Polyaromatic Naphthalene Derivatives as Heat Transfer Fluids

US Department of Energy CSP Program Review

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Golden CO

Outline of Presentation

- Description of concept and objectives
- Programmatic details
- Desired impact on concentrating solar power system performance
- Details of activities at ORNL and at Cool Energy
- Summary of progress to date
- Challenges to be addressed in the next year
- Future work

Description & Objectives: Addressing a need for a stable high-temp heat transfer fluid

STATUS QUO

CSP collectors are now limited to temperatures <400°C

- *Issues are fluid stability, vapor pressures, materials compatibility*

NEW INSIGHTS

Certain classes of organic molecules have not been considered as heat transfer fluids because of a lack of data.

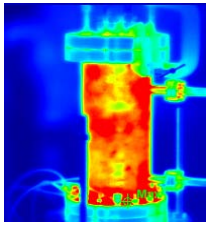
New data suggest that substituted naphthalenes have properties to allow repeated cycling above 500°C: stability to critical point, low vapor pressures, and low melting points.

Investigation of Thermal and Fluidic Properties of Substituted Naphthalenes:

- Synthesize phenyl naphthalene ✓
- Investigate materials interactions in static cell at high temperatures and pressures ✓
- Measure data that are lacking: viscosity, thermal conductivity
- Test for isomerization and hydrogen release at temperatures above 500°C. ✓

High Temperature Laboratory Scale Testing:

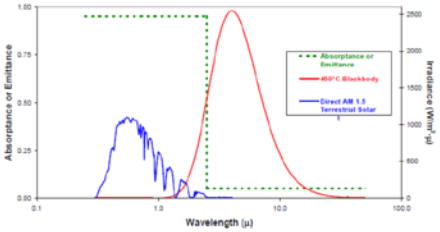
- Test performance in repeated and continuous cycling in ORNL high temperature test loop.
- On-line transducers for temperature and pressure profiles. ✓
- Off-line analysis for possible breakdown products. ✓



Medium Temperature Pilot Scale Testing:

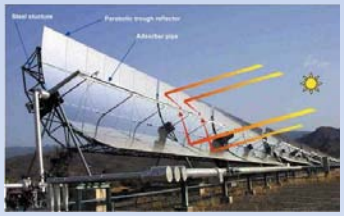
- Cool Energy Solar Field ✓
- Medium temperature operation
- Test assumptions used in system performance model

IMPACT



- Will develop dynamic system model to simulate performance in high temperature test loop
- Will carry out system performance modeling and economic analysis

END-OF-PHASE GOAL



Goal is to report on feasibility of using phenylnaphthalenes in high temperature (>500°C) solar field.

These fluids may allow CSP collectors to operate to 500°C

CSP should be more efficient at higher operating temperatures.

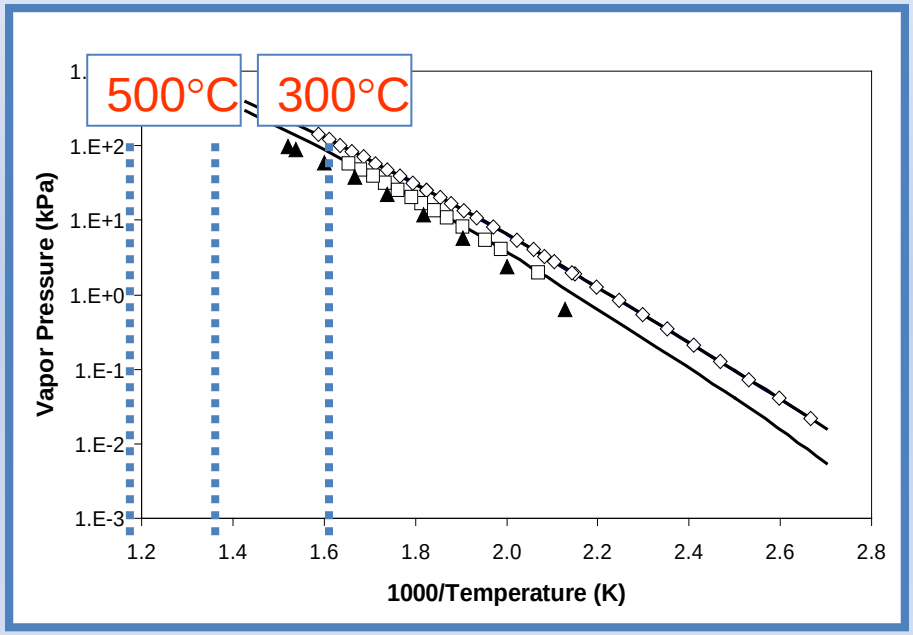
- DOE has identified five technical barriers to adoption of CSP
  - Capital cost. *The cost of the proposed heat transfer fluid will be reduced by optimizing the synthesis and selection of inexpensive reagents.*
  - Reliability. *The stability and compatibility of the fluid will be tested in high-temperature, high-pressure static tests in contact with loop materials.*
  - Performance. *The performance of the fluid will be tested by repeated cycling in a high-temperature test loop at ORNL.*
  - O&M costs. *Operations and maintenance costs will be reduced if the heat transfer fluid proves to be stable and non-reactive after repeated cycling.*
  - Technology Risk. *The heat transfer fluid will be tested in a pilot-scale solar field.*

- Polyaromatic naphthalene derivatives have physical properties that suggest they will be suitable as heat transfer fluids for concentrating solar power applications.
- ORNL is working with Cool Energy Inc to test aromatic heat transfer fluids at high temperatures and in a medium-temperature, pilot-scale solar field.
  - Three year project (February 2010 through January 2013)
  - Total Budget $935K

