Developing New Natural Gas (NG) Super-Absorbent Polymer

Project ID: ST215

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2020 DOE Hydrogen Program Annual Merit Review
May 19-21, 2020

Overview

Timeline

- Project start date: 1/22/2020
- Project end date: 1/31/2023
- % complete: 10%

Budget

- Total project funding: $1,119,095

- DOE share: $895,065
- Penn State share: $224,030

- Funding for FY2020-21: $368,455

Barriers

- System weight & volume
- System cost, efficiency, durability
- Charging/discharging rates
- Suitable NG binding energy
- High polymer surface area

Partners

- HyMARC consortium
- National Renewable Energy Lab.

Relevance: Current NG storage technologies and our research goals

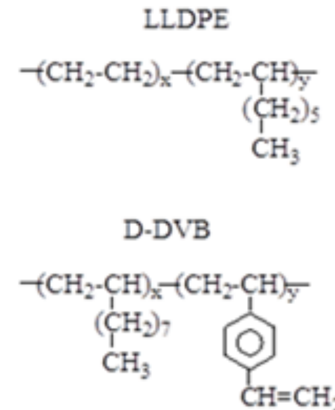
Method	Mass density (g/L)	Energy density (MJ/L)	Temperature (° C)	Pressure (bar)
Gasoline	740	34.2	25	1
Diesel	832	37.2	25	1
CNG	170	9.2	25	250
LNG	410	22.2	-162	<1
ANG	<140	<8	25	35 (500 psi)
1st year goal	>180	>10	25	<60
Project goal	>300	>16	25	35

Relevance: Absorption vs. Adsorption

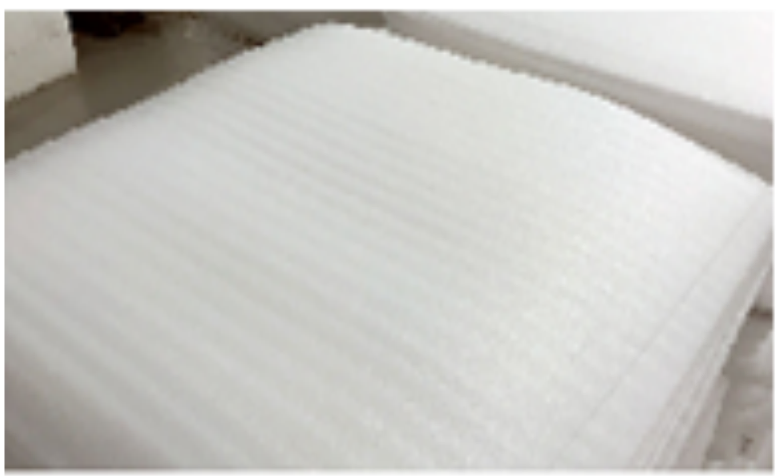
	Absorption	Adsorption
Phenomenon	A bulk phenomenon	A surface phenomenon
Mechanism	Molecules are dissolved in the absorbent to form a solution	Molecules are held loosely on the surface
Volume	Swollen matrix to accommodate the presence of absorbate molecules	No change
Kinetic	Happened at a uniform rate	Steadily increase and reaches equilibrium.
Concentration	Same throughout the material	Concentrated on the surface of adsorbent.
Sorption capacity	Up to >1000 times of polymer weight	Low capacity
Heat exchange	Endothermic process	Exothermic process
Temperature	Not affected by temperature	Favored by low temperature

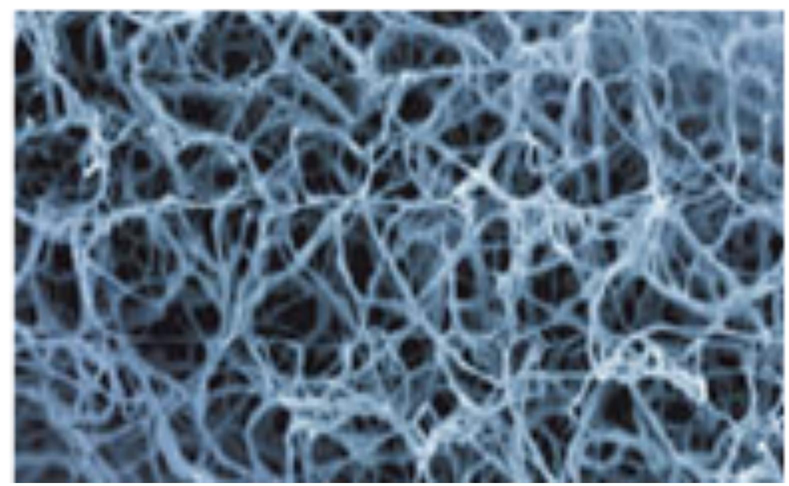
Relevance: Petrogel super-absorbent with IPN structure and porous morphology

