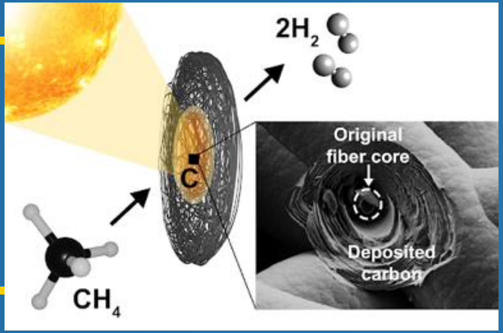
UCLA Samueli School of Engineering

Measurement and Computation of Reacting Flows with Carbon Nanoparticles (ISF) Workshop
Combustion Institute 40th Int'l Symposium
20 July 2024

Direct solar-thermal synthesis of flake graphite and hydrogen via methane decomposition



Prof. Timothy S. Fisher*
Schauerman Endowed Chair in Engineering
UCLA Mechanical & Aerospace Engineering Department

With Faculty: Mitchell Spearrin* (MAE), Yves Rubin (Chemistry)

Acknowledgement: Support from the CNSI Noble Family Innovation Fund, California Energy Commission, and US Dept of Energy is very much appreciated.

Students/Postdocs: Mostafa Abuseada (MAE), Abdalla Alghfeli (MAE), Chuyu Wei (MAE), Barathan Jeevaratanam (MAE), Julia Chang (Chemistry), Hengrui Xu (MAE), others as noted in slides

*also Co-Founder of SolGrapH Inc., a startup company involved with solar-thermal synthesis of materials; this talk is an academic briefing outside the scope of any commercialization activity.

Motivation – Clean/Circular Materials Production

- Manufacturing processes are often highly energy-intensive, even when the energy is primarily used for simple heating processes
- Direct solar-thermal green manufacturing provides a compelling, though seldom studied, option
- Reducing greenhouse gas emissions from the industrial sector can be achieved by utilizing renewable energy sources
- Semiconductor and electronic materials manufacturing is a major culprit of inefficient energy and resource use [2]

[1]

[1] https://blog.repurpose.global/green-manufacturing-the-business-benefits-of-sustainability/
[2] Krishna et al., Environ. Sci. Technol. 2008, 42, 8, 3069–3075

Introduction

- Methane decomposition global reaction

$$CH_4 \rightarrow C + 2H_2 \quad (\Delta H^o = 75.6\ \text{kJ/mol})$$

- Proceeds at T > 1000 K, enhanced by pressure reduction (Le Chatelier's principle), with a complex stepwise dehydrogenation mechanism

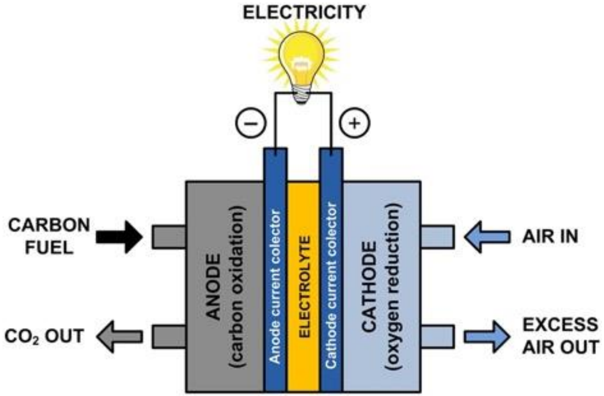
$$2CH_4 \xrightarrow{-H_2} C_2H_6 \xrightarrow{-H_2} C_2H_4 \xrightarrow{-H_2} C_2H_2 \xrightarrow{-H_2} 2C$$

- Provides storable and transportable solar fuel (H_2)
- Carbon product can be carbon black, graphite, nanotubes, etc., improving process economics
- With solar energy, ~ 14 kg-equivalent CO_2/kg H_2 emissions are avoided for H_2 + C production

Cost of H_2 production (per kg):

1) Steam Methane Reform. (SMR) = $1-1.5
2) SMR + CCUS > $2
3) **CH_4 pyrolysis ~ $2-3**
4) H_2O electrolysis > $4

*CCUS: Carbon capture, utilization, storage



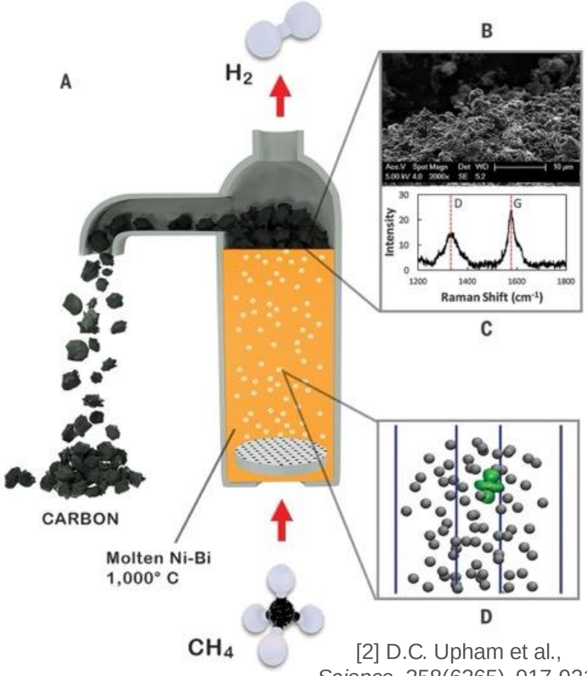
[1] A. Kacprzak, *International Journal of Energy Research*, *43*(1), 65-85, 2019

Challenges in Methane Pyrolysis

Challenges (solar and non-solar):