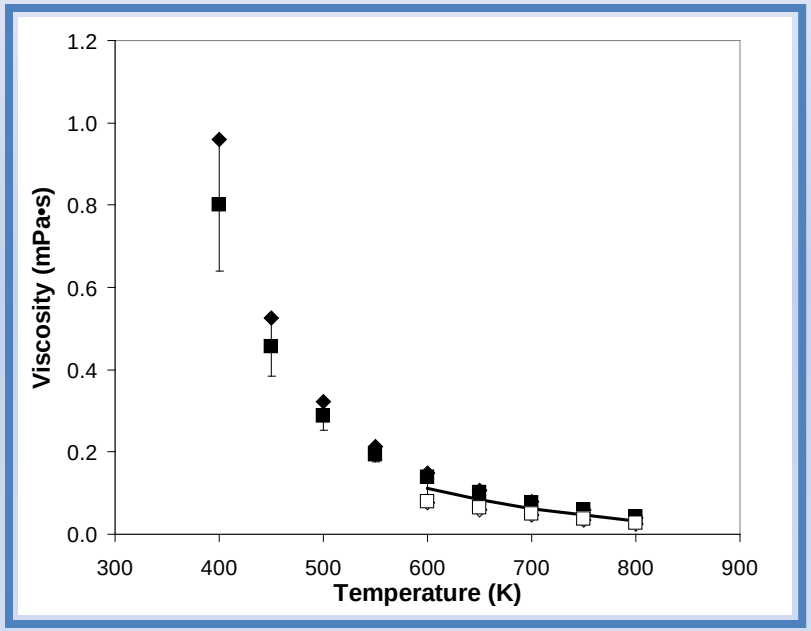
Substituted naphthalenes have physical properties attractive for CSP.

These fluids have potential to be used above 500℃ in CSP applications.

Measured Vapor Pressure



Calculated Viscosity

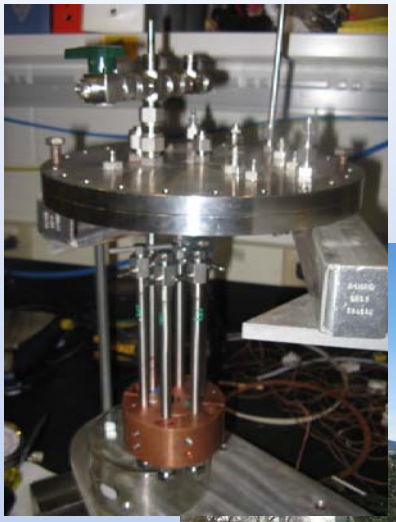


Liquid close to room temperature
Stable almost to critical point, 545℃
Relatively low critical pressure, 7 bar

McFarlane, Luo, Garland, Steele
Separation Science & Technology (2010)

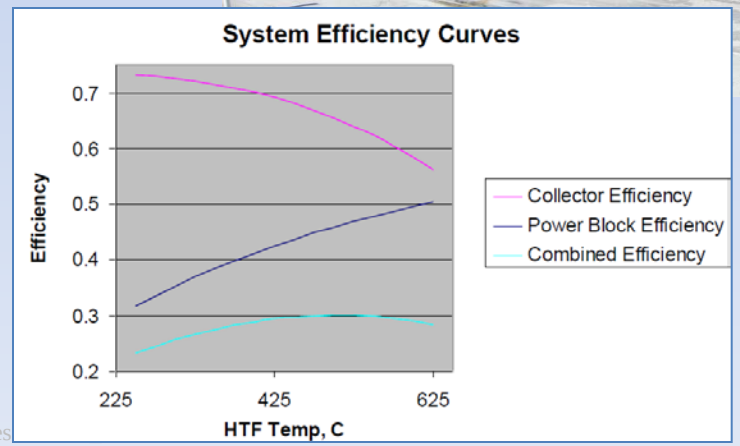
Activities this year have focused on testing high temperature performance of fluid

- Small scale high temperature heating with detailed chemical analysis

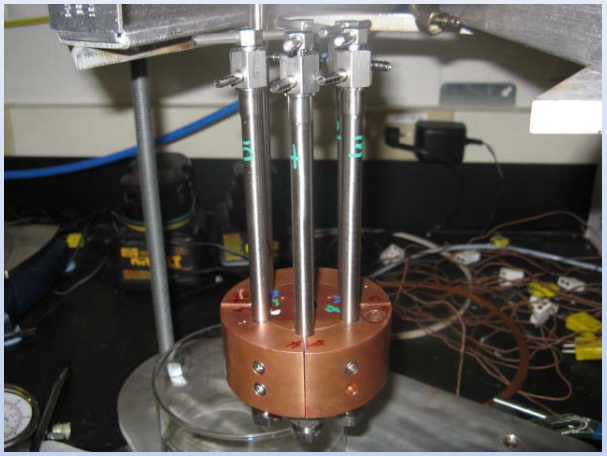


- Building and commissioning of pilot-scale test loop

- LCOE calculations on potential efficiency gains from use of high temperature HTF

