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PNNL-31038

Thermocatalytic Heat Pipes for Geothermal Resource Recovery

October 2020

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Mark D. White
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Jeromy J. Jenks

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Richland, Washington 99354

Abstract

Heat pipes are an important technology that allow orders of magnitude faster heat transfer than simple conduction. However, operating principles in heat pipes place fundamental bounds on their performance (critical heat flux and efficiency). Conventional heat pipe functionality is inherently tied to vaporization and condensation of the working fluid charged in the heat pipe. These fluids each have different operating temperature ranges based on the capillary, entrainment, sonic, and boiling limits of the heat pipe design. These limits, typically the capillary limit, dictate the maximum heat flux a heat pipe can carry, and most importantly for geothermal systems, the distance over which the pipes can operate (100 to 200 m maximum under optimum conditions). A thermocatalytic heat pipe breaks the inherent limitations of phase change thermo- and hydrodynamics and can transform heat pipe technology as a potentially more efficient means of extracting heat from a geothermal resource.

The thermocatalytic heat pipe uses a working fluid to transport both sensible and chemical heat. An endothermic chemical reaction at depth removes heat from the reservoir and produces reactive intermediates, which are transported to the surface and used to run a reverse exothermic reaction that releases heat for use in power generation or other useful purposes. This technology offers two distinct advantages over conventional geothermal heat recovery technologies: (1) lower heat loss to the rock outside of the geothermal reservoir, and (2) higher heat transfer rates to the well field within the geothermal reservoir. Both advantages offer opportunity to reduce risks and lower costs of geothermal energy recovery.

In this report, we discuss an initial effort to assess the efficacy and limitations of this technology for extracting heat from both porous/permeable and nominally impermeable geothermal reservoirs. Numerical simulation capabilities of the STOMP-GT code were enhanced to enable simulations of thermochemical heat pipes traversing geothermal reservoirs. An array of potential thermochemical reaction systems was evaluated and screened. Of these, an ethanol dehydration reaction was most promising in the vapor-liquid reaction set. A solid-phase dehydration reaction ($CuSO4 \cdot 5H2O$) showed the highest reaction enthalpy per unit volume but would require development of a nonaqueous carrier fluid to implement it in a heat pipe. Subsurface reservoir simulations predicted long-term performance of the heat pipes for each geothermal reservoir type. The performance of U-shaped wells and coaxial wells was evaluated for a suite of reactions for both hydrothermal and hot dry rock reservoirs and was compared with a baseline case of simply pumping water through the wells. The heat pipe technology was additionally evaluated for an enhanced geothermal system (EGS) with an injection borehole, production borehole, and intervening hydraulically conductive fracture. All reservoir types showed significant improvement in heat recovered over a 20-year operating period ranging from a 1.8X increase for the hot dry rock case to more than 2.5X more energy recovered for the EGS case.

Contents

Abstract iii
Thermocatalytic Heat Pipes for Geothermal Resource Recovery 1
Reservoir Simulation 2
Reversible Thermochemical Reactions and Reaction System Assessment 11
Summary 15
Overall Conclusions and Recommendations 15

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Thermocatalytic Heat Pipes for Geothermal Resource Recovery

October 29, 2020

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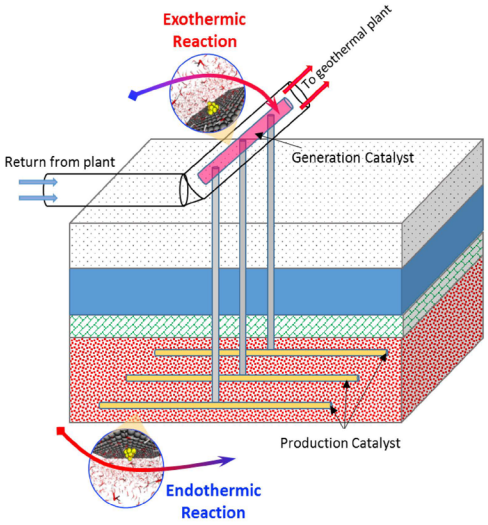
Project Overview

Scope

- Conduct simulations of a new class of heat pipe that enables nearly lossless transport of heat from deep geothermal reservoirs
- Instead of vapor-liquid condensation, thermochemical reactions with 10 to 50X higher heat carrying capacity are used to extract heat from the hot end of the heat pipe and produce reactive intermediates, which are transported to the “cold” end for heat recovery at the surface with a reverse reaction
- Heterogeneous catalysts (if required) are used in the heat pipe to control position where the thermochemical reactions occur

Project Impacts

- Geothermal resource recovery virtually anywhere
- Enable chemical heat pumping to thermally upgrade heat sources
- Reduce geothermal development risk due to adverse subsurface reservoir properties
- Reduce regulatory barriers and public perception concerns over fracking for EGS
- Eliminate surface heat exchanger fouling and maintenance issues from silica (and other mineral) precipitation
- Potentially reduce wellfield development costs with slim hole drilling techniques for heat pipes