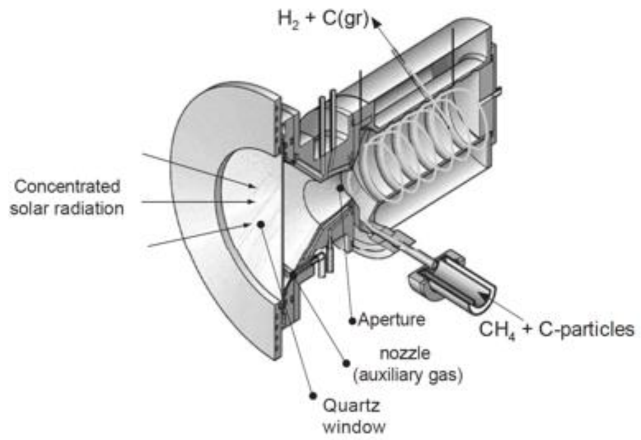
1) High operating temperatures or low product yields – catalysts
2) Reactor clogging and deposition on walls – avoid carbon product or use molten salts
3) Carbon deposition on window – indirectly irradiated solar reactors
4) Low-quality carbon black product: D/G Raman peak ratio > 1.5, no 2D Raman peak – use of metallic catalysts
5) Slow startup thermal response:
   > 1 hour
6) Catalyst sintering, deactivation, and purification (when applicable)

[1] A. Abánades et al., *International Journal of Hydrogen Energy*, 36(20), 12877-12886, 2011

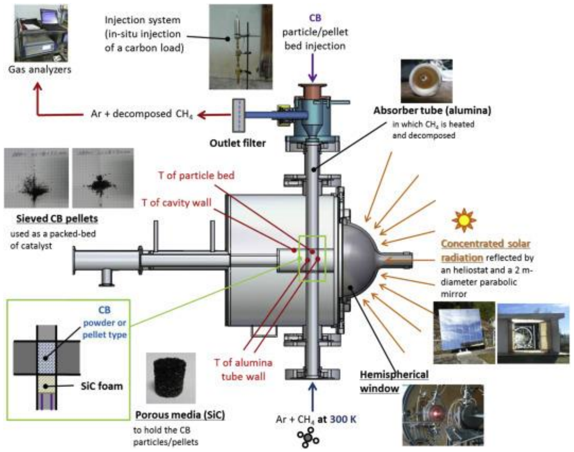


[2] D.C. Upham et al., *Science*, 358(6365), 917-921, 2017

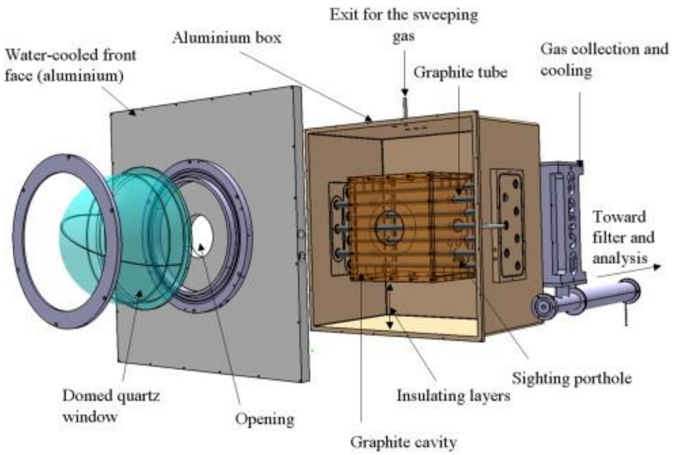
Prior work on solar-thermal CH_4 decomposition



Hydrogen from natural gas using a vortex-flow of carbon particles [1]



Hydrogen from methane using carbon black catalysts in an indirect packed bed [2]



Pilot-scale indirect reactor for hydrogen and carbon black from methane [3]

[1] Hirsch, D., & Steinfeld, A. (2004). International Journal of Hydrogen Energy, 29(1), 47-55.
[2] Abanades, S., Kimura, H., & Otsuka, H. (2014). International journal of hydrogen energy, 39(33), 18770-18783.
[3] Rodat, S., Abanades, S., Sans, J. L., & Flamant, G. (2010). International Journal of Hydrogen Energy, 35(15), 7748-7758.

Solar Methane Pyrolysis Process (lab)