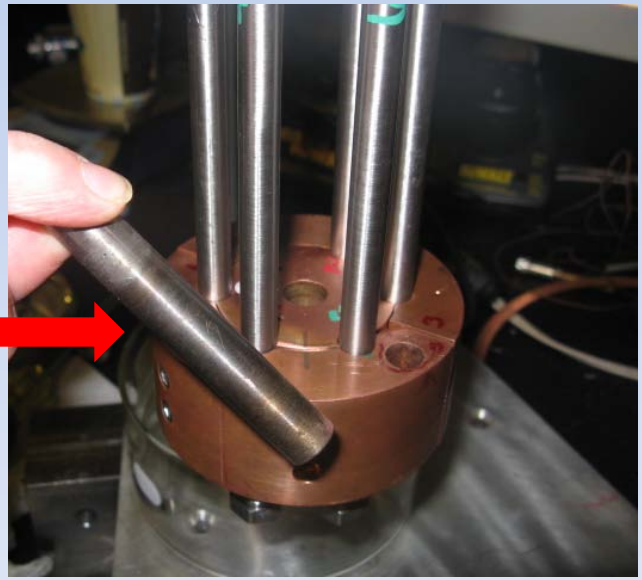


A furnace assembly was constructed to allow safe and efficient heating of the organic fluid to temperatures above 500°C.



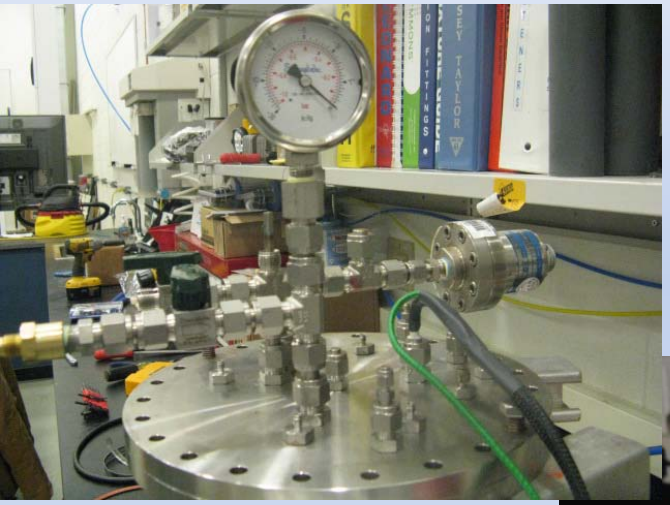
- Tubes welded on bottom and sealed on the top with valves or fittings
- Individual tubes can be removed and replaced

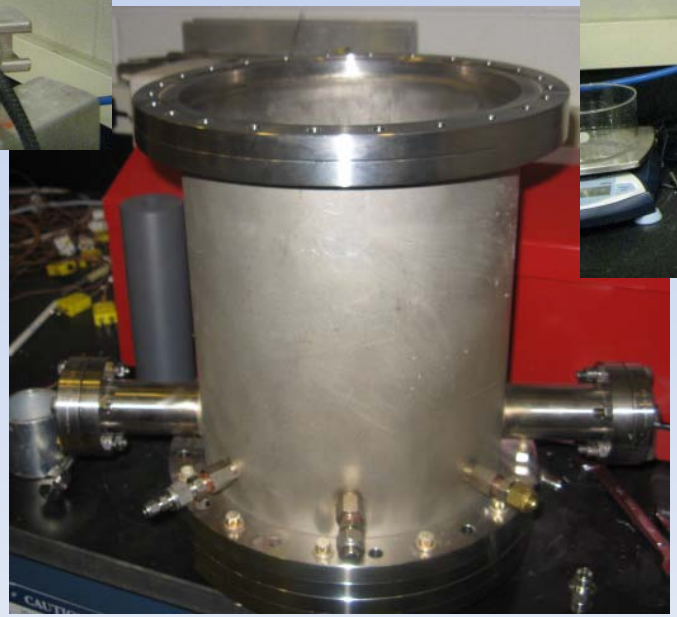
- Electrical resistance heating in center of copper block allows control to above 500°C

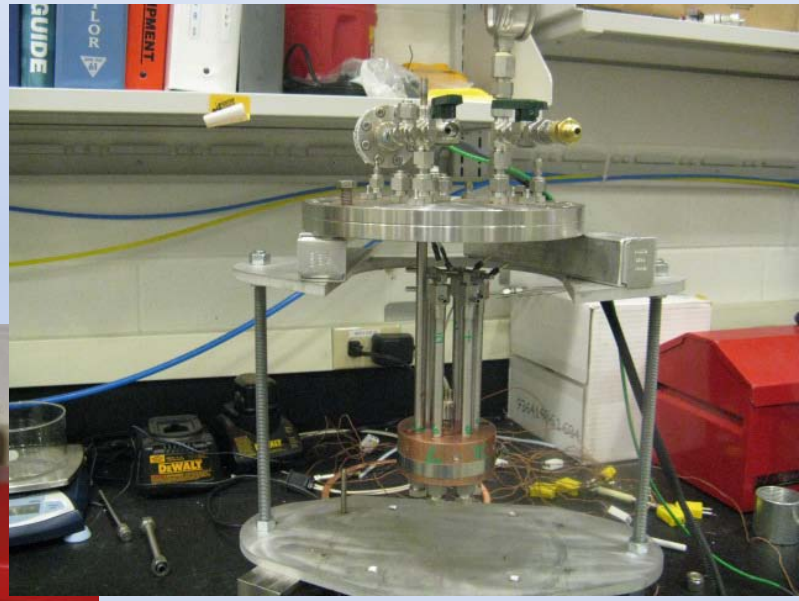


The heater assembly is housed in a vacuum chamber.