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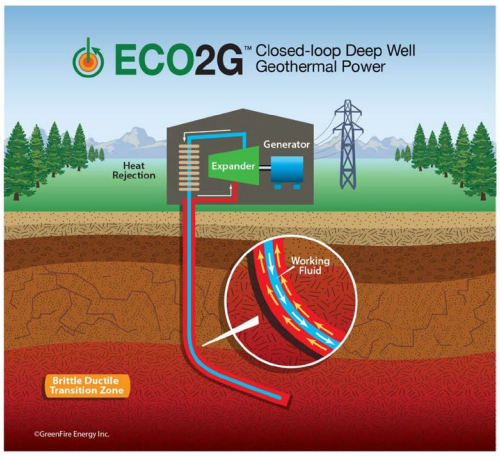
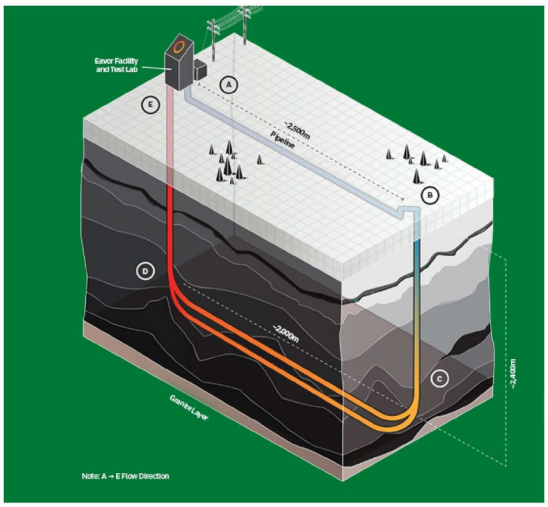
Greenfire Energy



Eavor



3

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Reservoir Simulation

Mark White
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Geophysics and Geomechanics
Pacific Northwest National Laboratory

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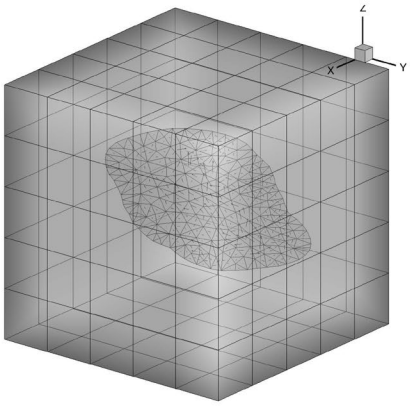
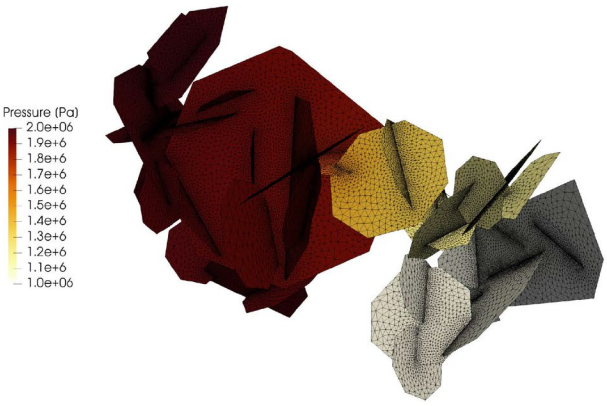
Embedded Borehole and Fracture Modeling w/ STOMP-GT



Discretized fracture embedded within a discretized rock matrix



dfnWorks (LANL) discrete fracture network model with a conforming grid without a surrounding rock matrix

5

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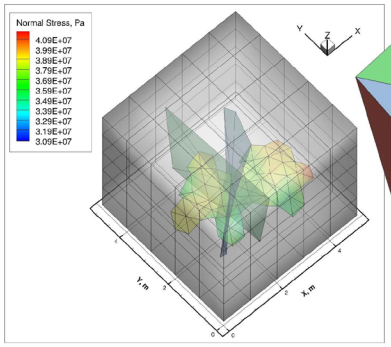
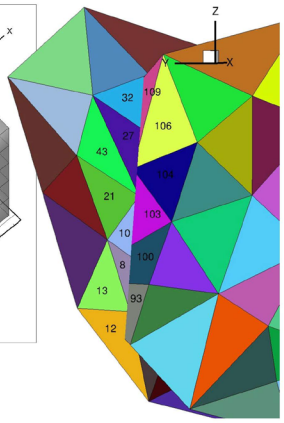
Embedded Borehole and Fracture Modeling w/ STOMP-GT



Discretized fractures embedded within a discretized rock matrix

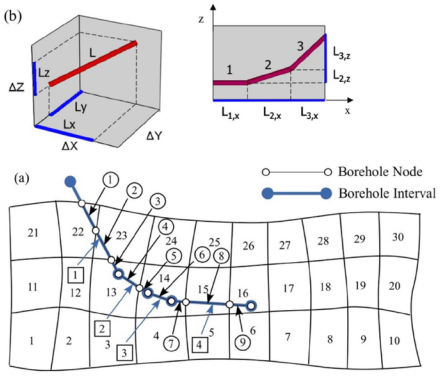


Fracture-fracture connection mapping

$$WI_x = \left[\frac{2\pi\sqrt{k_y k_z}\, t_x}{\ln\left(\frac{r_{0,x}}{r_{bh}}\right)+s_{bh,m}}\right];\ WI_y = \left[\frac{2\pi\sqrt{k_x k_z}\, t_y}{\ln\left(\frac{r_{0,y}}{r_{bh}}\right)+s_{bh,m}}\right];\ WI_z = \left[\frac{2\pi\sqrt{k_y k_x}\, t_z}{\ln\left(\frac{r_{0,z}}{r_{bh}}\right)+s_{bh,m}}\right]$$

$$r_{0,x} = \left[\frac{\left(\left(\frac{k_y}{k_z}\right)^{1/2}\Delta z^2+\left(\frac{k_z}{k_y}\right)^{1/2}\Delta y^2\right)^{1/2}}{\left(\frac{k_y}{k_z}\right)^{1/4}+\left(\frac{k_z}{k_y}\right)^{1/4}}\right];\ r_{0,y} = \left[\frac{\left(\left(\frac{k_x}{k_z}\right)^{1/2}\Delta z^2+\left(\frac{k_z}{k_x}\right)^{1/2}\Delta x^2\right)^{1/2}}{\left(\frac{k_x}{k_z}\right)^{1/4}+\left(\frac{k_z}{k_x}\right)^{1/4}}\right];\ r_{0,z} = \left[\frac{\left(\left(\frac{k_x}{k_y}\right)^{1/2}\Delta y^2+\left(\frac{k_y}{k_x}\right)^{1/2}\Delta x^2\right)^{1/2}}{\left(\frac{k_x}{k_y}\right)^{1/4}+\left(\frac{k_y}{k_x}\right)^{1/4}}\right]$$