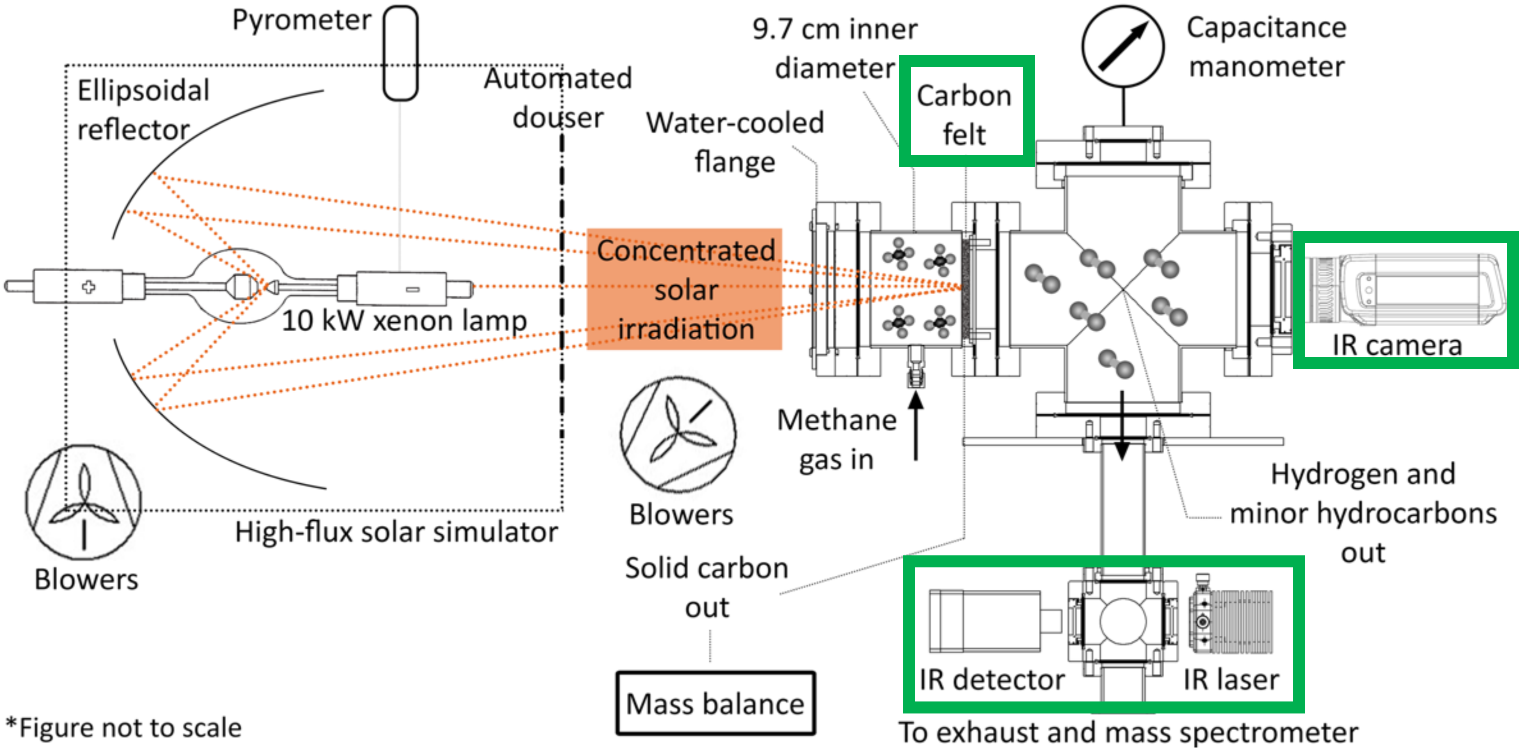
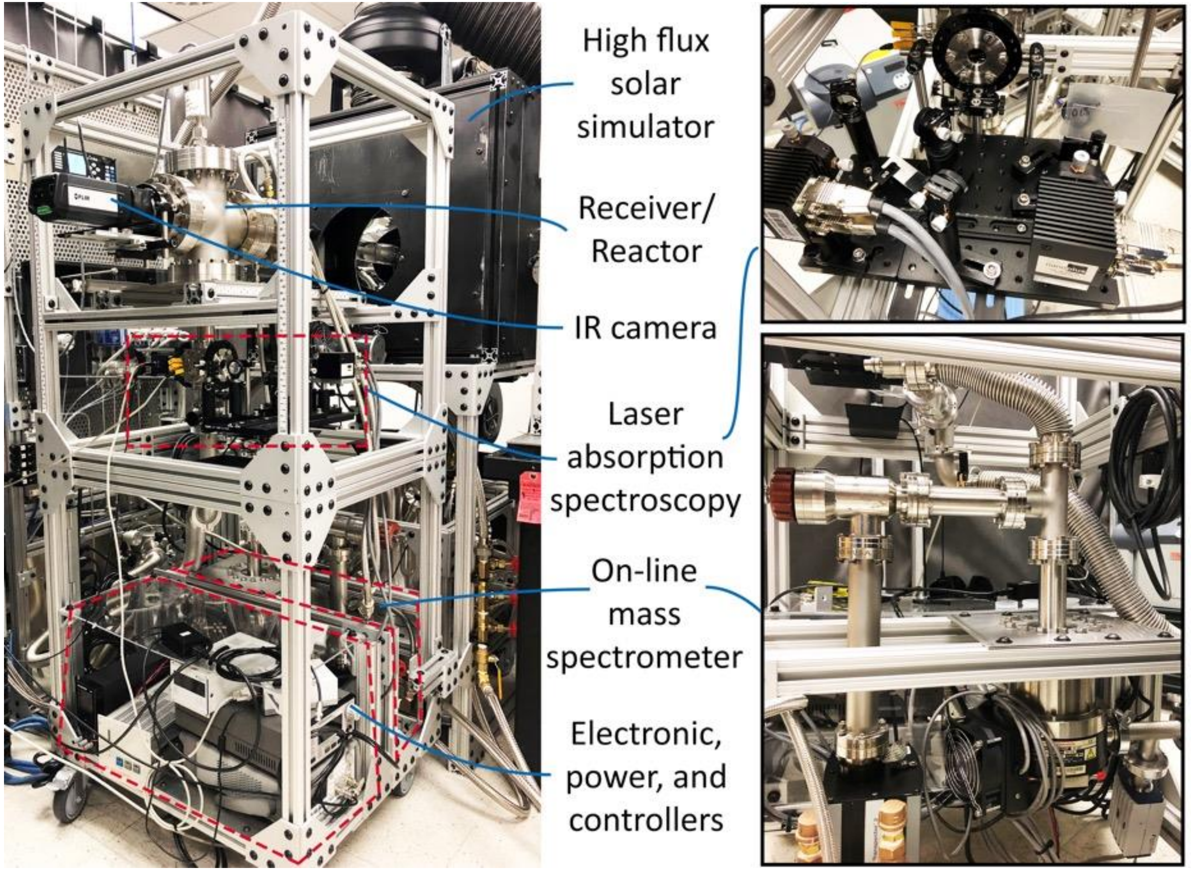