— Polyolefin thermoplastic (rigid segment)
— Polyolefin elastomer (soft segment)
● Chemical crosslinkers in soft segments
Physical crosslinkers in rigid segments



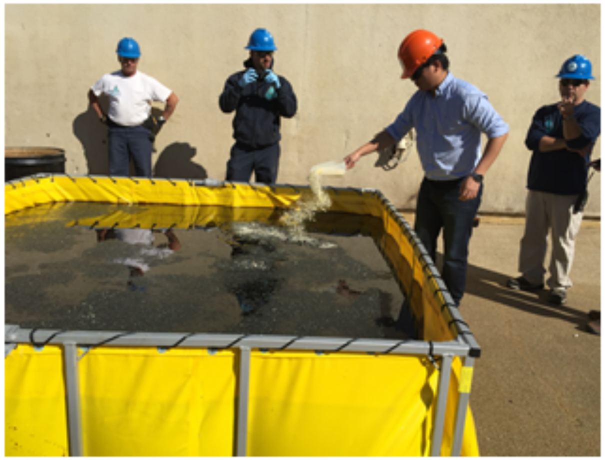
US patent 9,861,954

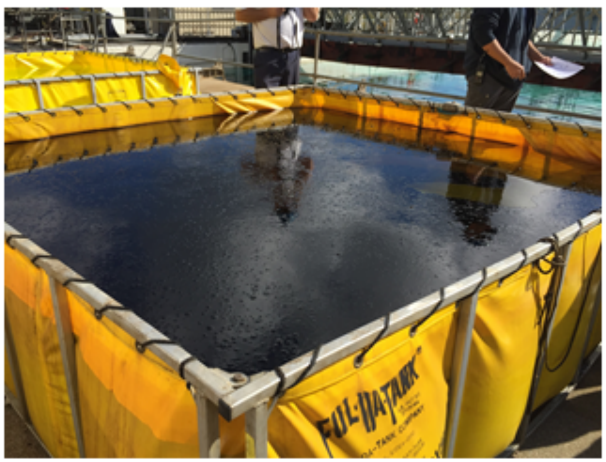


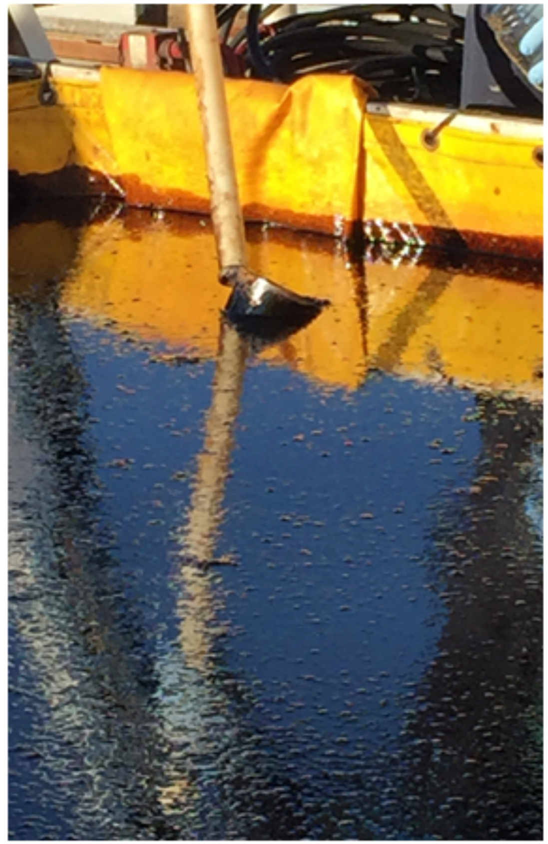


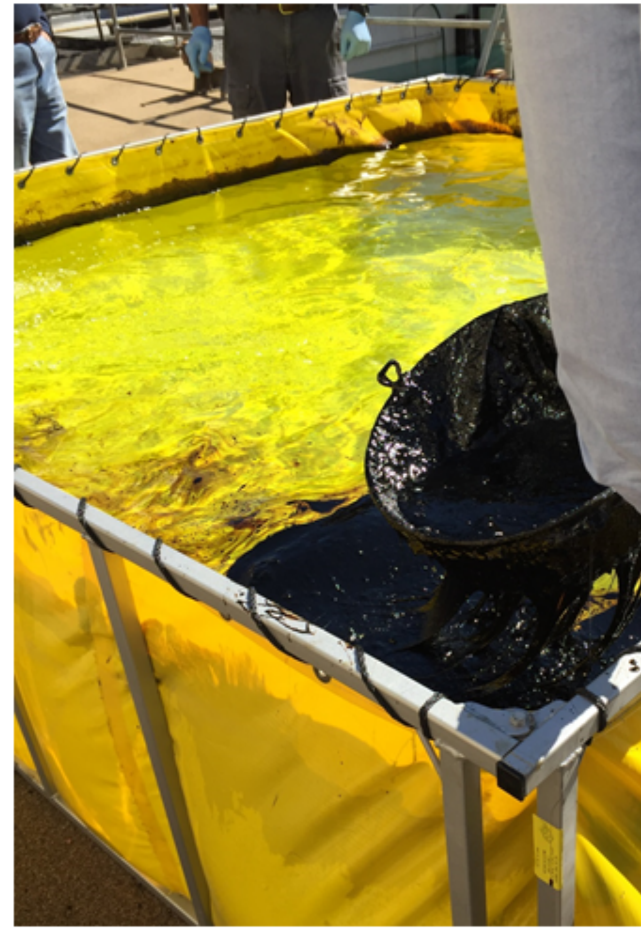
