Advanced Nanoporous Carbon for Natural Gas & Hydrogen Storage

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University of Missouri
Columbia, MO 65211

Alliance for Collaborative Research in Alternative Fuel Technology (ALL-CRAFT)

http://all-craft.missouri.edu

"Imagine paying as little as $1.25 a gallon to run your car. . . you would pump a fuel that's readily available, North American-produced and virtually pollution-free. Many motorists could even fill up in their own garages every night.

Now, what if this magical car were available today."

—USA Today
May 9, 2007

Feb. 16, 2007:

MEDIA ADVISORY:MU, MRI and Kansas City Showcase New Alternative Fuel Technology

WHAT: A press conference will showcase an innovation in vehicle natural gas storage technology that is being tested on a pickup truck owned by the Kansas City Office of Environmental Quality. Researchers from the University of Missouri-Columbia (MU) and Midwest Research Institute (MRI) have developed a natural gas tank filled with nanoporous carbon that is made from corncobs and can hold 180 times its own volume of natural gas at low pressure. This meets the storage target set by the U.S. Department of Energy and allows for a compact tank similar to current gasoline tanks. MU and MRI partnered with the City of Kansas City to install a prototype of the tank on a pickup truck, which is being monitored to test the tank's performance.

WHO: Speakers and experts at the event will include:
- Kay Barnes, mayor of Kansas City
- Brady Deaton, MU chancellor
- Jim Spigarelli, president and CEO of MRI
- Experts from MU, MRI and Kansas City, including Peter Pfeifer, professor of physics and principal project leader; Phil Buckley, principal engineer; and Sam Swearngin, superintendent of the Kansas City Central Fleet

WHEN: 10 a.m., Friday, Feb. 16

WHERE: MRI's Mag Auditorium, 4920 Cherry St., Volker Blvd., Kansas City, Mo.

National Science Foundation
WHERE DISCOVERIES BEGIN

SEARCH
NSF Web Site

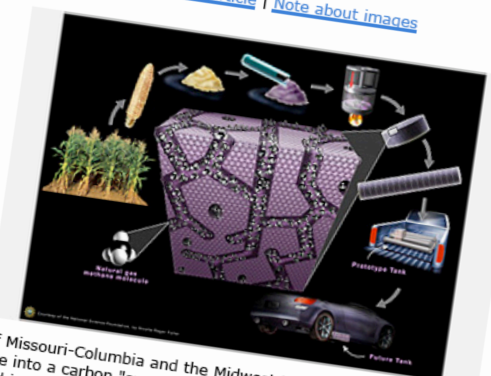
All Images

Press Release 07-011

From Farm Waste to Fuel Tanks

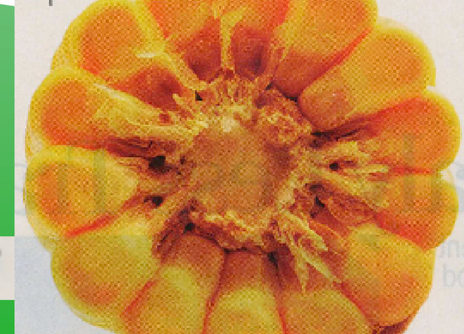
Record-breaking methane storage system derived from corncobs may encourage mass-market natural gas automobiles

Back to article | Note about images



Researchers at the University of Missouri-Columbia and the Midwest Resear... method to convert corncob waste into a carbon "sponge" with n... of natural gas and can be formed into a variety of shapes, ideal... methane-powered automobiles.

...elopments to Watch



ENERGY
NATURAL GAS IN THE COB

March 12, 2007 | BusinessWeek | 87

ALL-CRAFT Alliance for Collaborative Research in Alternative Fuel Technology

MRI Midwest Research Institute

ALL-CRAFT: Objectives

- Develop low-pressure, high-capacity storage technologies for natural gas (NG, methane, CH_4) and hydrogen (H_2), based on new adsorbent materials discovered at MU:
  — nanoporous carbon from waste corncob ("sponge for NG")
- Demonstrate low-pressure, flat-panel NG tank for
  — next-generation clean vehicles (NG internal combustion engines)
  — hydrogen fuel cell cars (with onboard reformers)
  — collection of biomethane from landfills, ... ("pollutant to renewable energy")
  — large-scale shipping of NG from/to locations not served by NG pipelines
- Develop low-pressure, flat-panel H_2 tank for
  — hydrogen fuel cell vehicles
  — other electric power supplies

Funded by:
– NG: NSF "Partnerships for Innovation;" California Energy Comm.
– NG: MU, MRI, Advanced Photon Source, DED/GAANN
– Total NG: \$1.1M (2004-07 NSF), \$1.3M (2009-11, CEC)
– H_2: DOE/BES, DOD/NSWC, DOE/EERE (2007-11), \$4.1M

Partners

- **MU (lead institution):** Physics (Pfeifer, Principal Project Leader; Wexler), Chemistry (Hawthorne), Chemical Engineering (Suppes), MURR (Robertson)
- Lincoln University, Jefferson City
- **Midwest Research Institute (MRI),** Kansas City: Energy-Storage Technology (Buckley)
- Clean Vehicle Education Foundation, Washington, DC
- DBHORNE, LLC, Atlanta
- Georgia NanoFAB, Atlanta
- Advanced Nanocarbon, Inc., Columbia, MO
- ANG Containment & Delivery Systems, Inc., Clermont, FL
- Missouri Dept. of Natural Resources (Energy Center), Jefferson City
- **Kansas City Office of Environmental Quality/Central Fleet**, Kansas City
- EMPA Materials Science & Technology, Zurich, Switzerland

Who we are—People

MU, Physics
Lauren Aston, Lin Bai (Tulane U.), Sarah Barker, Matt Beckner, Sam Bowman (NW MO State U.), Jacob Burress, Sara Carter, Raina Cepel, Elmar Dohnke, Carol Faulhaber (NW MO State U.), Lucy Firlej (U. Montpellier II, France), John Flavin, Monika Golebiowska, Lacy Hardcastle, Michael Kraus, Bogdan Kuchta (U. Marseille, France), Nick Kullman, Cintia Lapilli, Erik Norwald, Patrick O'Keeffe, Jeff Pobst, Sam Potts, Robert Schott, Demetrius Taylor, Matt Taylor, Carlos Wexler, Mikael Wood

MU, Chemistry
Jerry Atwood, Praveen Thallapally, Trevor Wirsig

MU, Chemical Engineering
Mona-Lisa Banks (Lincoln U.) Joshua Bulloc, Sean Crockett, Tarek Dannoon, Matt Factor, Mike Gordon, Monty Kemiki (Penn State U.), Eric Leimkuehler, Bryan Sawyer, Parag Shah, Serean Spellerberg, Galen Suppes, Ali Tekeei, Mustafa Yousif (Alabama A&M U.)