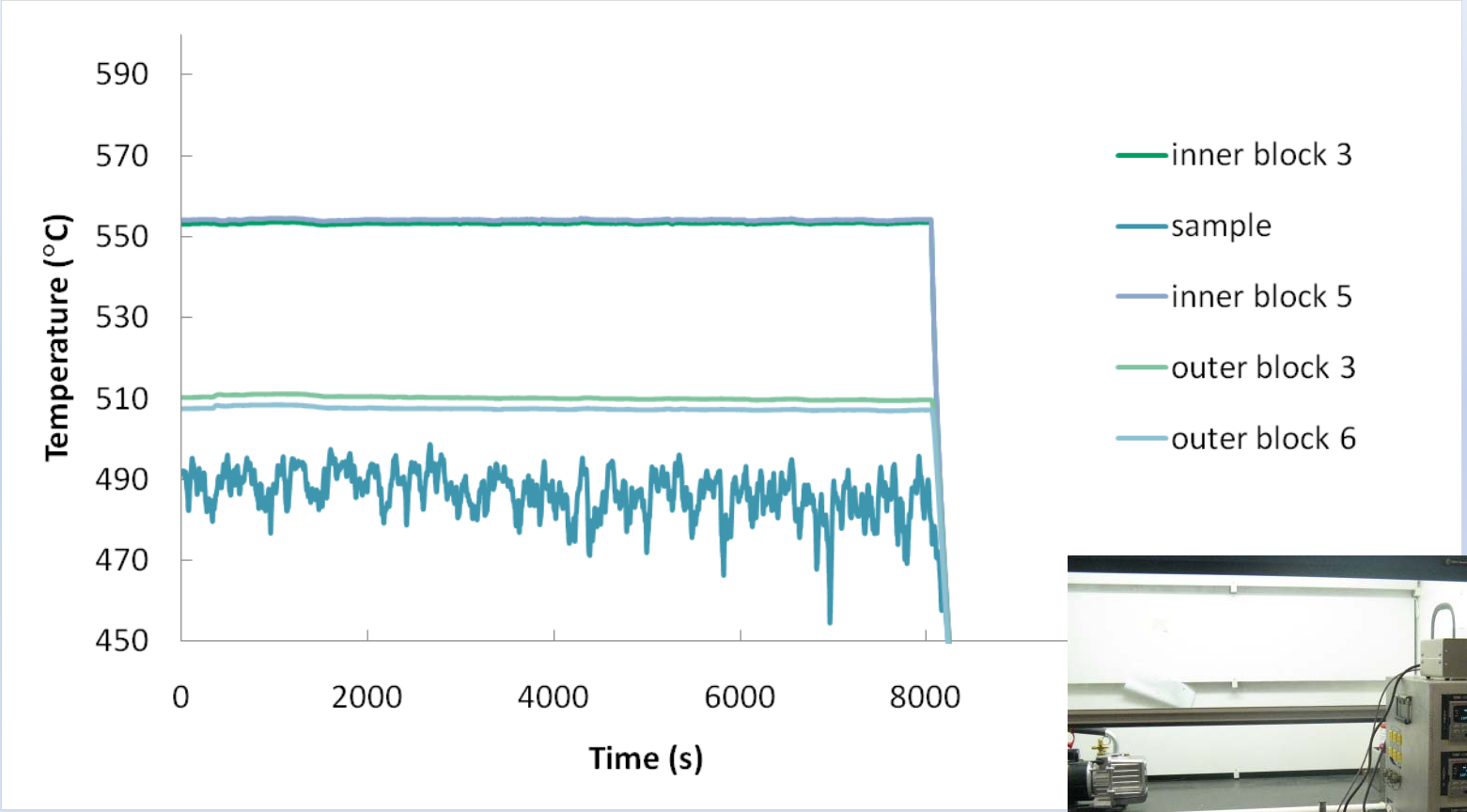
- The heated copper block is suspended from the top plate
- Pressure and temperature are measured in a sixth sample
- The chamber is evacuated during heating to reduce heat loss by conduction

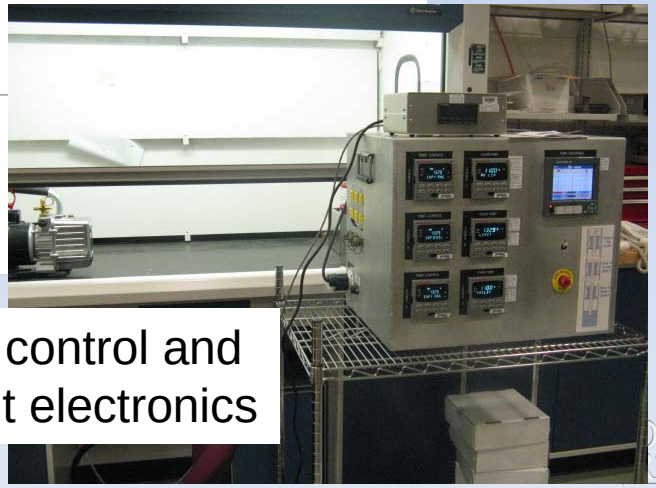






On-line temperature measurements are recorded during heating for inside and outside blocks and at sample.