*Figure not to scale

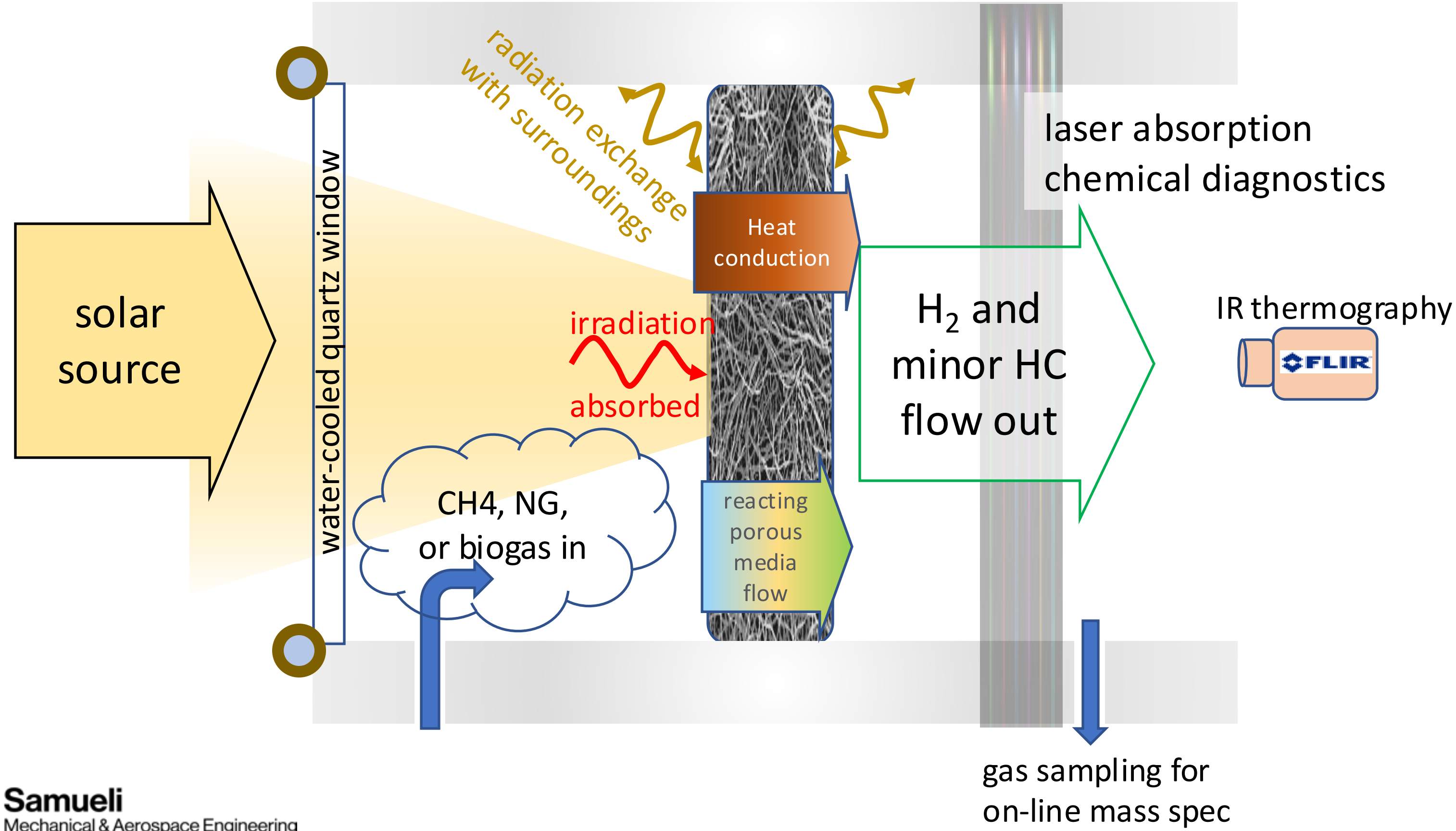
Reactor Assembly and Components



Mostafa Abuseada
PhD 2022

Abdalla Alghfeli
PhD 2022

Beautifully Complex Thermochemical Reacting Flow and Transport Problem



Methane Pyrolysis Conditions and Metrics

Operating conditions:

- Peak gross irradiance, 2000-4500 suns
- Total net radiant power, 1-4 kW
- Pure methane flow, 100-1000 sccm
- Pressure, 10-200 Torr
- Duration of decomposition, 5-100 min
- Typical gas residence time, 1-100 ms

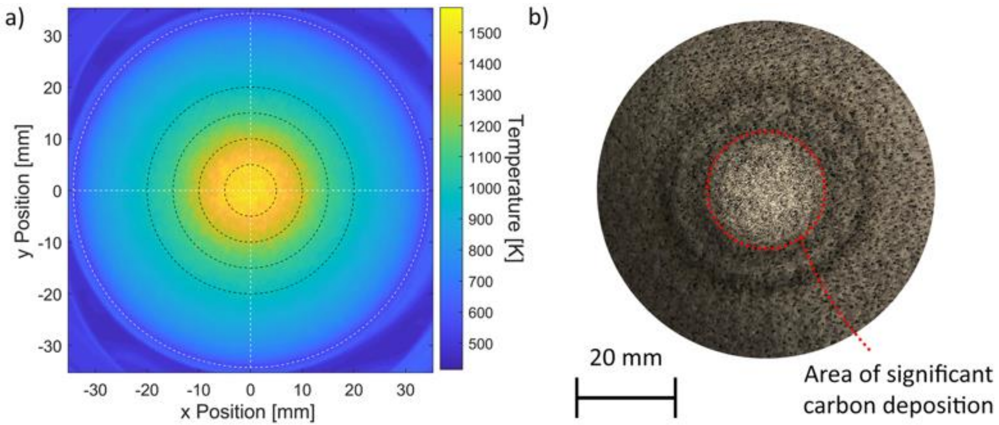
$$t_{\mathrm{res}} = \frac{L}{v} = \frac{\left(L\rho_{\mathrm{CH_4}}\pi D^2\right)}{4\dot{m}_{\mathrm{CH_4}}}$$

- Temperature, 700-2000 K

NO ADDED CATALYST!
MANY POROUS SUBSTRATES HAVE PRODUCED NEARLY IDENTICAL RESULTS

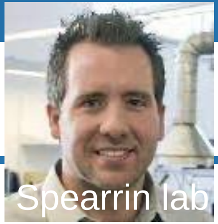
Chemical performance indicators (via mass balance):

- Methane conversion → $X_{\mathrm{CH_4}} = \frac{\dot{n}_{\mathrm{CH_4,in}} - \dot{n}_{\mathrm{out}} x_{CH_4}}{\dot{n}_{\mathrm{CH_4,in}}}$
- Hydrogen yield → $Y_{\mathrm{H_2}} = \frac{\dot{n}_{\mathrm{out}} x_{\mathrm{H_2}}}{2\dot{n}_{\mathrm{CH_4,in}}}$
- Carbon yield → $Y_{\mathrm{C}} = \frac{\dot{m}_{\mathrm{C}}}{M_{\mathrm{C}}\dot{n}_{\mathrm{CH_4,in}}}$