MU, Civil & Environmental Engineering
Joshua Bergsten, John Bowders

MU, MURR
Dave Robertson

MU, Intern. Inst. Nano & Molecular Medicine
Fred Hawthorne, Hanbaek Lee, Mark Lee, Satish Jalisatgi, Zhi Yang

MRI
Bob Barton, Phil Buckley, Tom Breier, Joe Clement, David Dolson, Jason Downing, Steve Eastman (MU), Phil Freeze, Sam Grinter (MU), Steve Graham, Antonio Howard (Lincoln U.), Greg Jones, Juan Martinez, Darren Radke, Todd Vassalli (MU)

Kansas City Office of Environmental Quality
Dennis Murphy, Sam Swearngin

Consultants
Christian Bach, EMPA/ETH, Zurich, Switzerland
Cindy Carroll, MO Dept. of Natural Resources
Doug Horne, Clean Vehicle Education Foundation
Signe Kjelstrup, Norwegian U. Sci. & Techn., Trondheim
Cynthia Mitchell, Columbia Municipal Landfill
John Noller, MO Dept. of Natural Resources
David Quinn, Royal Military College of Canada
Francisco Rodriguez-Reinoso, U. Alicante, Spain
Szczepan Roszak, Wroclaw U. Technology, Poland
Louis Schlapbach, EMPA/ETH, Zurich, Switzerland
Rusty Sutterlin, Renewable Alternatives LLC
Jim Wegrzyn, Brookhaven National Laboratory
Andreas Züttel, EMPA/ETH, Zurich, Switzerland

Low-tech waste material → high-tech product

VOLUME 88, NUMBER 11 PHYSICAL REVIEW LETTERS 18 MARCH 2002

Nearly Space-Filling Fractal Networks of Carbon Nanopores

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F. Rodríguez-Reinoso,[5] P. W. Schmidt,[1,‡] and D. J. Voss[1]
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[2]*Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
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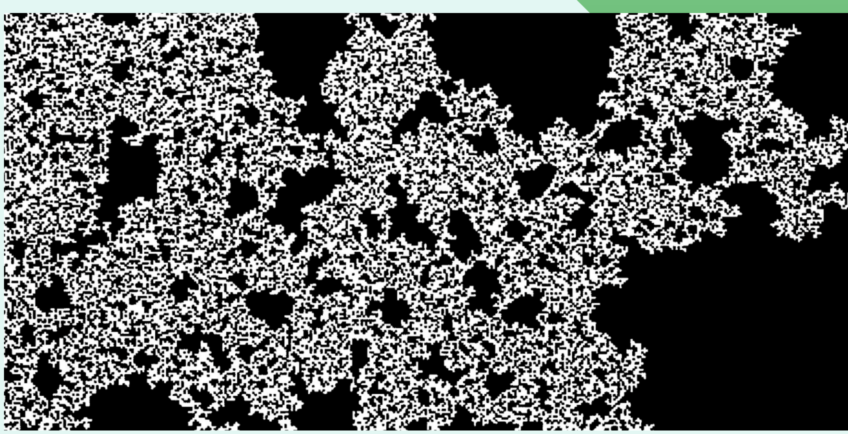
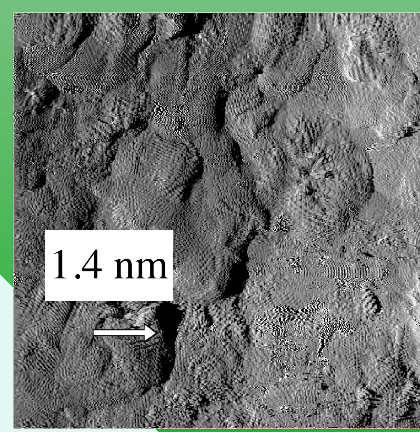
[4]*Center for Microengineered Materials, University of New Mexico, Albuquerque, New Mexico 87131*
[5]*Departamento de Química Inorgánica, Universidad de Alicante, E-03080 Alicante, Spain*
[6]*Air Force Research Laboratory, Edwards Air Force Base, California 93524*
(Received 11 January 2001; revised manuscript received 17 October 2001; published 28 February 2002)

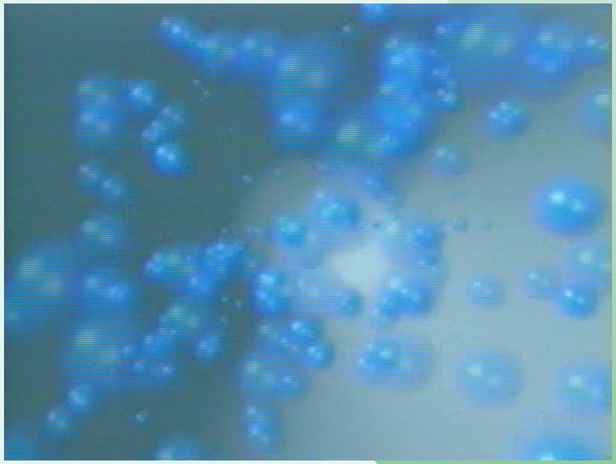
Small-angle x-ray scattering, nitrogen adsorption, and scanning tunneling microscopy show that a series of activated carbons host an extended fractal network of channels with dimension $D_p = 2.8-3.0$ (pore fractal), channel width 15–20 Å (lower end of scaling), network diameter 3000–3400 Å (upper end of scaling), and porosity of 0.3–0.6. We interpret the network as a stack of quasiplanar invasion percolation clusters, formed by oxidative removal of walls between closed voids of diameter of ~10 Å and held in registry by fibrils of the biological precursor, and point out unique applications.

