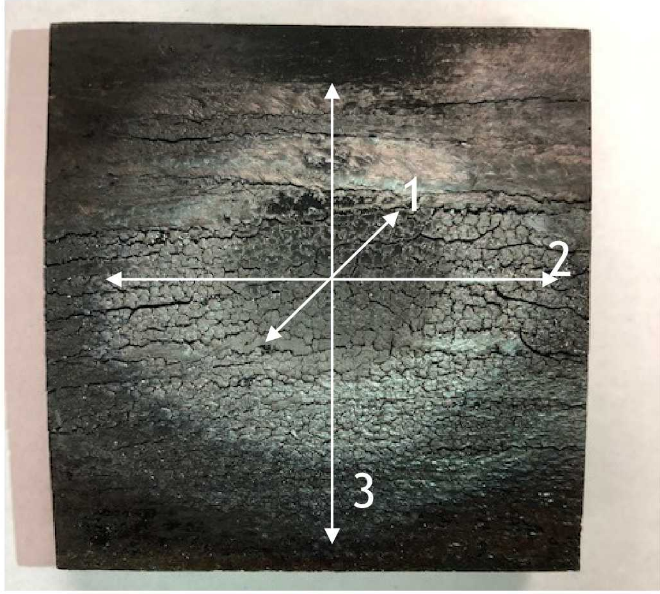


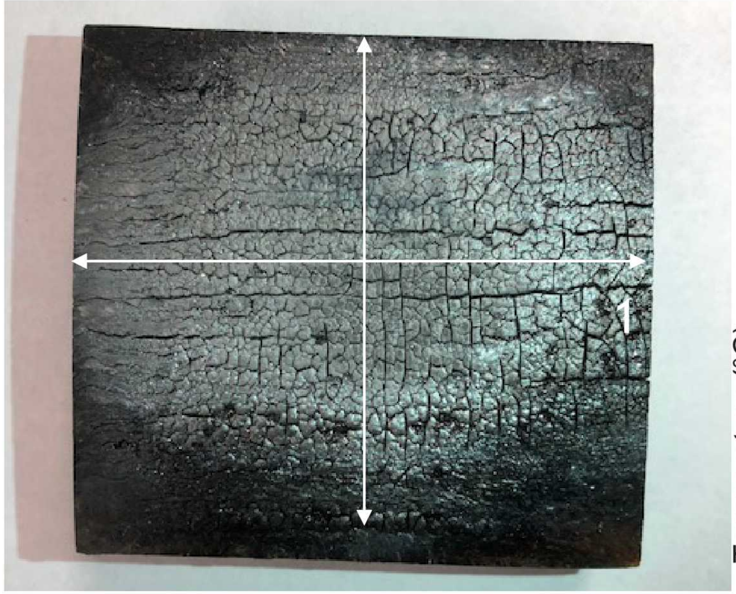


Thermocouples are placed at various depths within sample

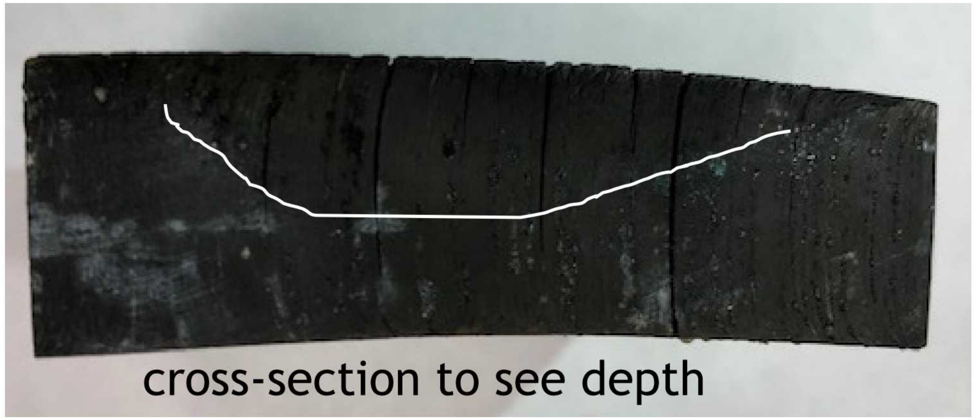
Samples were evaluated outside and within chamber.