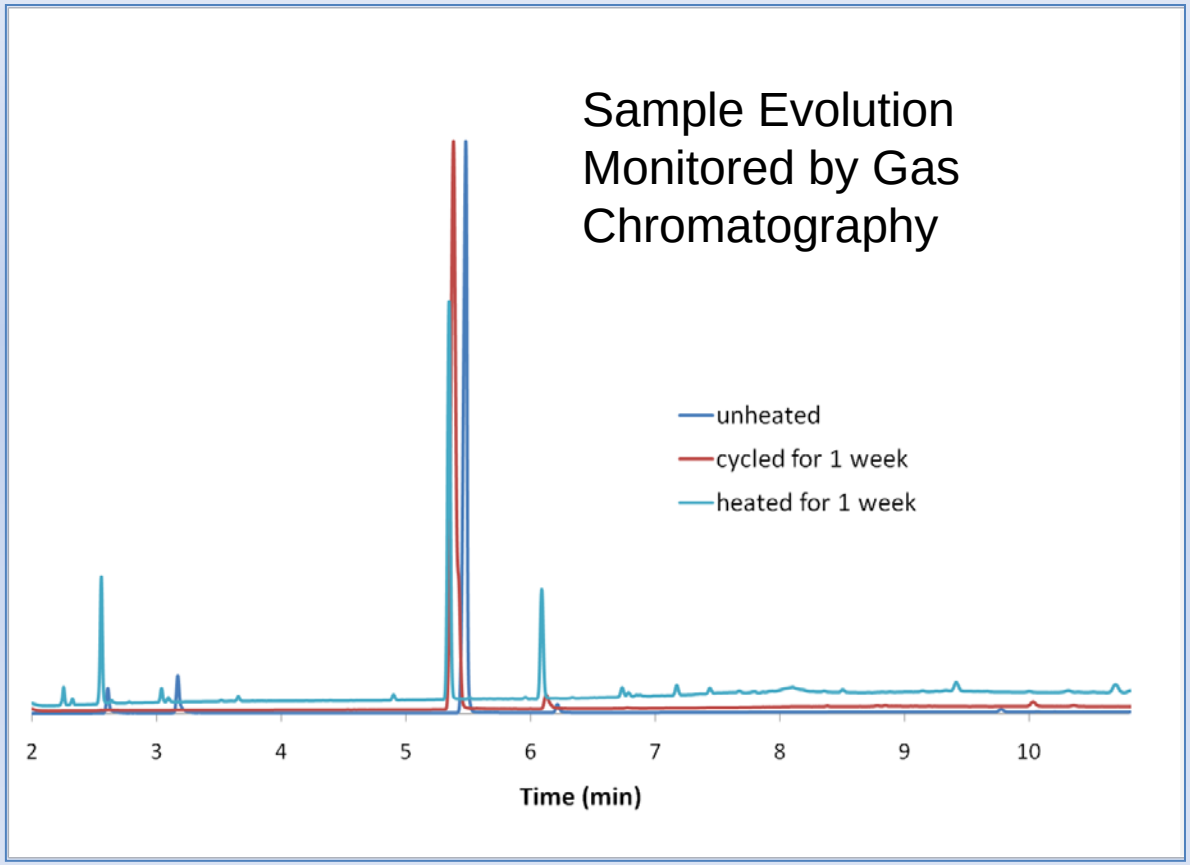




Temperature control and measurement electronics

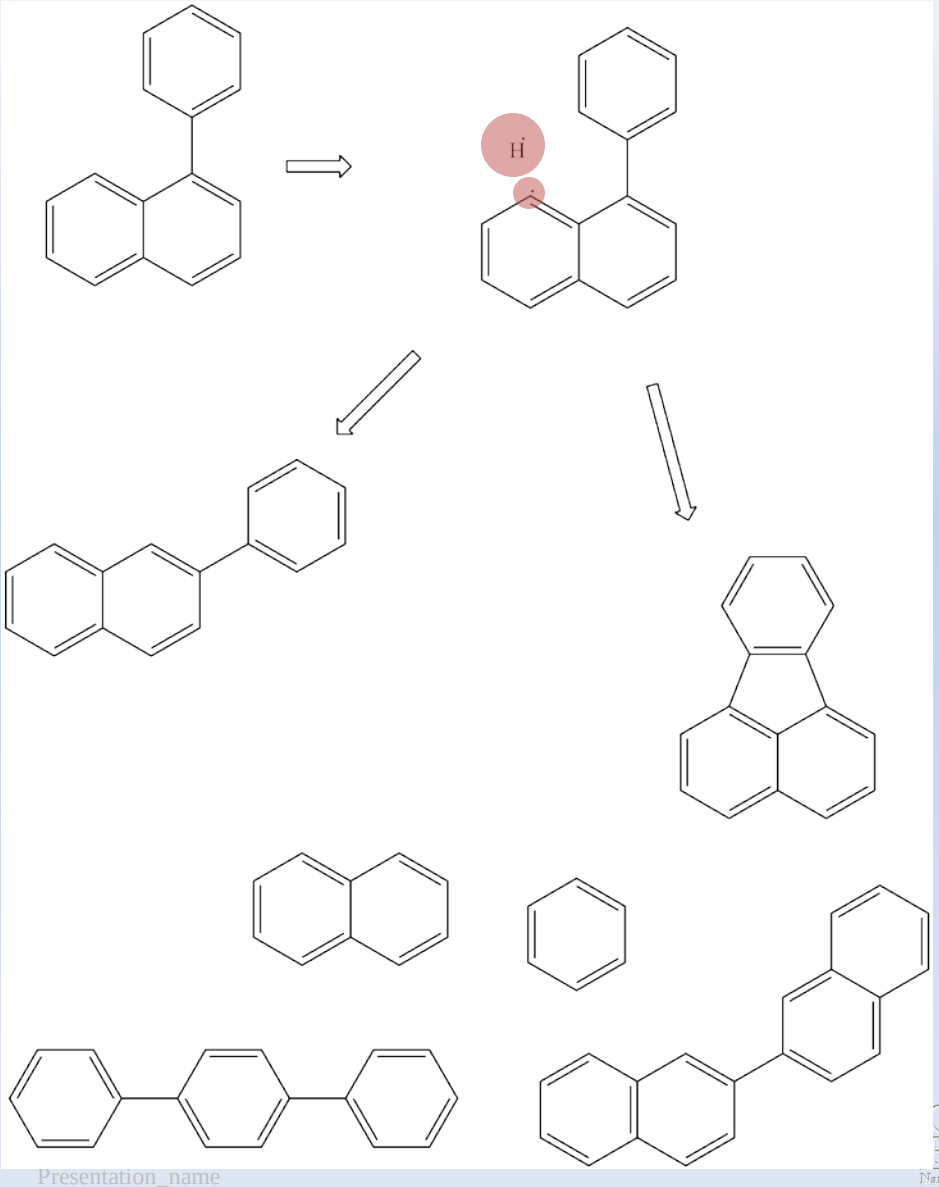
Changes have been observed in samples during extended duration thermal tests.