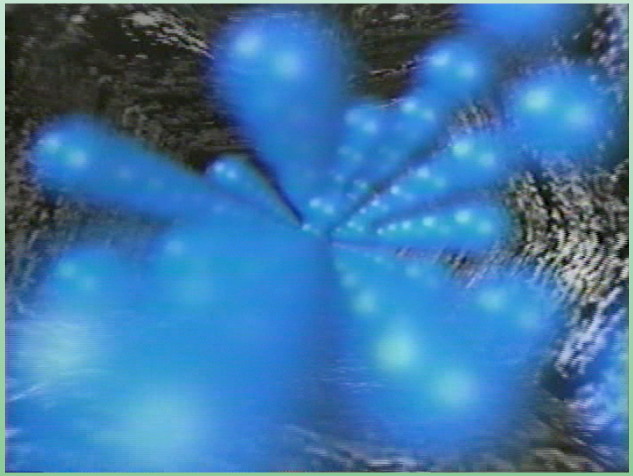


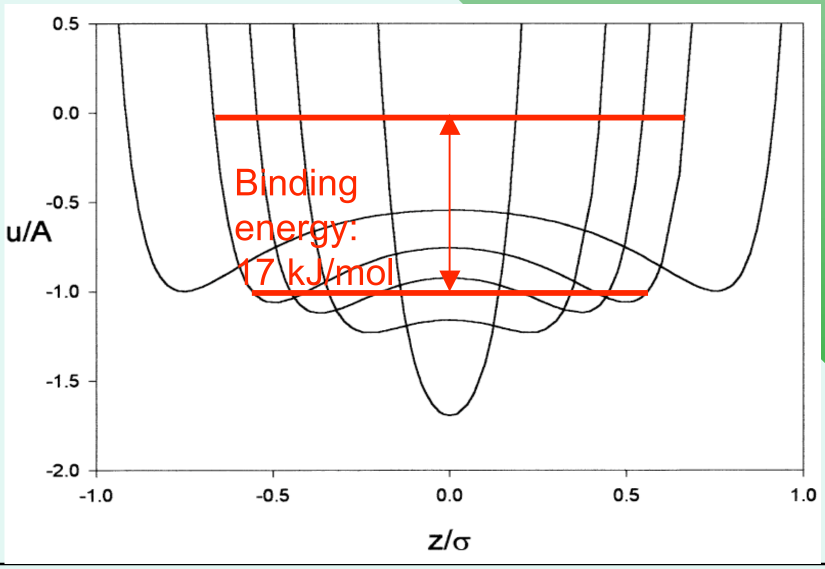


Van der Waals attraction in nanopores forces NG into liquid-like dense fluid (170 g/l at 35 bar)

Why are nanopores important?







1) In narrow pores, van der Waals potentials overlap; create deep energy well: Max. CH_4 / H_2 capacity in pores of width 1.1 nm / 0.7 nm. Molecules are held in tight-packed configurations.

2) Narrow pores create large surface area: >3000 m^2/g (football field)

Why alternative fuels?

- Reduce dependence on foreign oil
- Harness domestic renewable energy sources
- Create new opportunities for domestic agriculture
- Create clean air in cities
- Reduce transportation costs by improving energy efficiency
- Reduce greenhouse gas emissions

} Develop sustainable transportation in U.S.

What are alternative fuels?

- Ethanol (from corn, wood, …)
- Natural gas*‡ (NG; from domestic gas fields, deep-sea methane hydrate fields, landfills, biomass); 85% of NG used in U.S. is domestic
- Biodiesel (from soybeans, vegetable oils, …)
- Hydrogen* (from NG, water & electricity, coal, …)
- Electricity (from coal/nuclear/hydroelectric/solar/wind power plants)

* ALL-CRAFT ‡At pump currently: $0.8-1.2/equivalent gallon of gasoline

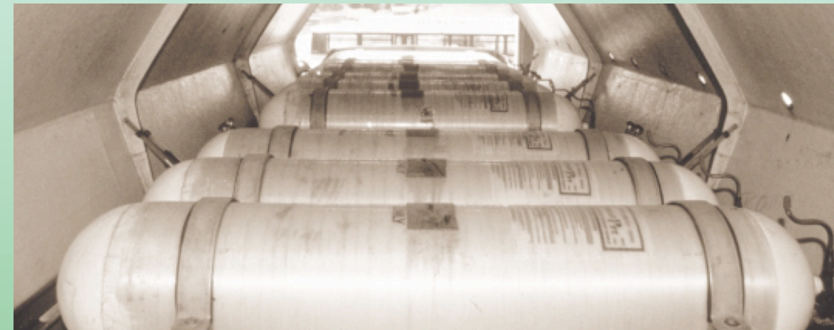
Current natural-gas vehicles

- Low emission of hydrocarbons (/ ozone, smog), CO, NO_x, particulate matter. Up to 40% reduction of CO_2. NG stored as compressed natural gas (CNG) in steel or composite cylinders at 250 bar (3600 psi).
- Clean Cities Coalitions:
  - Los Angeles: >1500 CNG buses
  - Kansas City: >200 CNG public utility vehicles
  - U.S.: 150,000 CNG vehicles
  - Worldwide: over 5 million CNG vehicles

Why are we not already driving NG-fueled cars?

- High-pressure cylindrical/spherical tanks take up passenger or trunk space.