Examples of coupons after testing



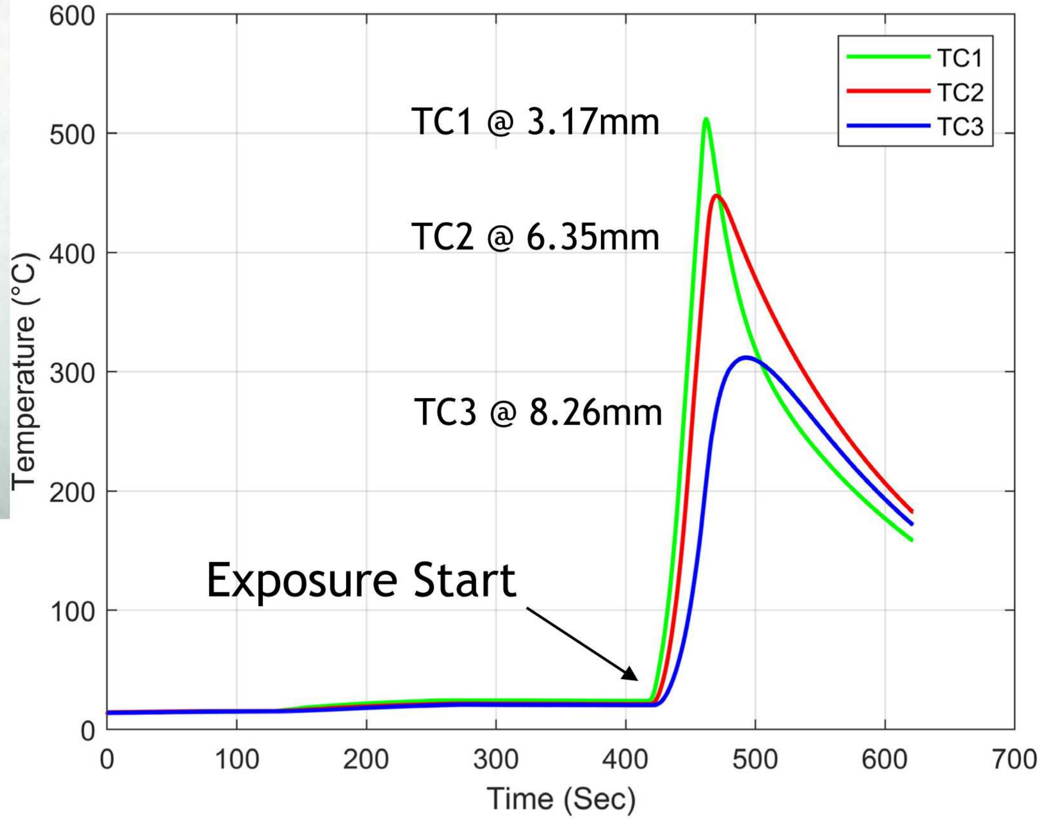


Surface char effects based on condition used to evaluate coupon



cross-section to see depth

Thermocouple temperature readouts



Example Pyrometer Surface Temperature Range: 1600-2500 °C

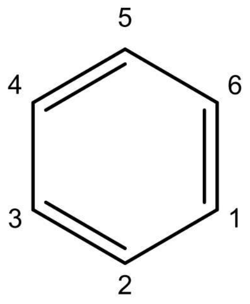
Example Mass Losses:
~13 g in air, ~6 g under nitrogen