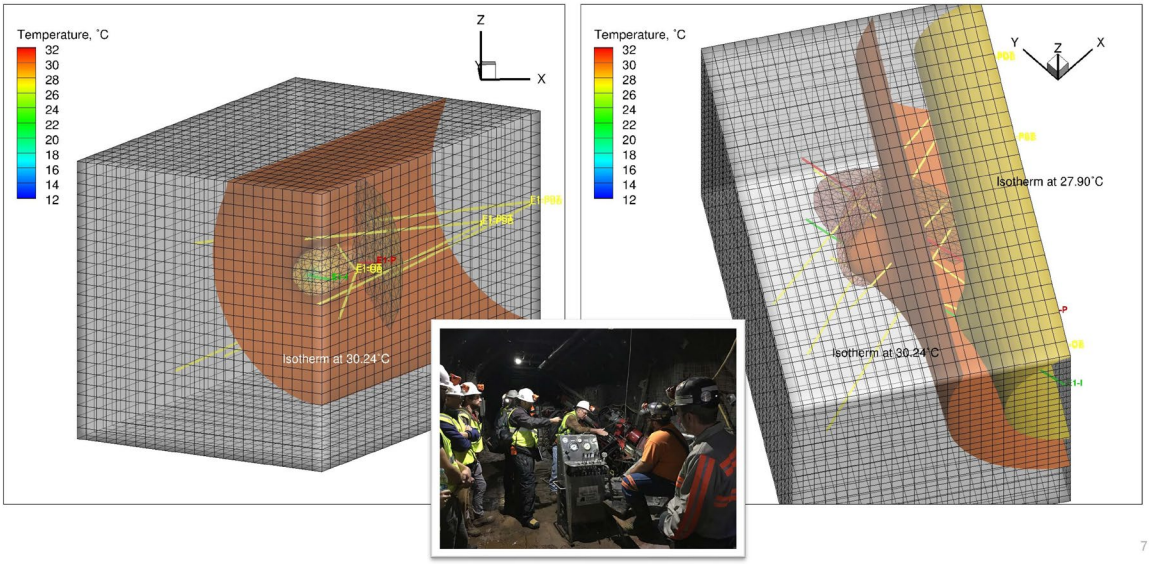
$$WI = \sqrt{(WI_x)^2+(WI_y)^2+(WI_z)^2}$$



Borehole trajectories translated into borehole nodes

6

Embedded Borehole and Fracture Modeling w/ STOMP-GT

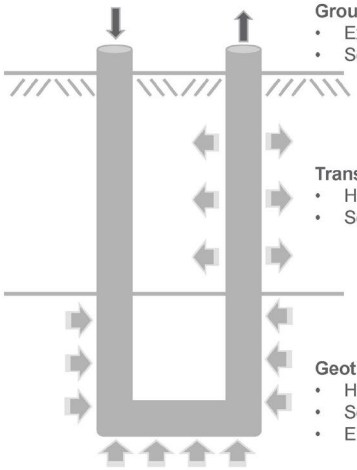


7

U-Pipe Modeling Approaches and Concepts

- Injection Flow Rate
- Fluid Temperature
- Reactant Concentration

- Pressure
- Fluid Temperature
- Reactant Concentration



Ground Surface
- Exothermic chemical reaction
- Sensible heat gain by working fluid

Transition Zone
- Heat transfer to/from working fluid
- Sensible heat gain/loss

Geothermal Reservoir
- Heat transfer to working fluid
- Sensible heat gain
- Endothermic chemical reaction

Pipe Flow
- Darcy-Weisbach Equation
- Colebrook Equation

$$\Delta P = \lambda \frac{L}{D_h} \frac{\rho u^2}{2}$$

$$\frac{1}{\sqrt{\lambda}} = -2 \log \left[\frac{2.51}{R_e \sqrt{\lambda}} + \frac{r_f}{3.72 D_h} \right]$$

Heat Transfer
- Peaceman conduction model between outer pipe wall and rock matrix
- Radial conduction across pipe wall
- Fully developed flow advection between inner pipe wall and working fluid

Endothermic Chemical Reaction
- Temperature controlled first-order reaction rate

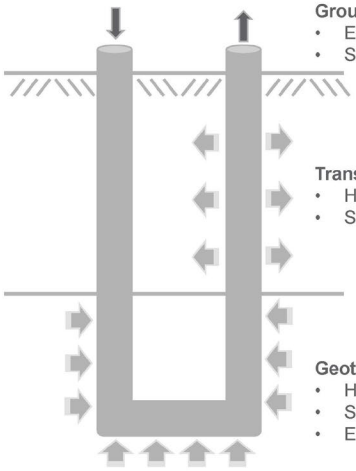
$$r = \frac{k\,[C_s]}{\left(1 + \exp\left(\frac{(T^* - T)}{\beta}\right)\right)}$$

8

U-Pipe Modeling Approaches and Concepts

- Injection Flow Rate
- Fluid Temperature
- Reactant Concentration

- Pressure
- Fluid Temperature
- Reactant Concentration



Ground Surface
- Exothermic chemical reaction
- Sensible heat gain by working fluid

Transition Zone
- Heat transfer to/from working fluid
- Sensible heat gain/loss

Geothermal Reservoir
- Heat transfer to working fluid
- Sensible heat gain
- Endothermic chemical reaction

Pipe Flow
- Darcy-Weisbach Equation
- Colebrook Equation

$$\Delta P = \lambda \frac{L}{D_h} \frac{\rho u^2}{2}$$

$$\frac{1}{\sqrt{\lambda}} = -2 \log \left[\frac{2.51}{R_e \sqrt{\lambda}} + \frac{r_f}{3.72 D_h} \right]$$