- ***Open microporous channels for fast kinetics during the sorption-desorption cycles***
- ***Minimum change of absorbent external shape and size during the cycles***
- ***Offer good mechanical strength.***

Relevance: Petrogel for oil spill recovery







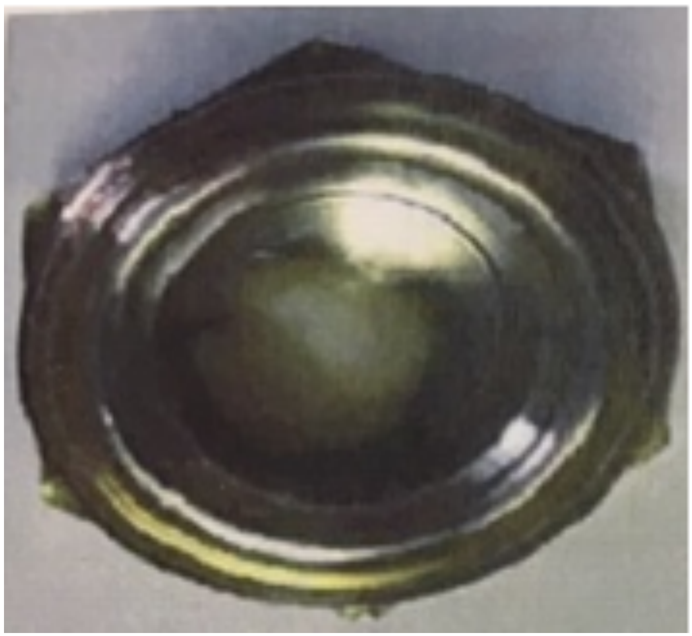


Operational Test at Ohmsett Facility

ACS Sustainable Chemistry & Engineering **2018**, 6, 12036-12045.