- Evidence of changes to phenylnapthalene fluid
  - Isomerization to 2-phenylnaphthalene
  - Slow conversion to fluoranthene, terphenyls
  - Gas accumulation in vessel
  - However, little pressure rise in monitored sample vessel



Ways to address challenges encountered when using an organic fluid

- Strategies developed to suppress radicals
  - Functionalize aromatics at where C-H bonds most vunerable
  - Add suppression agents
  - Start tests with fluoranthene, stable end product



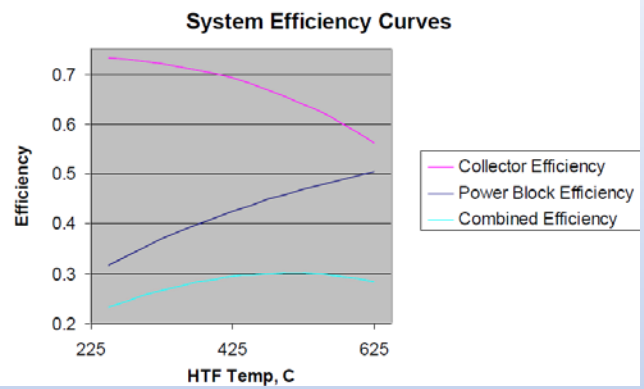
A pilot scale loop facility has been designed, built and commissioned in Boulder.

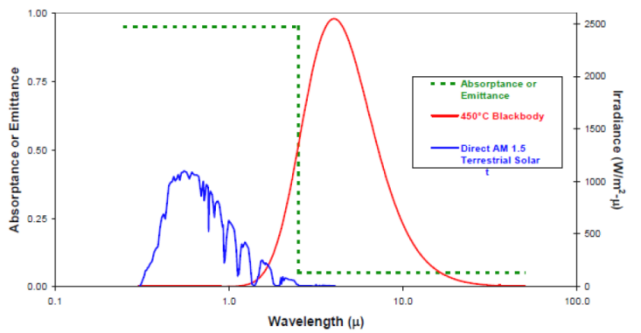
Cool Energy

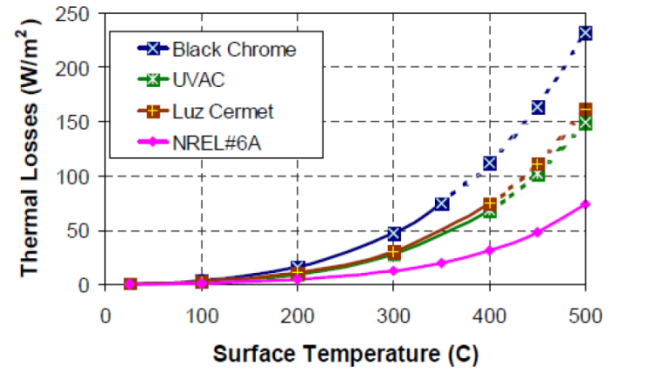
Powering a Clean Tomorrow®

Preliminary LCOE calculations indicate that fluids operating at average temperatures of 500°C will give 30% sunlight-to-electricity efficiency

- Collection efficiency has trade off between trends for conversion of sunlight into thermal energy, and from thermal-to-electric power device
- Used the NREL Solar Advisory Model to perform an initial study of the relationship between receivers, turbine performance, and HTF properties
  - Simulated use of VP-1 (300-400 °C) and Hitec XL (up to 550 °C)
  - With thermal energy storage, get better performance at high temperatures
  - Projected reductions in LCOE are small (~4%), but with improved HCE's could increase to 8%.