Heat Transfer
- Peaceman conduction model between outer pipe wall and rock matrix
- Radial conduction across pipe wall
- Fully developed flow advection between inner pipe wall and working fluid

Endothermic Chemical Reaction
- Temperature controlled first-order reaction rate

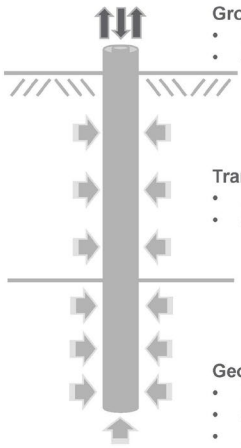
$$r = \frac{k\,[C_s]}{\left(1 + \exp\left(\frac{(T^* - T)}{\beta}\right)\right)}$$

8

Coaxial-Pipe Modeling Approaches and Concepts

- Injection Flow Rate
- Fluid Temperature
- Reactant Concentration

- Pressure
- Fluid Temperature
- Reactant Concentration



Ground Surface
- Exothermic chemical reaction
- Sensible heat gain by working fluid

Transition Zone
- Heat transfer to/from working fluid
- Sensible heat gain/loss

Geothermal Reservoir
- Heat transfer to working fluid
- Sensible heat gain
- Endothermic chemical reaction

Pipe Flow
- Darcy-Weisbach Equation
- Colebrook Equation

$$\Delta P = \lambda \frac{L}{D_h} \frac{\rho u^2}{2}$$

$$\frac{1}{\sqrt{\lambda}} = -2 \log \left[\frac{2.51}{R_e \sqrt{\lambda}} + \frac{r_f}{3.72 D_h} \right]$$

Heat Transfer
- Peaceman conduction model between outer-outer pipe wall and rock matrix
- Radial conduction across outer pipe wall
- Fully developed flow advection between inner-outer pipe wall and working fluid
- Fully developed flow advection between outer-inner pipe wall and working fluid
- Radial conduction across inner pipe wall
- Fully developed flow advection between inner-inner pipe wall and working fluid

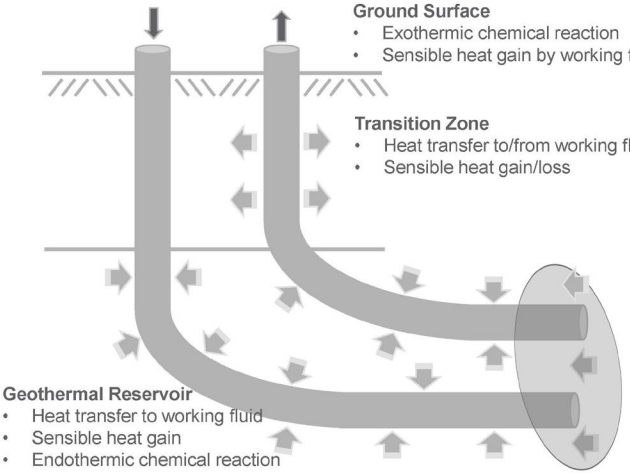
Endothermic Chemical Reaction
- Temperature controlled first-order reaction rate

$$r = \frac{k\,[C_s]}{\left(1 + \exp\left(\frac{(T^* - T)}{\beta}\right)\right)}$$

9

EGS Modeling Approaches and Concepts

- Injection Flow Rate
- Fluid Temperature
- Reactant Concentration
- Pressure
- Fluid Temperature
- Reactant Concentration



Pipe Flow
- Darcy-Weisbach Equation
- Colebrook Equation

$$\Delta P = \lambda \frac{L}{D_h} \frac{\rho u^2}{2}$$

$$\frac{1}{\sqrt{\lambda}} = -2 \log \left[\frac{2.51}{R_e \sqrt{\lambda}} + \frac{r_f}{3.72 D_h} \right]$$

Heat Transfer
- Peaceman conduction model between outer pipe wall and rock matrix
- Peaceman conduction model between fracture plane and rock matrix
- Radial conduction across pipe wall
- Fully developed flow advection between inner pipe wall and working fluid

Endothermic Chemical Reaction
- Temperature controlled first-order reaction rate

$$r = \frac{k\,[C_s]}{\left(1 + \exp\left(\frac{(T^* - T)}{\beta}\right)\right)}$$

10

Computing and Comparing Outputs

Water vis-à-vis Thermocatalytic Fluid

- Water

$$P = \dot{m}\,(h_o - h_i)$$

$$P_{Carnot} = P\left(1 - \frac{T_i}{T_o}\right)$$ ← Value of the Power Produced

$$E_{Carnot} = \int P_{Carnot}\, dt$$

- Thermocatalytic Fluid

$$P = \dot{m}\,(h_o - h_i + \Delta h_{reaction})$$

$$T_o' = T_{sat}(h_o + \varepsilon\, \Delta h_{reaction})$$

$$P_{Carnot} = P\left(1 - \frac{T_i}{T_o'}\right)$$ ← Value of the Power Produced

$$E_{Carnot} = \int P_{Carnot}\, dt$$

E_{Carnot} - integrated Carnot efficiency x power, J
h_i - enthalpy of inlet water, J/kg
h_o - enthalpy of outlet water, J/kg
$\Delta h_{reaction}$ - heat of reaction, J/kg
$\dot{m}$ - mass flow rate, kg/s
P - produced power, W
P_{Carnot} - Carnot efficiency x produced power, W
t - time, s
T_i - inlet temperature, K
T_o - outlet temperature, K
T_{sat} - saturated liquid water temperature at enthalpy, K
ε – reaction conversion efficiency (assumed 1.0)