GC-MS (Bench Top) Results from Solar Furnace Chamber

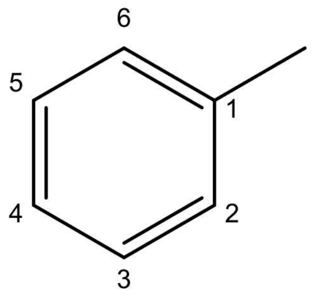
Example of Gases Collected (RT; PA%)
Cyclopropane (4.345; 4.84)
Cyclopropene (4.467; 1.93)
1,3-butadiene (4.481; 3.29)
1,2-butadiene (5.337; 0.15)
Acetone (6.008; 5.10)
Isopropyl alcohol (6.194; 13.23)
4-heptyn-2-ol (6.259; NA)
1,3-cyclopentadiene (7.007; 4.91)
4-methylene-cyclopentene (10.144; 2.76)
1,4-cyclohexadiene (10.312; 1.62)
Benzene (10.995; 9.90)
Toluene (15.17; 8.21)
p-xylene (19.177; 3.71)
Styrene (19.909; 3.30)
Phenol (21.956; 1.89)
alpha-phellandrene (22.799; 2.06)
1-methyl-4-(1-methylethyl)-1,3-cyclohexadiene (23.024; 0.63)
m-cymene (23.184; 0.67)
17 of 69 listed

Snap Shot of Pyrolysis Gases collected during High Heat/High Flux testing from Carbon Phenolic.

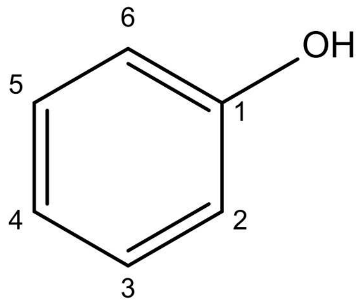
Product Species:



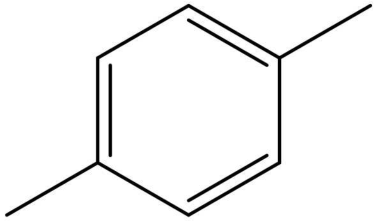
Benzene



Toluene

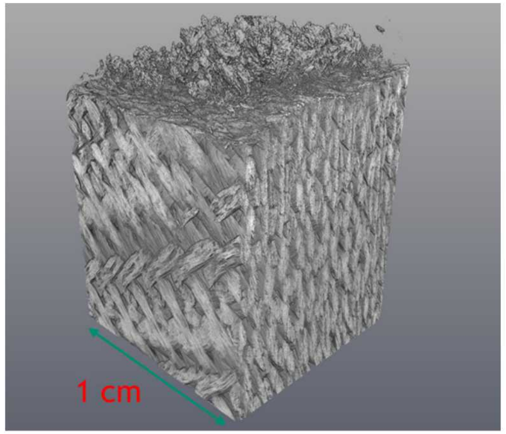


Phenol

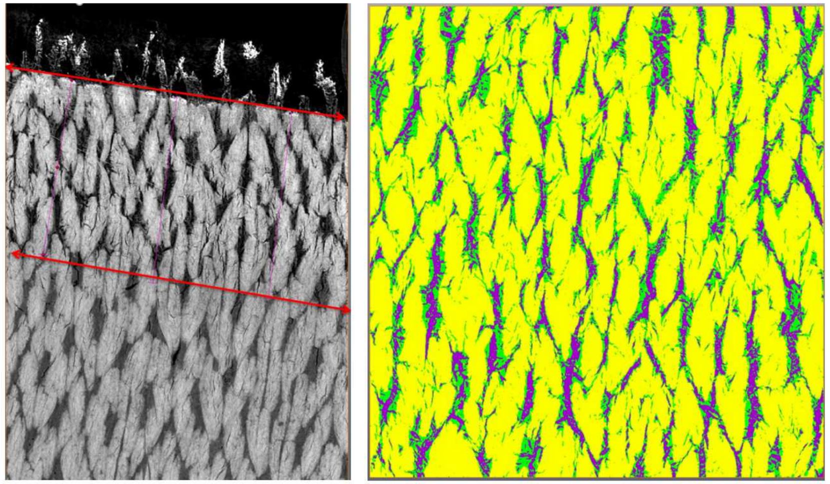


p-xylene

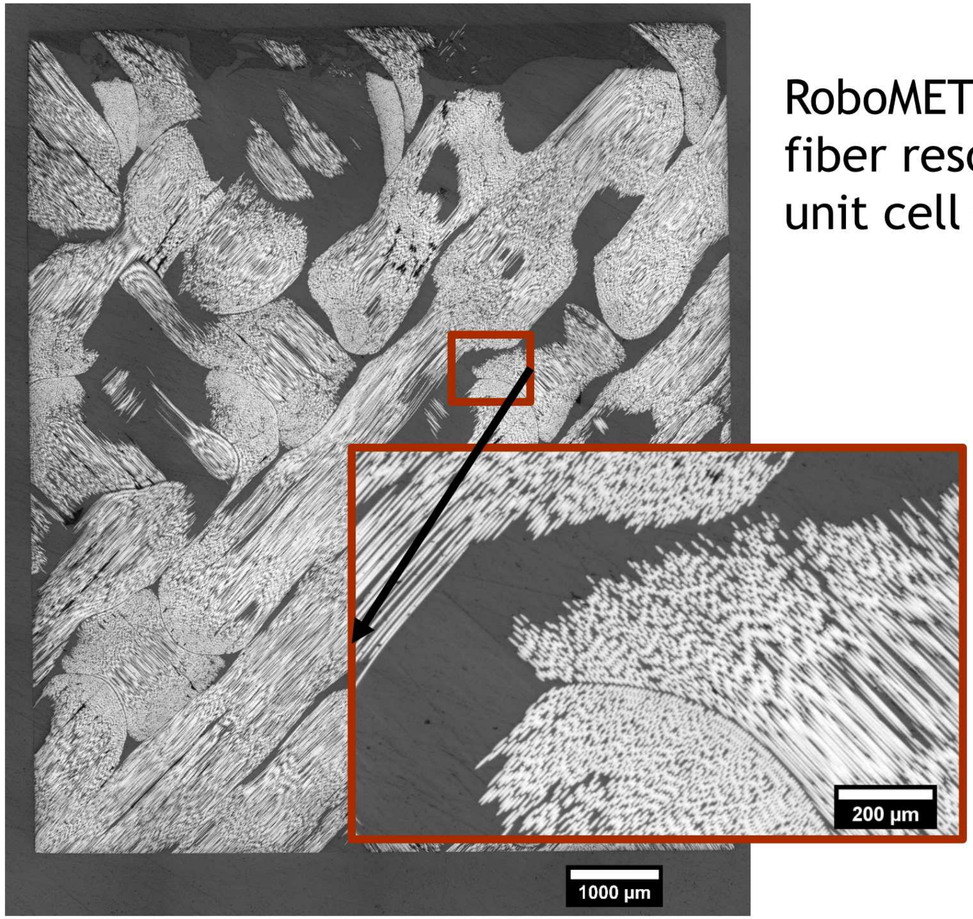
Using 3D Mesoscale Imaging to Understand Char



X-ray CT shows weave at coupon scale

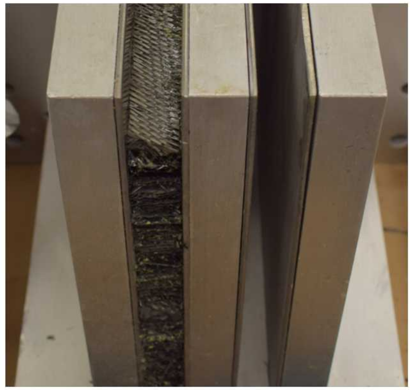


Char can be imaged/measured



RoboMET provides fiber resolution at unit cell scale

Summary



We have developed a novel solar furnace chamber used to investigate ablation chemistry and behavior.

To examine insights our team has provided:

- Custom materials manufacturing
- Material characterization and ablation testing
- Ablation chemistry: some compounds identified were reported in the literature.
- Solar Furnace Chamber allows us to study ablation under a controlled environment.

Acknowledgments

- Team: J. Coleman, J. Nicholas, L. Collins, P. Salinas, E. Coker, T. Alam, S. Meserole, T. Chavez, K. Armijo, J. Lassa, C. Roberts, J. Madison, S. Roberts