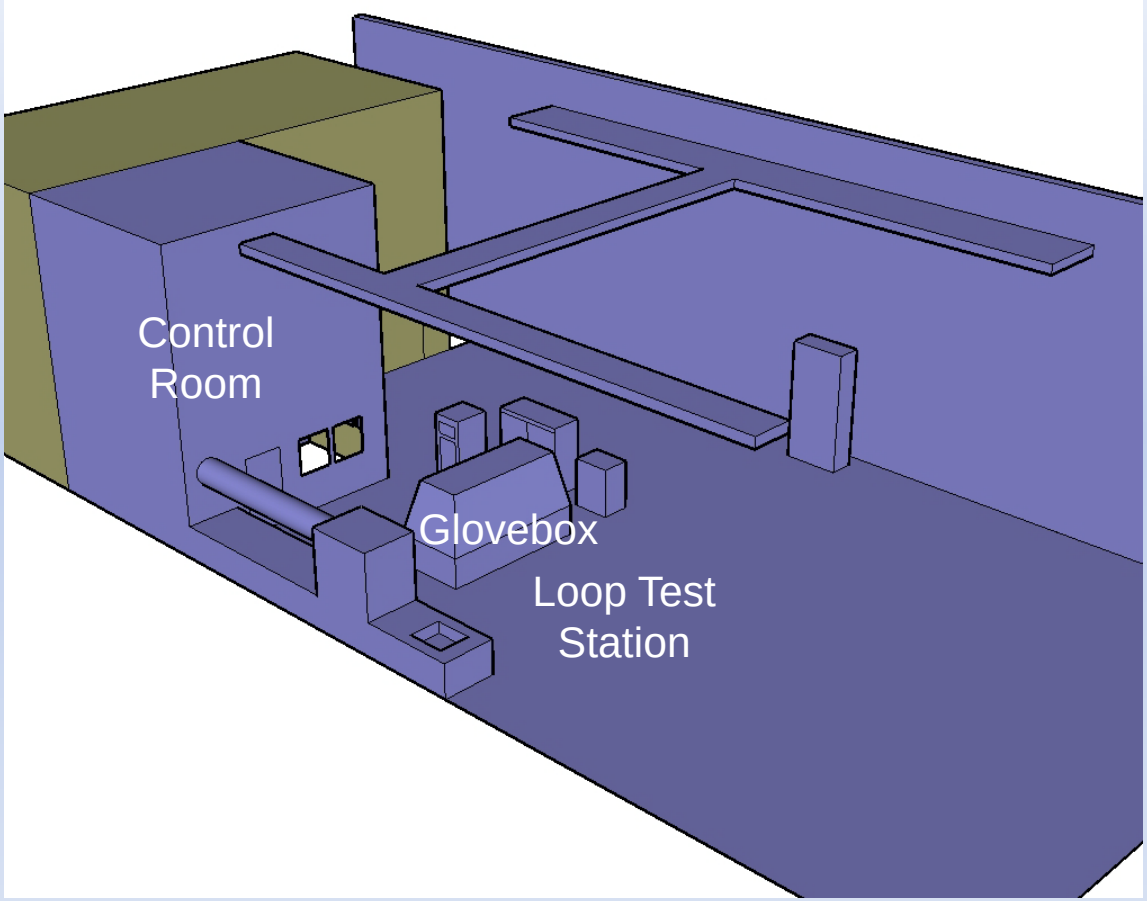


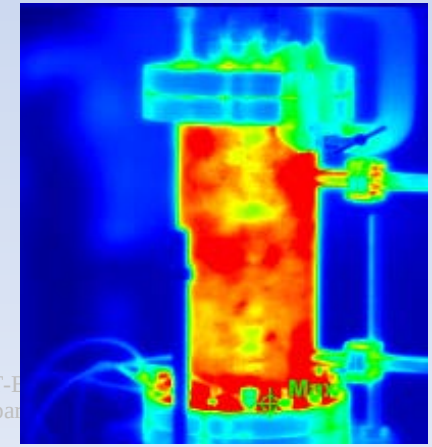




2011: Test performance of fluid in flow loop

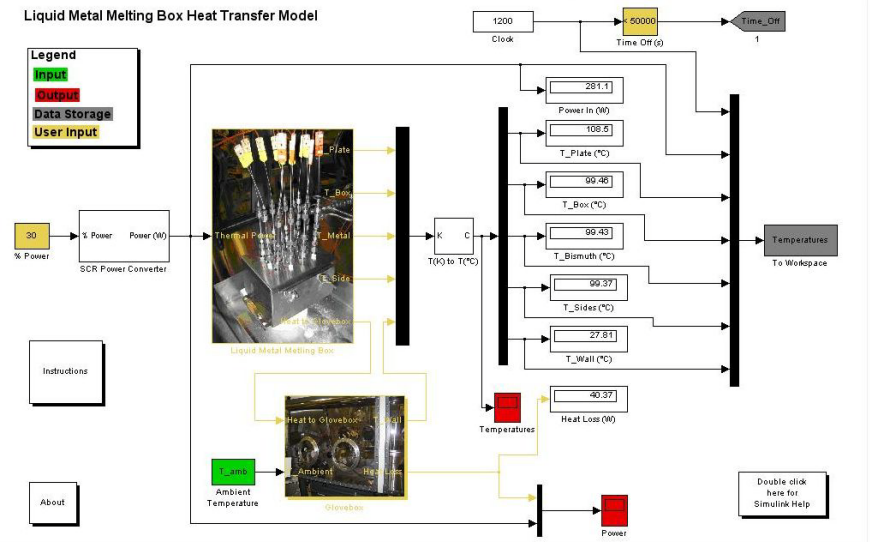
- **ORNL's Small Power Systems Testing Facility for Component and Loop Development**
- Electrical power supplies (20 kW(e) through 10 control circuits)
- Chilled water system
- Facility Instrumentation
- Remote control capability
- Thermal imaging