Abuseada *et al. ACS Energy & Fuels*, **38** 3920 (2022)

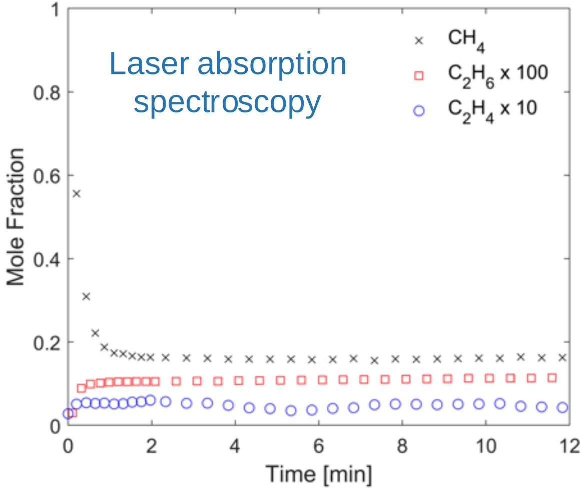
Pyrolysis Performance

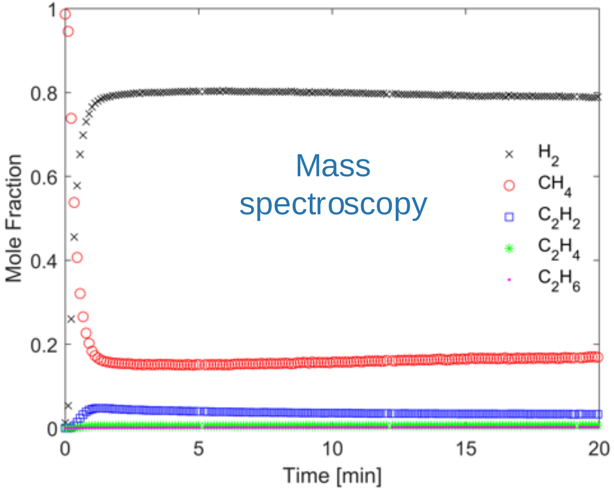


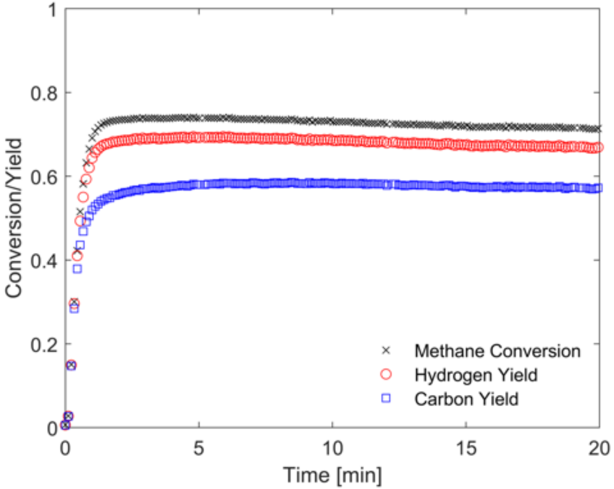
Barathan J.
PhD student
(Spearrin group)

Process stable over time (~20 min)

- CH_4 conversion = 73% and H_2 conversion = 69%
- Carbon felt weight increase by 0.62 g → C yield (actual) = 58%
- C theoretical yield (mass balance) = 58.3% → indication that nearly all carbon captured in felt
- Largest byproduct is acetylene (C_2H_2) – likely due to short residence time