11

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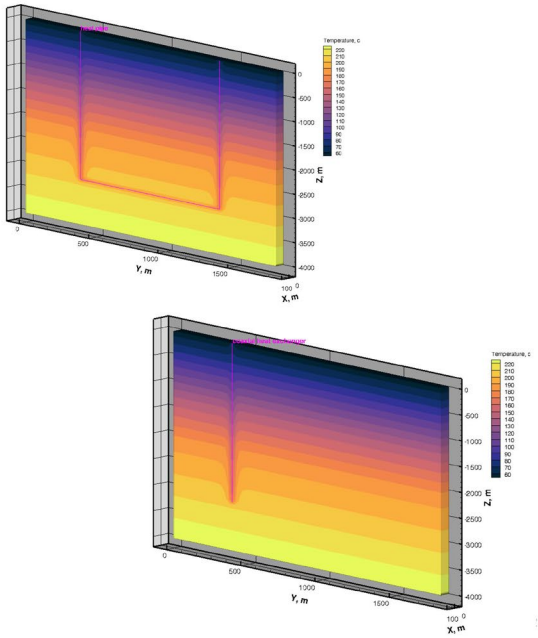
Hot Dry Rock

- Model based on data from FORGE deep well site
- U-shaped well and coaxial well (with no insulation between inner and outer pipes)
- Depth to horizontal section of well = 3015 m
- Temperature at bottom of reservoir = 230º C
- Flow rates 5 kg/s and 20 kg/s



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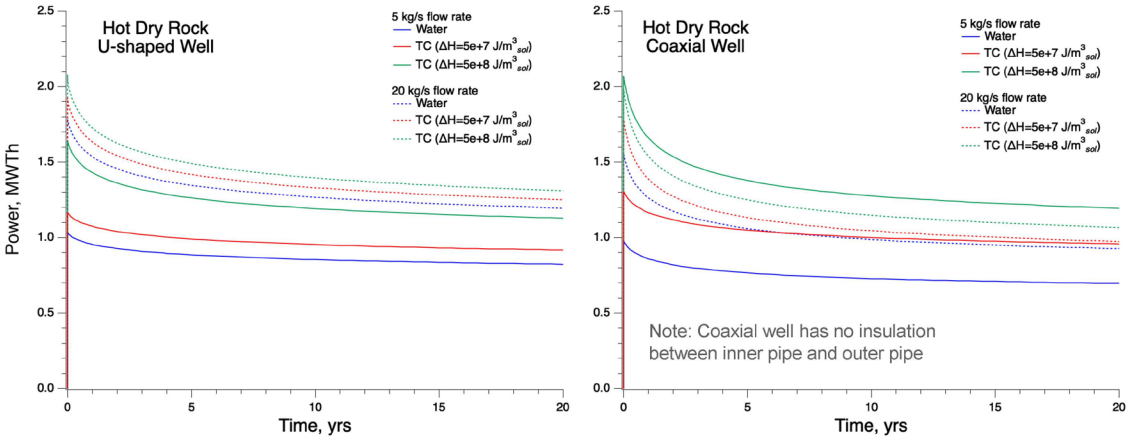
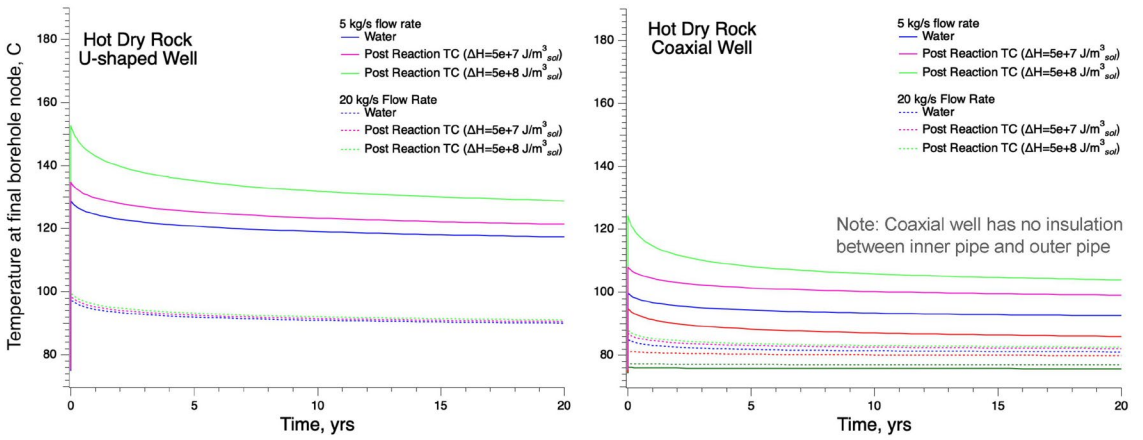
Hot Dry Rock Simulation Results



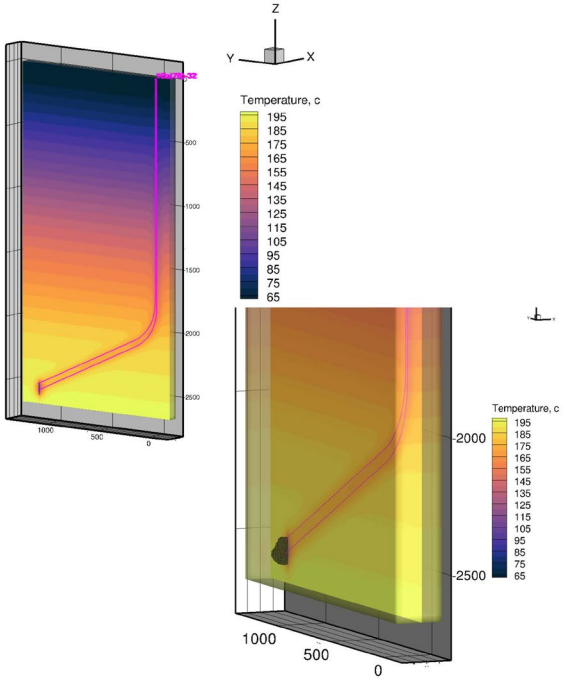
Hot Dry Rock Simulation Results



14

EGS Utah Forge

- Model based on Utah FORGE EGS with two boreholes 16A(78)-32 and 16B(78)-32, connected by a fracture with a 50-m radius
- Depth to bottom of wells = 2585 m
- Temperature at bottom of reservoir = 230ºC
- Flow rates 5 kg/s and 20 kg/s