  CNG cylinders in transit bus:



- Only NG passenger car in U.S.: Honda Civic GX; CNG tank in trunk:

Goal: Develop low-pressure (35 bar, 500 psi), "flat-panel" tank, like gasoline tank. Store NG in nanoporous carbon; pores adsorb NG like a sponge: ANG tank

Best flat-panel tank previously

Atlanta Gas Light Adsorbent Research Group (AGLARG), 1997:

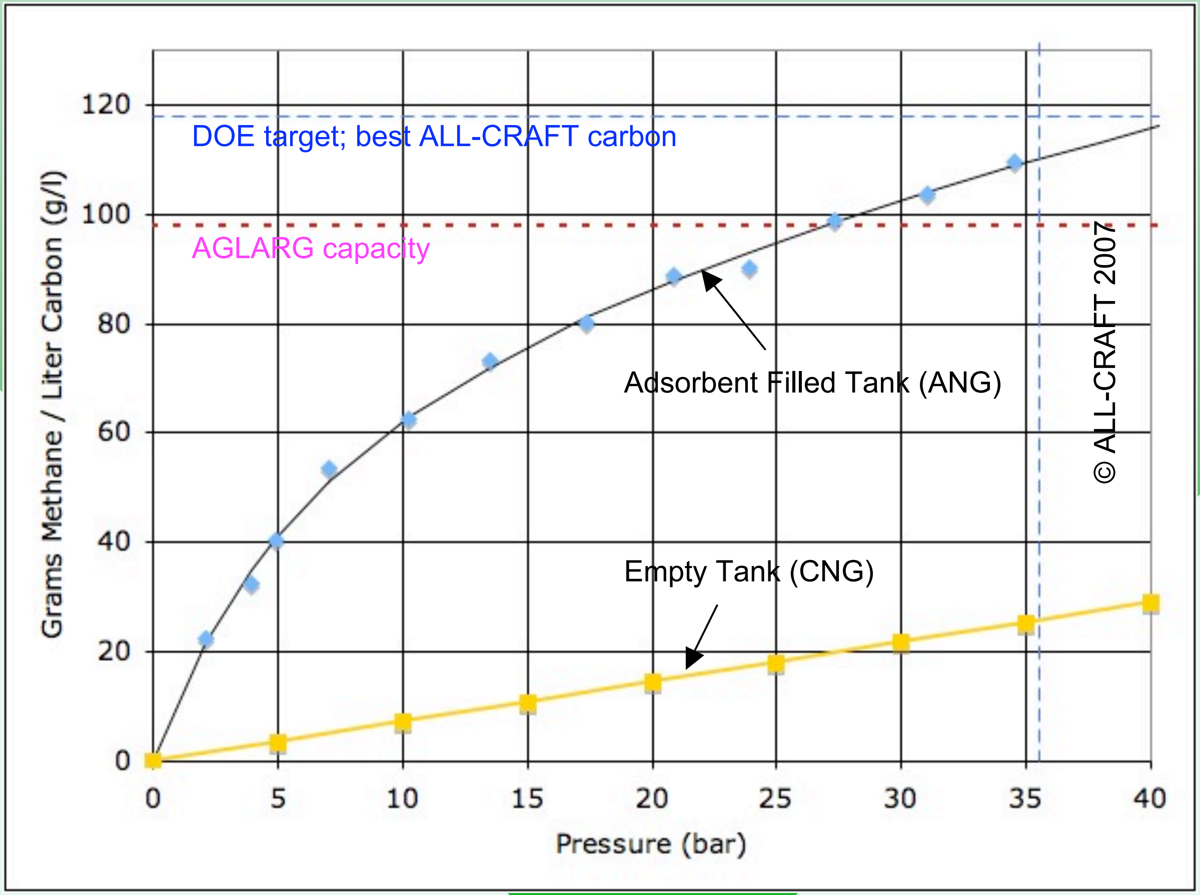
Adsorbent: monolithic activated carbon ("briquettes") from peach pit; troublesome maintenance of consistent quality of briquettes; binder blocks pores

4 tanks in bed of NG Dodge Dakota

ALL-CRAFT: Monolithic carbon, with superior performance, from corncob. Missouri corn can supply raw material for NG tanks of all cars in the U.S.

Performance of ALL-CRAFT tank

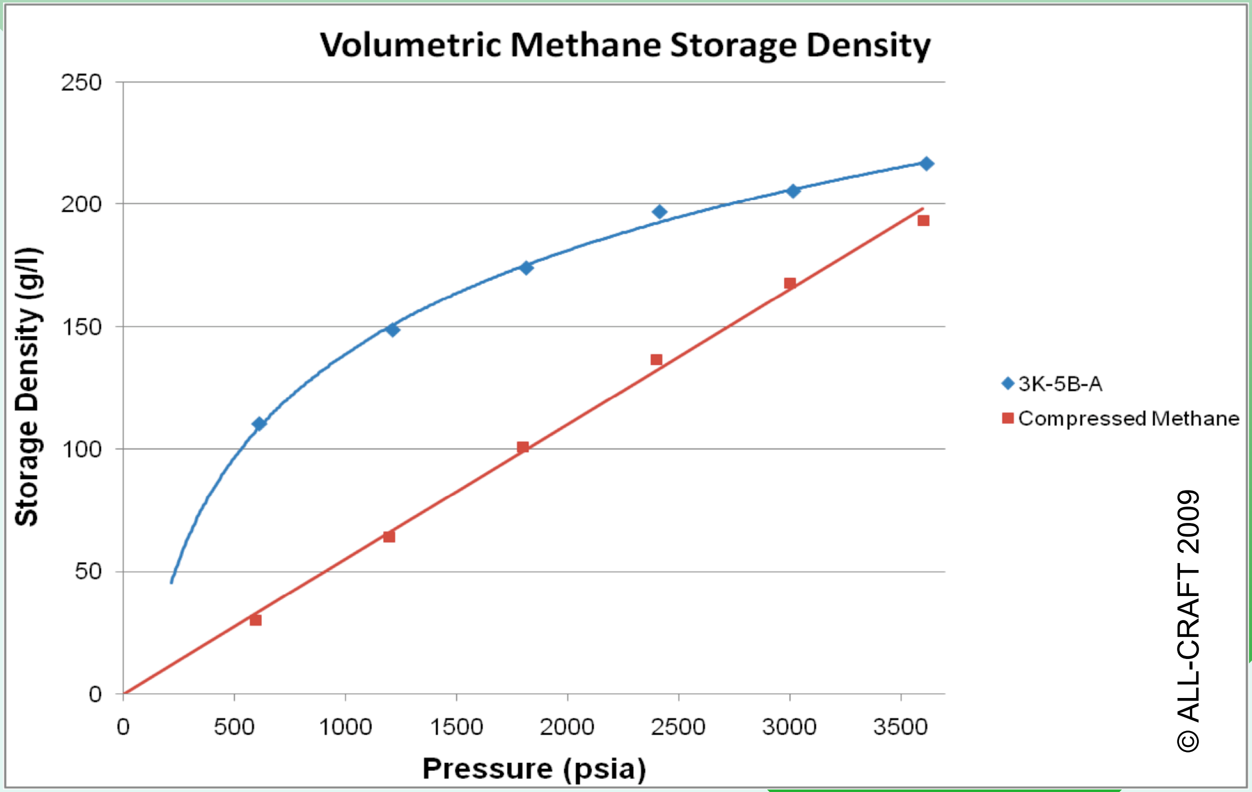
- Target pressure for flat tank: 35 bar (35 atm, 500 psig *); without adsorbent, pressure would have to be 150 bar, much more than what a flat tank can bear
- DOE target capacity: 118 g/l (vol. CH_4 at 25 ^{o}C & 1 bar, per vol. tank: 180 V/V)
- AGLARG tank: 98 g/l
- ALL-CRAFT target: >100 g/l achieved! DOE target achieved!