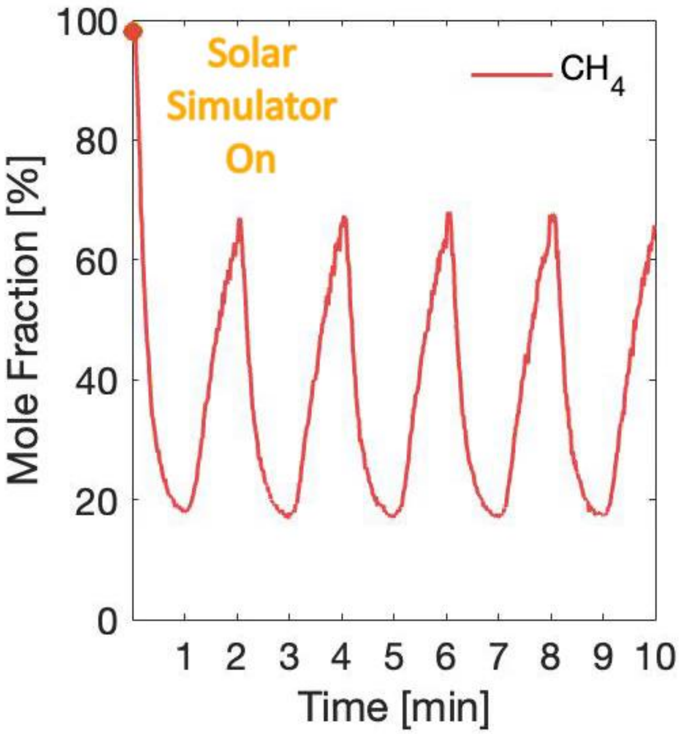


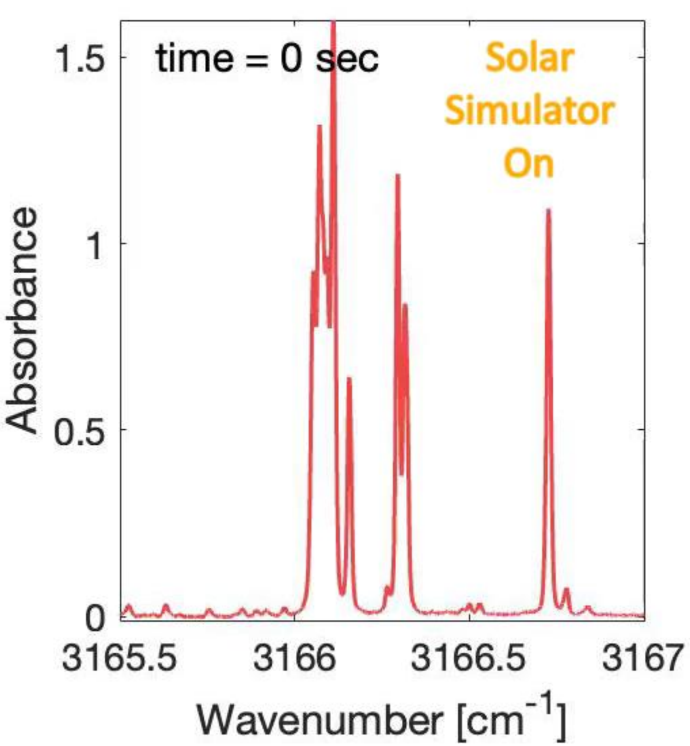




Wei *et al.*, *Proc. Comb. Inst*, **39** 5581 (2023)

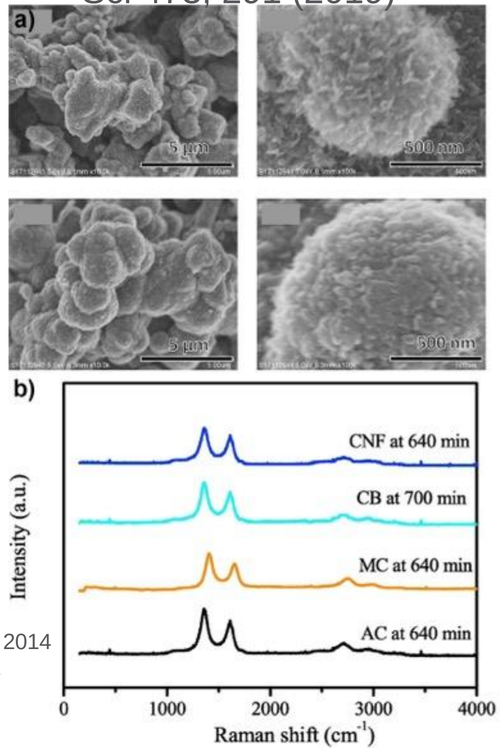
Process Time Response



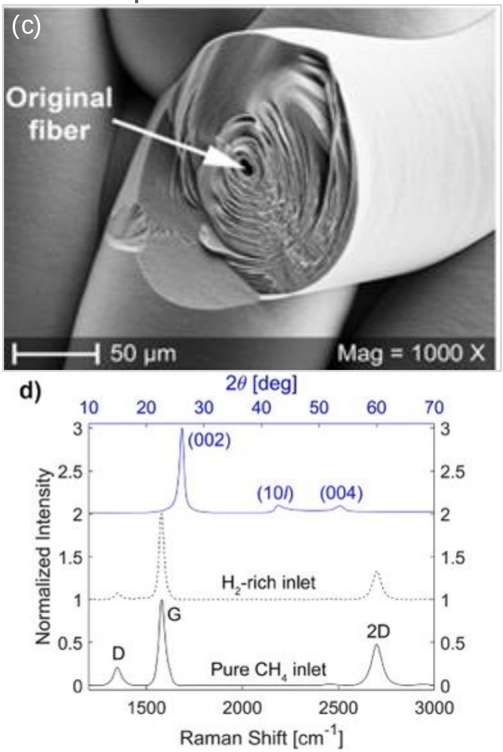


Not All 'Graphitic' Materials are the Same…

Nishii et al., Appl Surf Sci 473, 291 (2019)



present work



Prior work:

- Carbon catalysts produce amorphous carbon [1-3]
- No Raman 2D peak or XRD peaks [4,5]
- Raman D/G ratios ~0.5 with metal catalysts [6,7] (typically 0.2 or less in central zone here)

[1] S. Abanades, H. Kimura, H. Otsuka, *Fuel*, 153, 56-66, 2015
[2] G. Maag et al., *International Journal of Hydrogen Energy*, 34(18), 7676-7685, 2009
[3] S. Abanades et al., *International Journal of Hydrogen Energy*, *39*(33), 18770-18783, 2014
[4] J.L. Pinilla et al., *International Journal of Hydrogen Energy*, 37(12), 9645-9655, 2012
[5] S. Rodat et al., *Solar Energy*, *85*(4), 645-652, 2011
[6] Y. Pan et al., Carbon, 192, 84-92, 2022
[7] X. Guo et al., Carbon, 50, 321-322, 2012

Processing Time for Graphitization

Conventional Pet Coke Graphitization
(Jäger et al, Industrial Carbons,
DOI: 10.1002/14356007.n05_n03, 2012)