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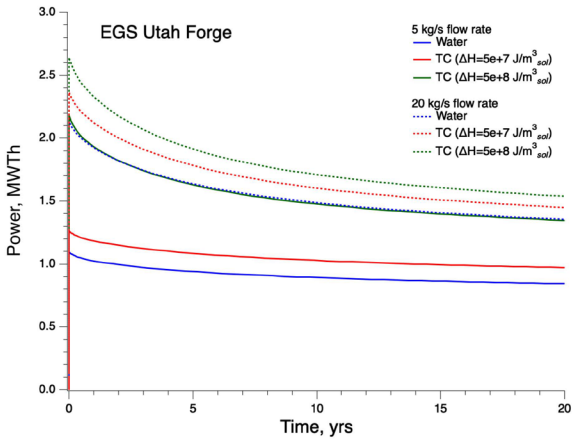
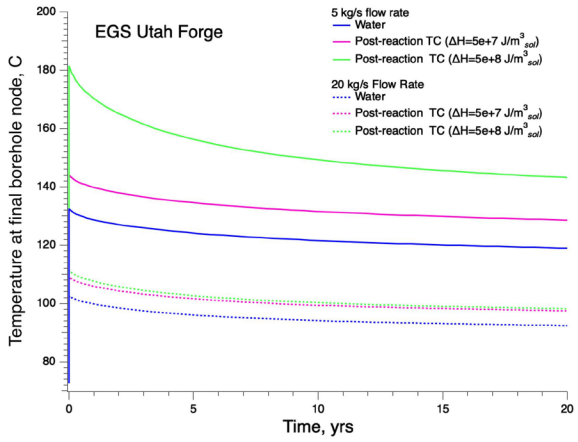
EGS Utah Forge Simulation Results





16

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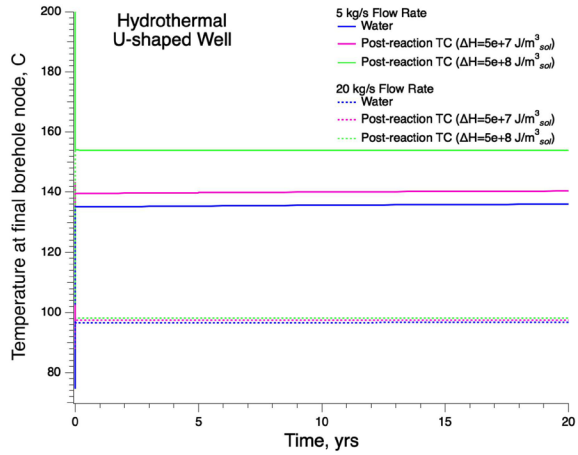
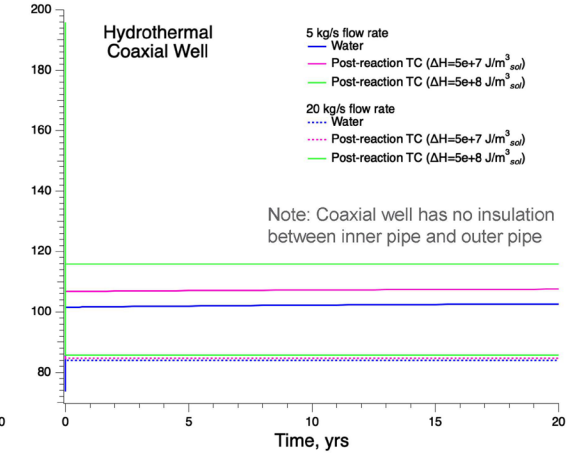
Recirculating Hydrothermal Simulation Results





19

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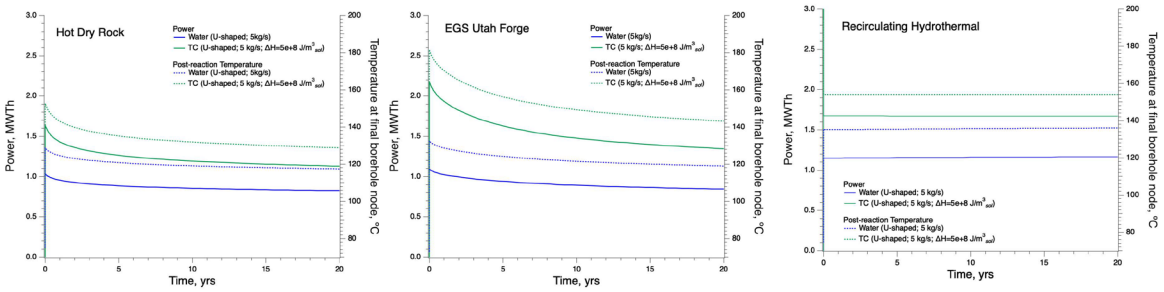
Summary of Best Cases based on Carnot Power



20

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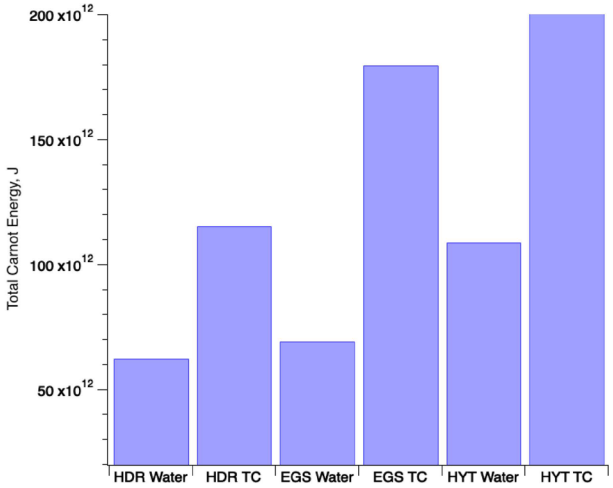
Summary of Total Carnot Energy produced over 20 years