*) 500 psi: pressure in NG pipelines

ANG vs. CNG at high pressures

- For heavy-duty vehicles, cylindrical tanks (CNG at 3600 psi) are fine
- Can ANG tank at 3600 psi beat CNG tank at 3600 psi?
- Yes, ANG storage capacity is ~20% higher:

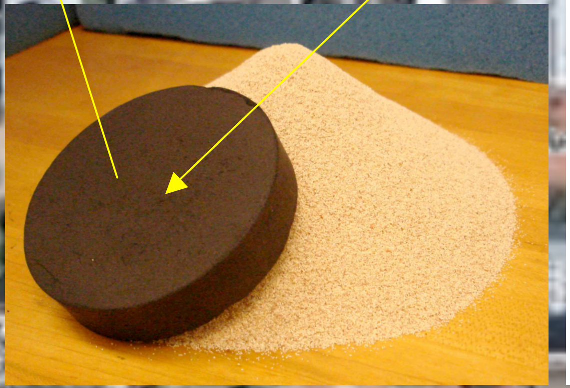


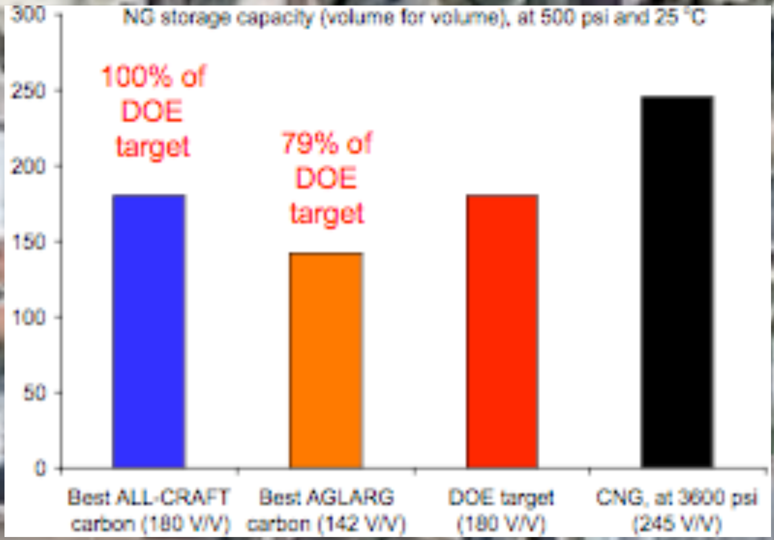
Carbon production and NG storage capacity

Produced over 100 different carbons from corncob (variable formulations) & searched for maximum storage capacity

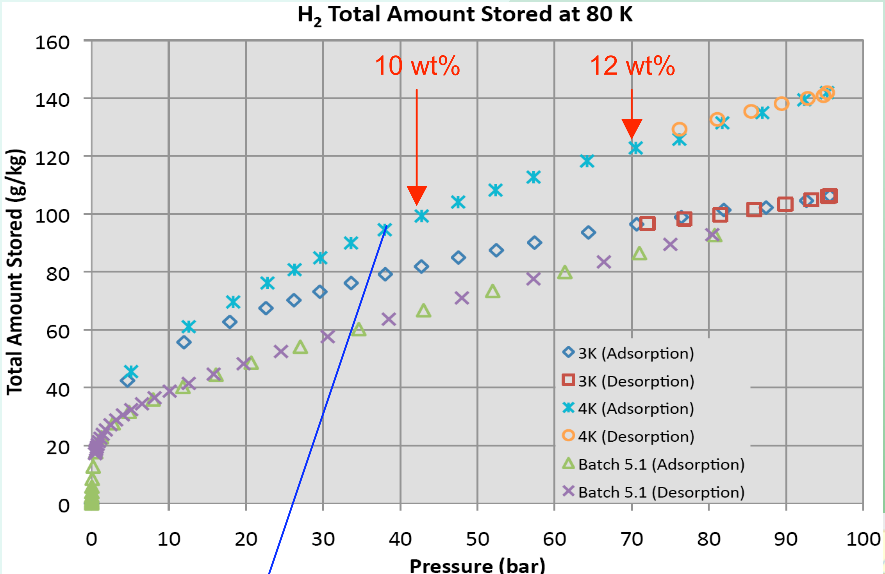
NREL: "Missouri Hockey Puck"