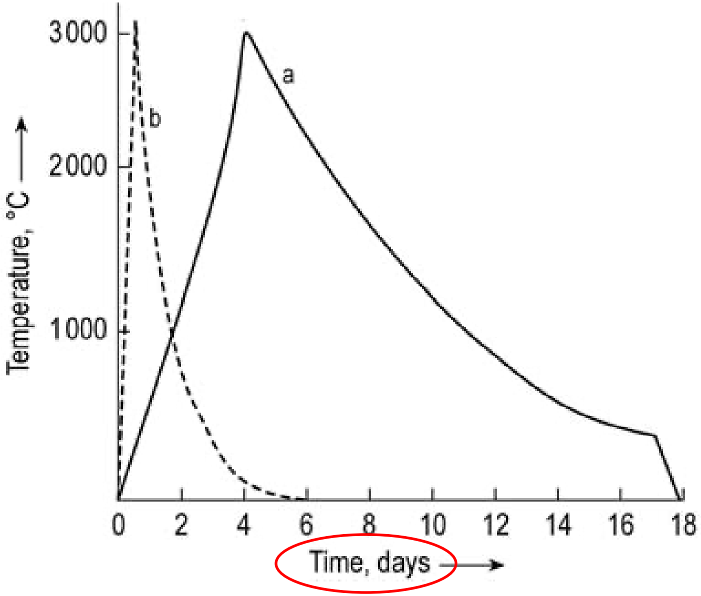
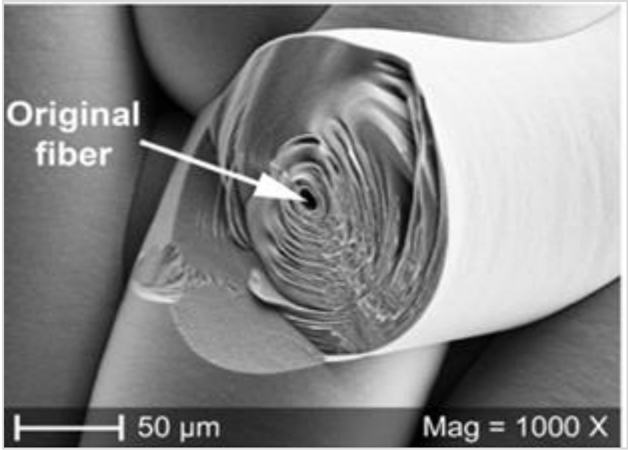


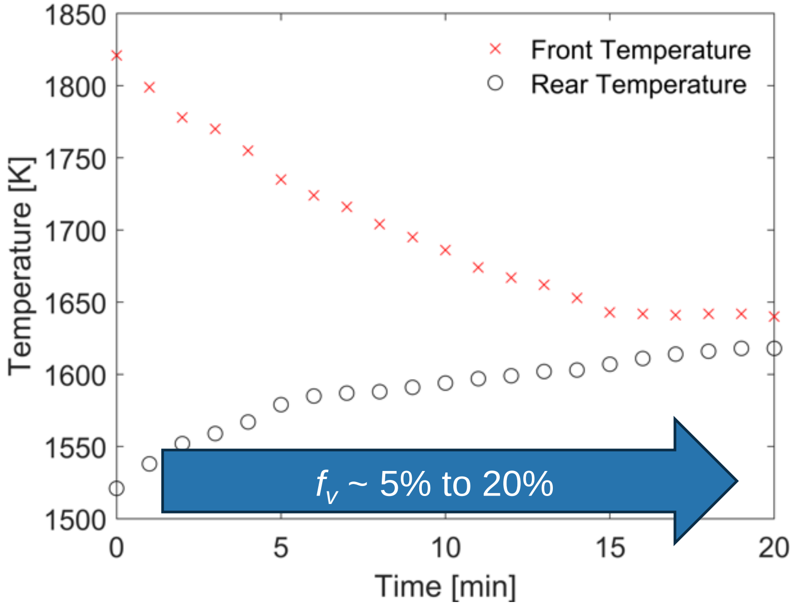
Figure 12. Temperature cycles of the Acheson furnace (a) and Castner furnace (b)

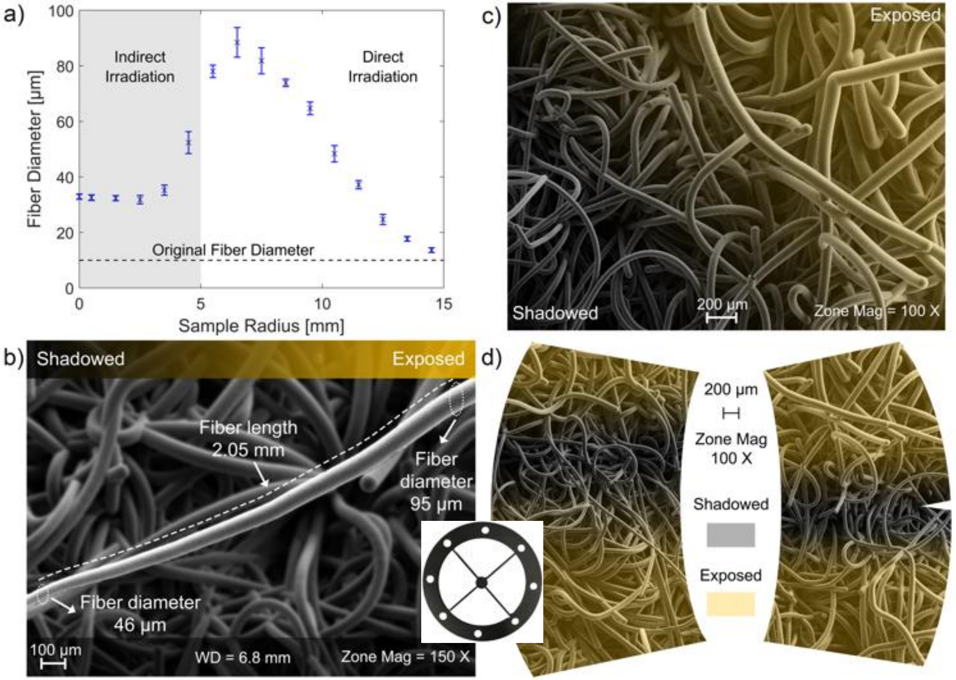
This Process
CH_4 residence time: 1-100 ms
Diameter growth < 20 min: 10 to 100 µm