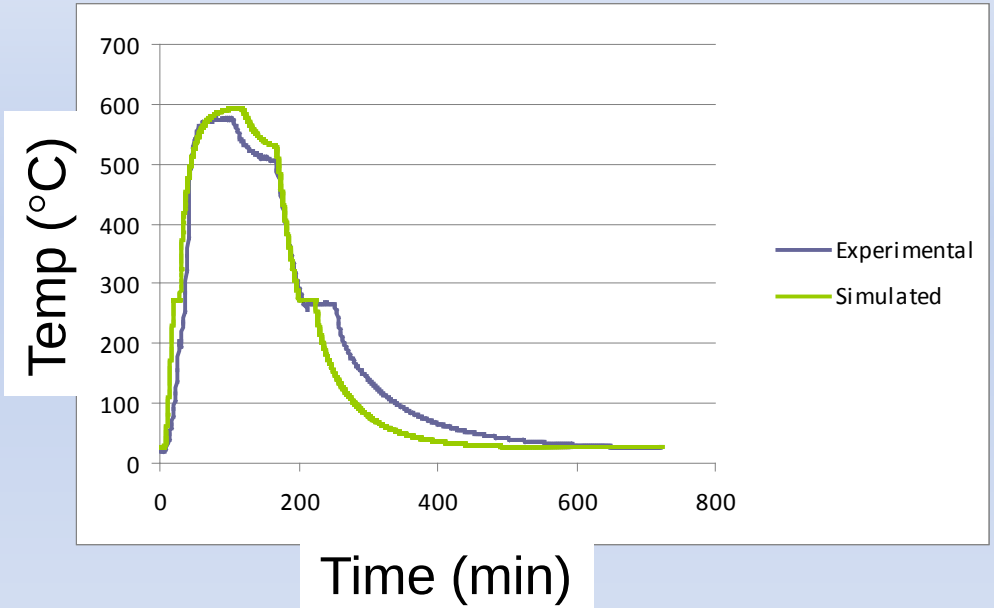




2011: Predictions of Loop Transient Performance at High Temps

- LabView Simulink based dynamic system models
  - Heat balance
  - Pump power requirements

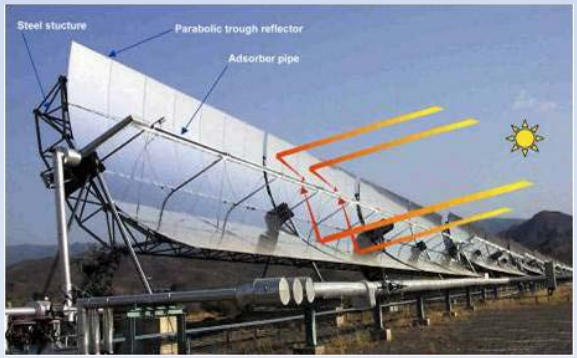




The project has made progress towards goal, but more left to be done

- Towards Advanced HTF
  - Technical barriers are primarily related to performance and the cost of operations, resulting in a relatively low plant capacity of 25%.
  - The capacity can be improved by increasing the maximum operating temperature
  - The goal is to develop an organic heat transfer fluid
    - Liquid at room temperature
    - Low vapor pressure
    - Stable above 500°C
    - Relatively inexpensive to manufacture.

- Testing Phenylnaphthalene as HTF
  - Route to increased stability
    - Radical suppression
    - Functionalization
    - Fluoranthene
  - Viscosity measurements
    - Reduce viscosity at low temperatures
  - High temperature pumping experiments
  - Low cost manufacture
  - Lower temperature pilot scale testing at temperatures from 180-220°C



Additional slides

Results: Thermophysical Properties Show Feasibility for High Temps

Compound	T_m T_b **(K)**	C_p **(kJ·kg^{-1}K^{-1})**	ρ **(kg·m^{-3})**	T_c **(K)** P_c **(bar)**	**Vp** **(bar)**	λ **(W·m^{-1}·K^{-1})**	υ **(mPa·s)**
Dowtherm A Therminol VP-1 (678 K)	285.2 530.2	2.725	672.5	770 31.34	11.32	0.0771	0.12
Xceltherm 600-C_{20} paraffin oil (588.8 K)	T_b range 574–741	3.001	672.36	768 10.7	0.2499	0.1122	0.252
H_2O (563 K, 7.5 MPa)	273.15 373.15	5.5	732	646.95 220.64	Super- heated	0.56	0.13
Li_2BeF_4 (973 K)	732 1703	2.42	1940	Not available	Not available	1.0	2.9
Na (823 K)	370.95 1156	1.27	820	2503.75 256.4	~10–16	62	0.12
Helium (7.5 MPa)	T_b 4.22	5.5	3.8	5 2.26	Super- heated	0.29	11.0
Biphenyl (500 K)	342 559	2.03	869	773±3 33.8±1	0.531	0.118	0.32
p-Terphenyl (500 K)	485 623	1.98	947	908+10 29.9±6	0.0199	0.135	0.73
phenylnaphthalene (600K)	**297–318 598**	**2.6**	**849**	**818 7.1**	**0.820**	**0.077**	**0.11**

Summary: Project Activities

Performance Metric	Goals	Result in FY11*	Milestone Dates
Down-selection of candidate fluids	Synthesis & modeling	Investigating sources for fluid	09/11
Measurement of stability at high T & P	Static, small-scale lab tests	Analysis of fluid and possible breakdown products	Go/No Go 09/11
Commission high temperature loop	Complete design & safety envelope	Design and build	Summer 2011
High temp lab testing and models	Confirm performance, stability	Tests to be conducted with 1 L fluid	Start fall 2011
Med temp testing at solar field pilot plant	Demonstrate scale-up	Facility commissioned	Tests to start 2012
High temp conceptual design & economic analysis	Including LCOE, performance criteria	Preliminary LCOE analysis completed	Final version 01/2013

*Project started in February 2010