Has surface area that could cover much of MU campus





Hydrogen storage capacities

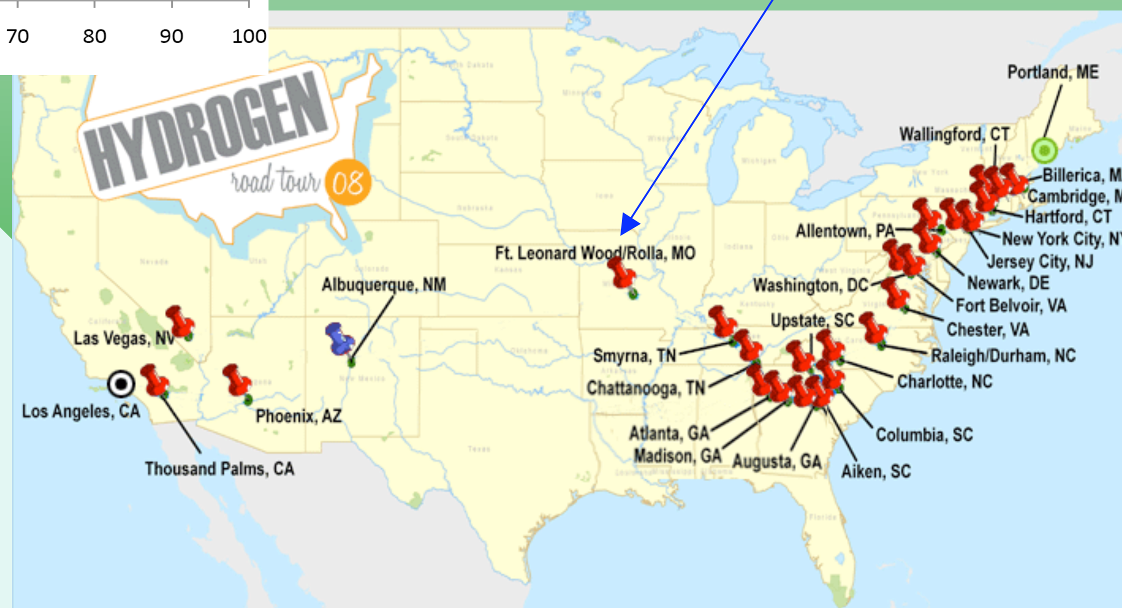


DOE 2010 target: 6 wt% at ambient temperature and ~ 50 bar

DLA/NSWC:

Hydrogen fuel cells on forklifts, …

Rolla, MO: 1st hydrogen fueling station in Midwest

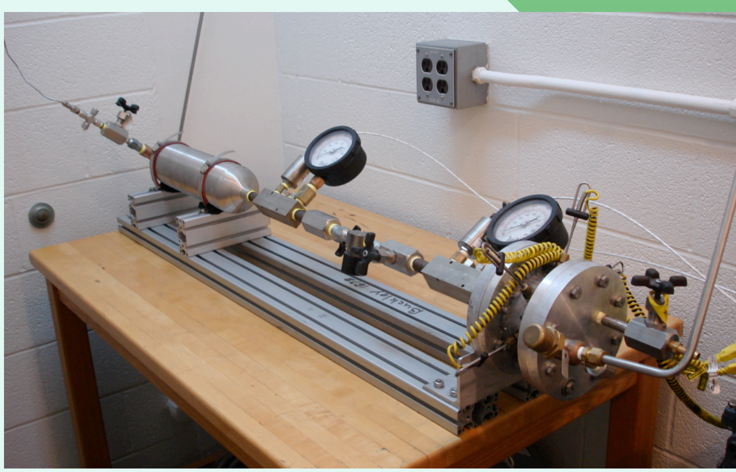


Research & development in the lab

CH_4 uptake on small samples

X-ray analysis at Advanced Photon Source

CH_4 uptake on briquettes (MRI test fixture)



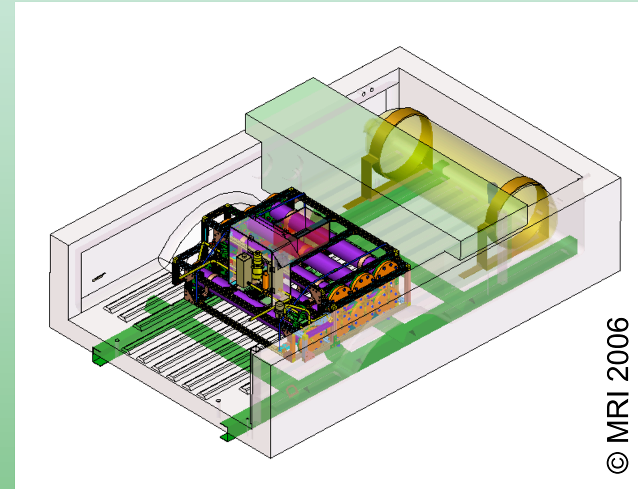
150-ton press to make briquettes

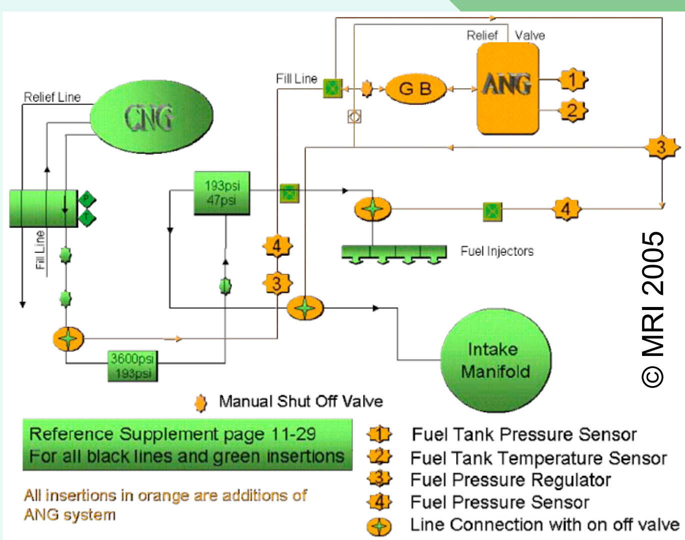
ALL-CRAFT Alliance for Collaborative Research in Alternative Fuel Technology