Effects of Variable Volume Fraction and Shadowing

Mostafa Abuseada
PhD student





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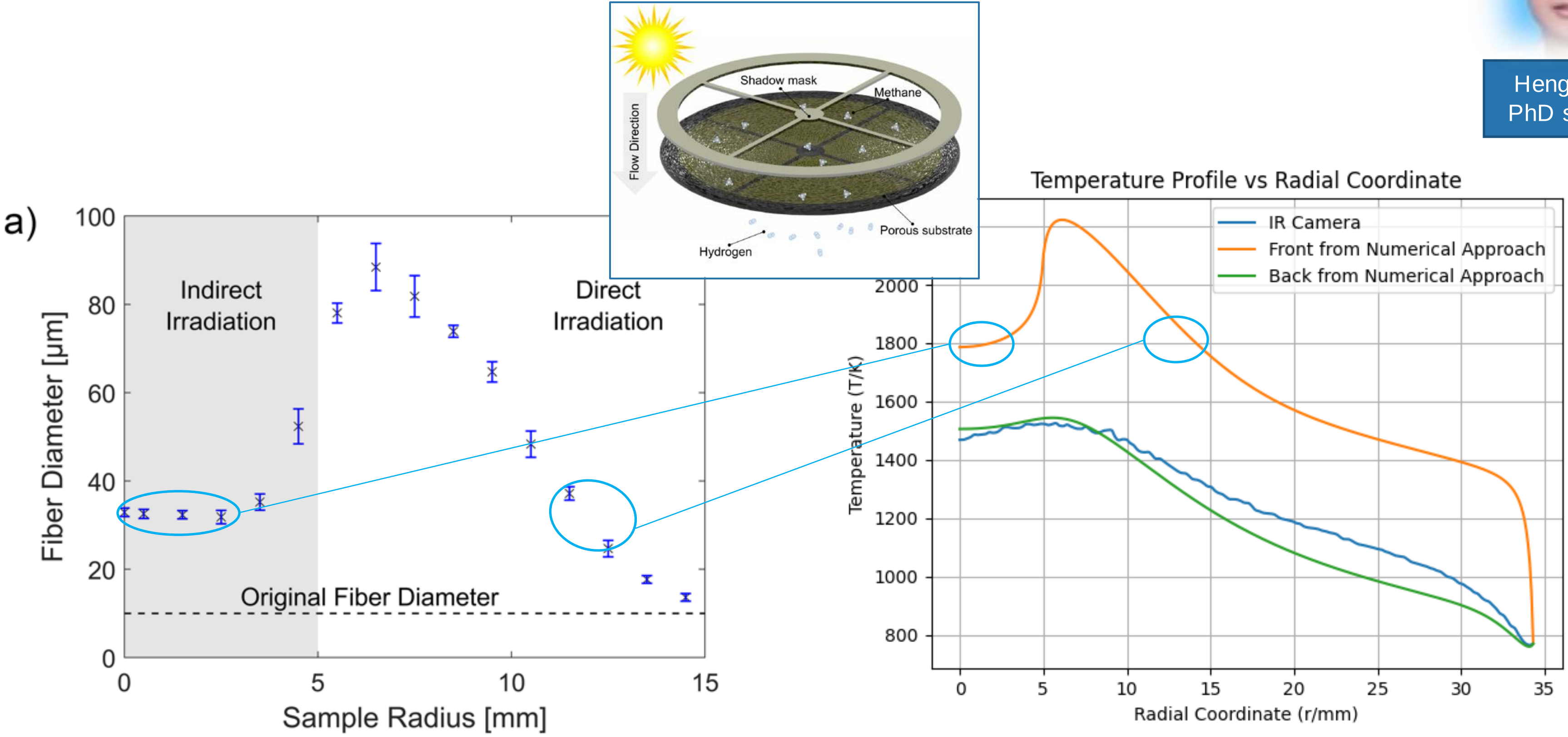
Unraveling photoexcitation effects



Local thermal transport is complex

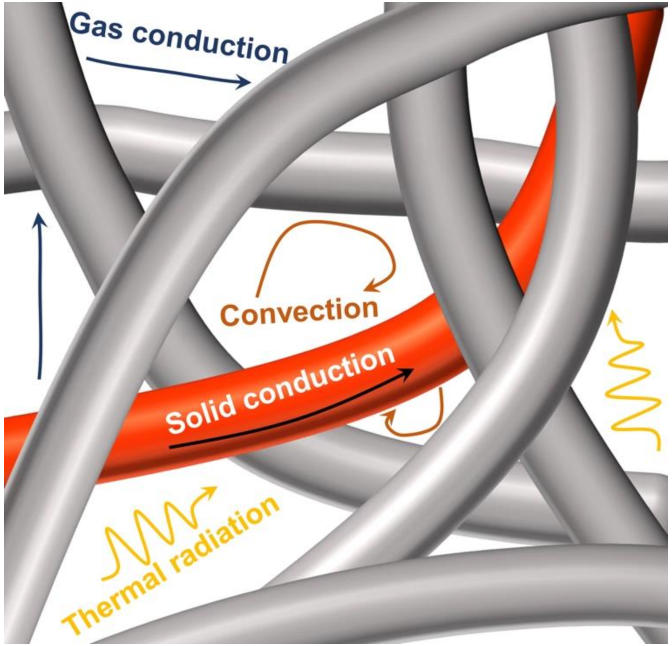
$$\frac{1}{r}\frac{\partial}{\partial r}\left(kr\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(k\frac{\partial T}{\partial z}\right) = 0$$

$$k(T) = w_0 T^3 + w_1 T^{-1}$$

$$-k(T)\frac{\partial T}{\partial r}\bigg|_{r=R} = q_R''$$

$$-k(T)\frac{\partial T}{\partial z}\bigg|_{z=0} = \alpha_s q_s'' + \alpha_{sur}\sigma T_{sur}^4 - \varepsilon\sigma T^4$$

$$-k(T)\frac{\partial T}{\partial z}\bigg|_{z=Z} = \alpha_{sur}\sigma T_{sur}^4 - \varepsilon\sigma T^4$$



Field scale-up (many additional challenges)

CA Energy Commission (10kW)
with SEMPRA/SoCalGas (biogas focus)

US Dept. of Energy (50kW)
1. BES (solid C focus)
2. NETL (H_2 focus)

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Thank you!

See related poster at CI 40:

Kuenning et al., “Direct solar-thermal pyrolysis of biogas for graphite and syngas production assessed via laser spectroscopy”

Poster #4P126
Th 25 July, 1000-1700