21

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Reversible Thermochemical Reactions and Reaction System Assessment

Jian Liu

Satish Nune

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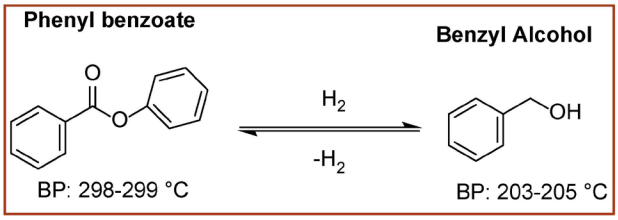
Reversible Thermochemical Reactions: Heat Pipes

- High heat of reaction (Exothermic)
- Boiling point temperature difference between the two components should be large enough so phase difference exists.
- Faster kinetics (reversibility)
- Minimal degradation
- High operation temperature.



23

Reversible Organic Transformations Studied: Alcohols

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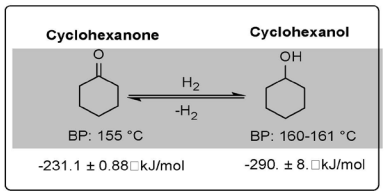
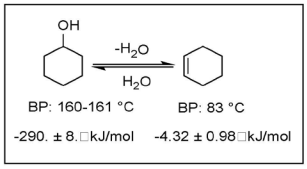
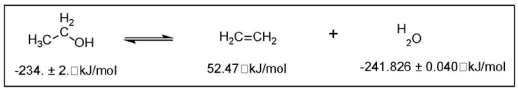
Dehydrogenation

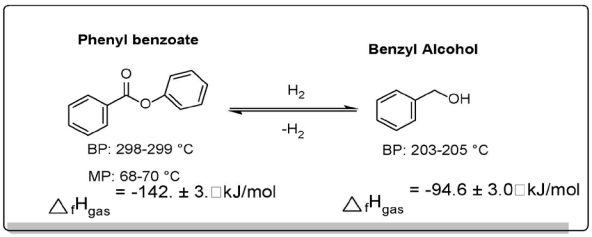


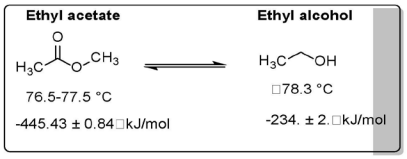
Dehydration





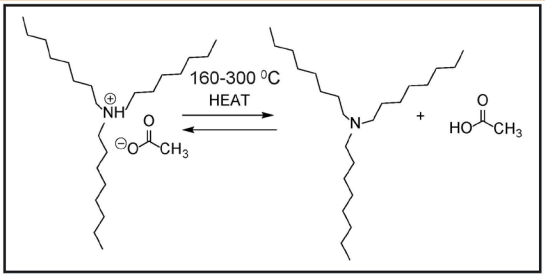
Esterification





NIST: $\Delta_f H_{gas}$ Enthalpy of formation of gas at standard conditions

Reversible Acid-Base Reactions

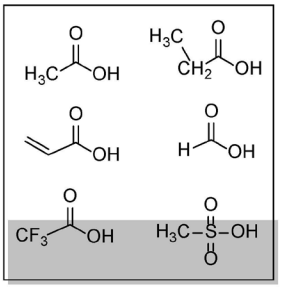


BASES

- Tripentylamine
- Trihexylamine
- Trioctylamine
- Tridodecylamine
- 1-Methylimidazole
- Tetramethylguanidine(TMG)

ACIDS

- Acetic Acid
- Propionic acid
- Butanioic acid
- Vinylacetic acid
- Formic acid
- Trifluoroacetic acid
- Methane sulfonic acid



Acids: The alkyl group (CH_3) in acetic acid can be changed with electron rich and electron poor groups

Reversible Transformations Studied

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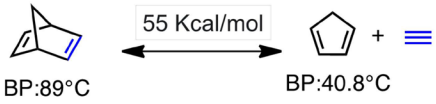
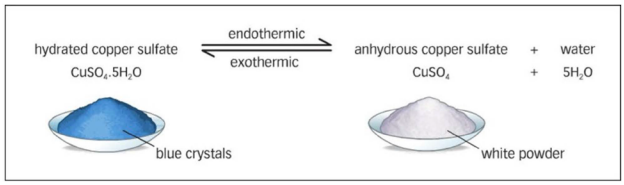
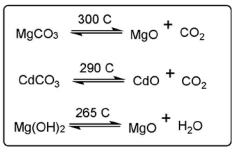
Diels Alder Reaction

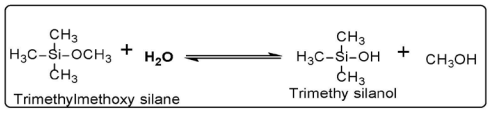


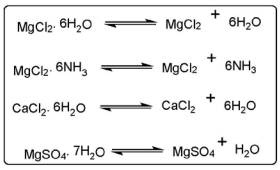
Inorganic Reactions





Silane Hydrolysis





Heat Pipe Model in Aspen Plus

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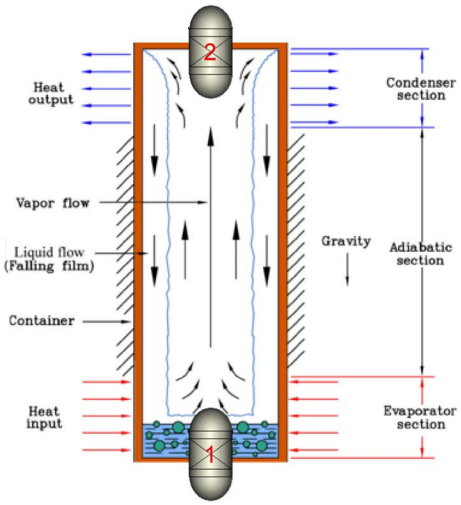