MRI Midwest Research Institute

NSF

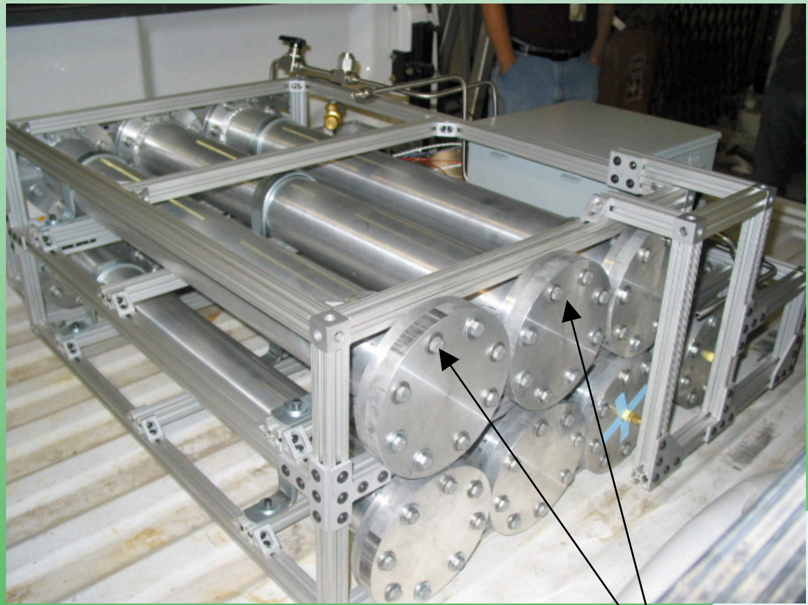
ALL-CRAFT ANG tank on Ford F-150: MRI, Kansas City Office of Environmental Quality—October 2006 to present





6 Al tubes holding 300 carbon briquettes

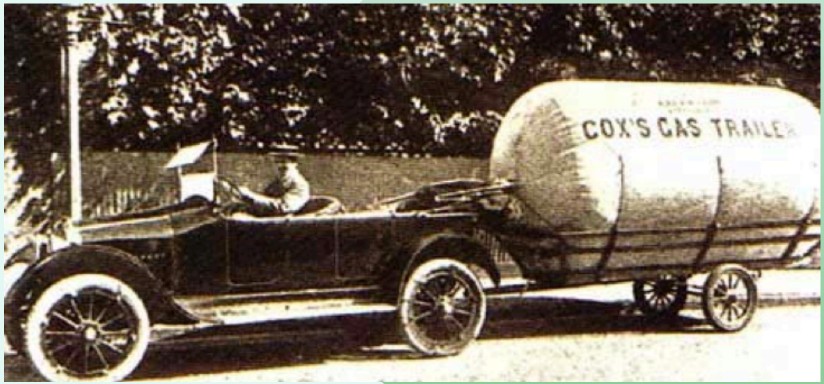
ALL-CRAFT tank on Ford F-150: MRI, Kansas City Office of Environmental Quality—February 2007 to present



6 Al tubes holding 300 carbon briquettes

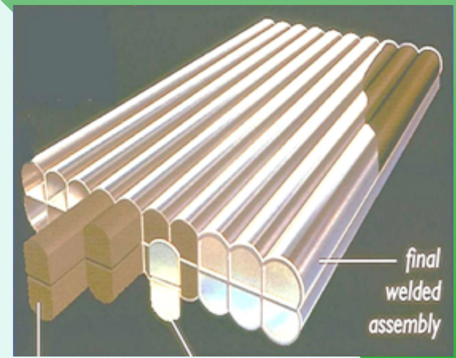
Natural gas vehicles over time

First NG vehicle 1910 (USA) with balloon tank on trailer



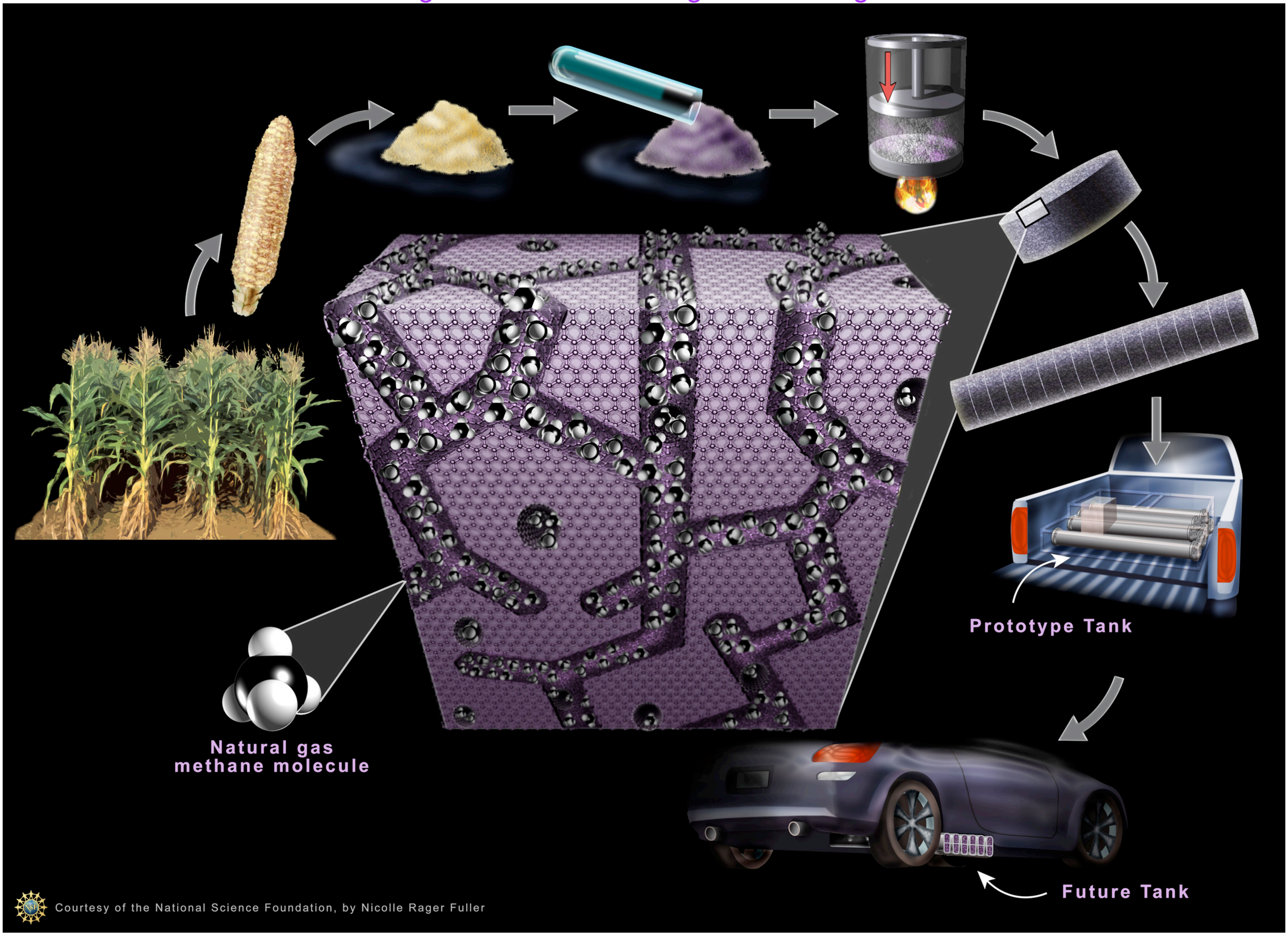
NG vehicle ~1930 (France) with balloon tank on roof

Current NG vehicle with high-pressure tank in trunk

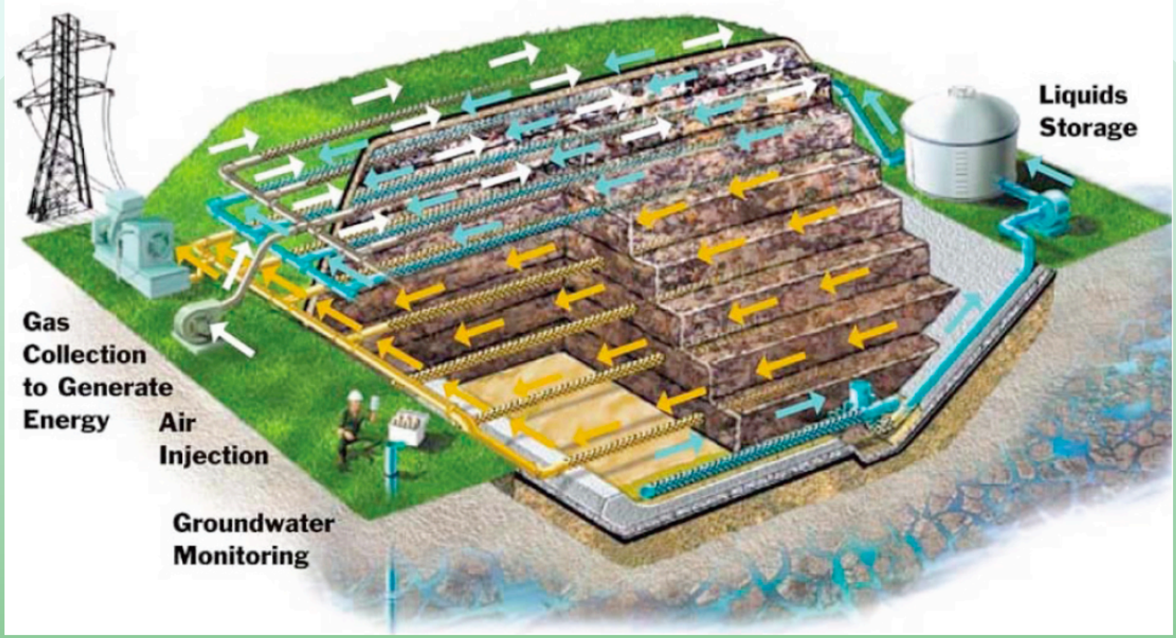


Future NG vehicle with low-pressure tank under floor

From agricultural waste to high-tech storage tanks



Recovery of biomethane from landfills and farms



- Landfills: largest human-made source of methane (CH_4) in U.S.
  Landfill gas (LFG): ~ 50% CH_4, ~ 50% CO_2
- CH_4: 20 times more potent greenhouse gas than CO_2
  Capture CH_4 at landfill: "pollutant to renewable energy"
  If no power plant: recover CH_4 in 60,000 pound ANG tanks
- Annual CH_4 emission from landfills in U.S.:
  - Could power 4 million homes: $5 billion/yr
  - Greenhouse equivalent to emission from 90 million cars (~1/2 of cars in U.S.)
  - If captured, equivalent to planting forest 2 x area of MO

Commercialization

- MU filed USPTO and WIPO patent application, Nov. 2007

- MU issued license, for mobile applications of ANG technology, to ANG Containment & Delivery Systems, Inc., March 2009

Opportunities

National level

- NG fueled cars = next-generation clean vehicles
  1. Reduce smog, respiratory disease, cardio-vascular disease, …
  2. Reduce greenhouse gas emissions
  3. Reduce dependence on foreign oil ***now***
  4. Harness domestic NG fields (Alaska), deep-sea methane hydrate fields (Oregon), renewable NG from landfills & biomass (Missouri, …)
- Recovery of NG from landfills
  1. Pollutant to energy
  2. Economic growth in rural areas

State level

- Produce NG tanks, from MO corn cob, for 10 million cars/year: $10 billion/yr
- Produce & operate NG tanks, from MO corn cob, for 2,500 landfills: $10 billion/yr
- Produce NG tanks, from MO corn cob, for large-scale NG shipping: $5 billion/yr