- Simple steady state model
- Thermodynamic method: Activity coefficient (NRTL etc.) or Equation of State (Peng-Robinson, SRK etc.)
- Use Gibbs reactors to calculate heat duty
- Obtain thermodynamic and thermohydraulic properties
- Identify promising candidates for thermocatalytic heat pipes

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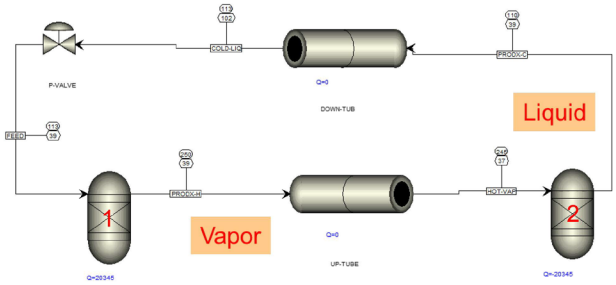
Task 1-Aspen plus model-Ethanol dehydration example

aspentech



Gibbs reactor-Hot

Gibbs reactor-Cold

Feed liquid volume: 71.05 L/h
Enthalpy change: 1198.01 kJ/L

	Hot	Cold
ETHANOL	0.799	0.049
ETHYLENE	0.101	0.475
WATER	0.101	0.475

- Use two Gibbs reactors to simulate equilibrium for reactions and neglect kinetics.
- The hot side temperature (250 °C) and cold side temperature (110 °C) is used.
- The initial flowrate of the feed line is set to 1 kmol/hr for the starting and the initial compositions is set to match stoichiometric composition.
- The heat duties of the reactors combining the liquid flow rate are used to estimate the amount of heat that can possibly be extracted per volume base.
- Simulations could not be performed in cases where data on reactants and products was not available

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Task 1-Reaction System Simulations-Results Summary

	Reaction	Highest normal b.p. (°C)	Temperature range (°C)	Pressure (atm)	Enthalpy change (kCal/hr)	Feed volume (L/hr)	Enthalpy per volume (MJ/m^3)	Effective conversion	*ΔG_foward (kJ/mol)	*ΔG_reverse (kJ/mol)	Both ΔG negative (Y/N)
L-L	Current geothermal power	100	165-75	10	N/A	N/A	360.33	N/A	N/A	N/A	N/A
V-L	H_2O phase change	100	250-110	39	10723	19.90	2254.67	N/A	N/A	N/A	N/A
	EtOH phase change	78.4	250-110	39	11611	67.09	724.10	N/A	N/A	N/A	N/A
	EtOH dehydration	100	250-110	39	20345	71.05	1198.01	70.5%	-5.49	-11.87	Y
	1-Propanol dehydration	97	250-110	39	13881	121.98	476.14	2.8%	-20.11	4.51	N
	1-Butanol dehydration	117.7	250-110	39	17748	132.94	558.58	0.9%	-22.33	7.25	N
	1-Pentanol dehydration	138	250-110	39	21405	134.16	667.55	23.6%	-22.71	8.35	N
	Cycloheaxnol dehydration	160.9	250-110	39	22063	127.87	721.94	4.8%	-34.29	16.73	N
	2,5-Norbornadiene DA	89	250-110	26	12322	108.78	473.93	Negligible	205.40	-219.56	N
S-V	$CuSO_4$-$5H_2O$ dehydration	650	250-110	39	79425	30.00	11077.14	100%	-16.86	-16.97	Y
V-V	Steam methane reforming (HT)	100	825-600	40	9185	1986.87	19.34	53.8%	-15.47	-37.43	Y
	Steam methane reforming (LT)	100	250-110	40	7564	277.69	113.97	0.8%	76.22	-139.07	N

- Ethanol dehydration reaction was most promising in the V-L reaction set
- Low effective conversions under the simulated conditions limited effectiveness of many systems
- Having both forward and reverse reactions with negative ΔG helps achieve a higher conversion efficiency
- Inorganic solid dehydration reaction ($CuSO_4 \cdot 5H_2O$) looks particularly attractive
  - High reaction enthalpy per unit volume
  - Excellent conversion efficiency
  - High density of reagent
  - Will require dispersal in non-aqueous heat transfer fluid (nanofluid technology)

29

Summary

- Several promising thermochemical systems were identified with volumetric reaction enthalpies that are consistent with values that show significant benefit in subsurface reservoir simulations
- From a traditional heat pipe design perspective with V-L reactants/products, ethanol dehydration appears to be a promising candidate
- Exploiting the dehydration of copper sulfate pentahydrate could be very promising provided cycling between the anhydrous and hydrous copper sulfate can be achieved in an appropriate carrier fluid
- Many other potentially promising reaction systems were identified that will require collection of additional thermochemical data to simulate properly with ASPEN Plus and may require development and testing of catalysts that could improve conversion efficiency under relevant geothermal conditions

30

Overall Conclusions and Recommendations

- Subsurface simulations conclusively illustrate potential of thermochemical heat pipe technology to increase quality of heat brought to the surface from a wide variety of geothermal reservoir types
- Technology offers significant potential to reduce geothermal well field development costs per MW of power generation
- Several thermochemical reaction systems were identified, some of them that avoid need for catalyst development to implement, which could significantly compress R&D timeline from Lab → Field Trial → Commercial Application
- PNNL recommends proceeding with a Phase 2 development effort directed at demonstrating operational performance of selected thermochemical heat pipe systems

31

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