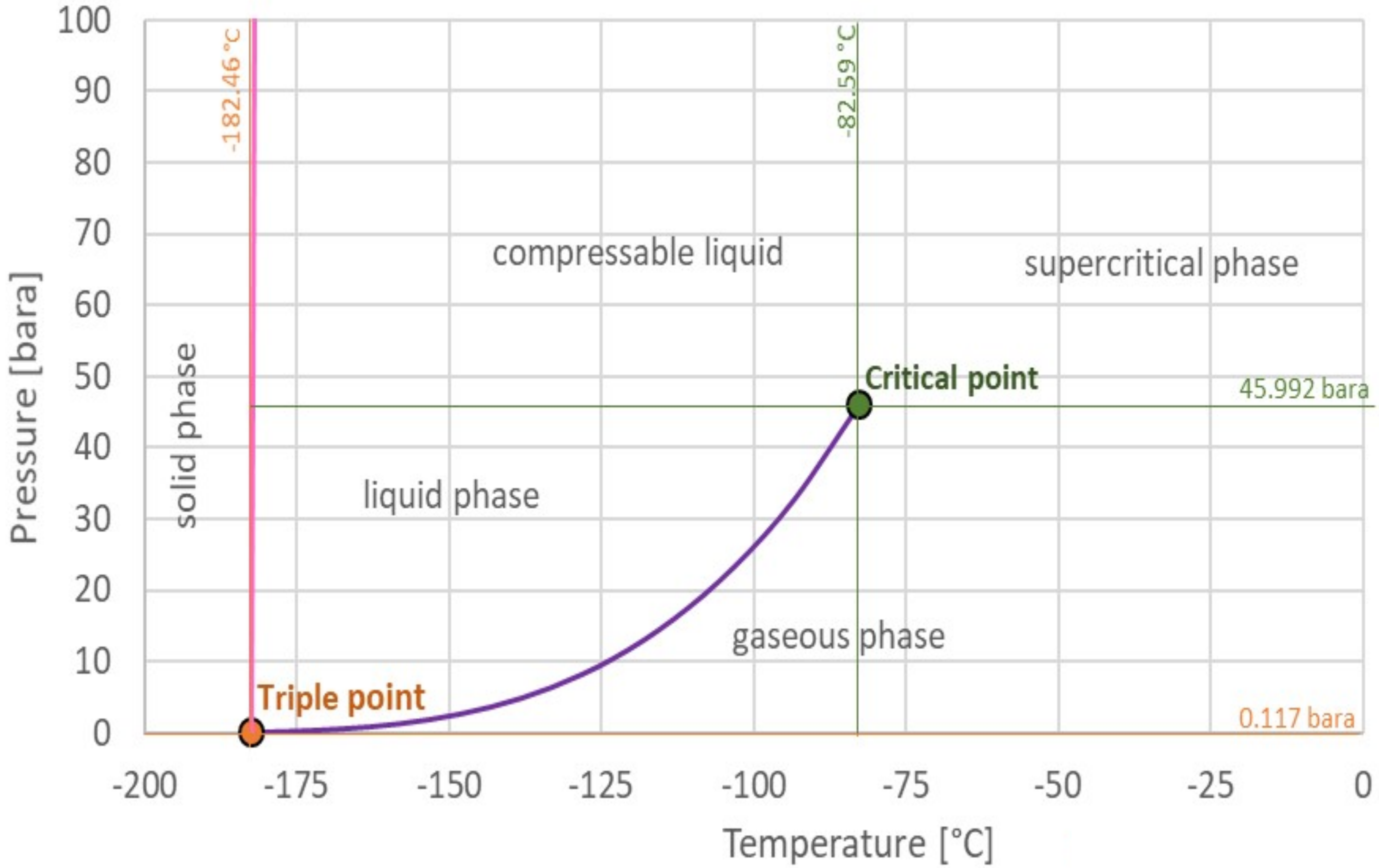
Relevance: Petrogel super-absorbent for C_2 gas

(left) A Petrogel particle (2-3 mm size) inside a stainless cell, which was exposed to C_2 ethylene gas under 500 psi pressure at ambient temperature for a few minutes. (right) After opening the cell, Petrogel shows the desorption of C_2 gas with the gradual expanding volume (>20 times that of its starting volume).



What is the suitable Petrogel structure for Natural gas (C_1 gas)?

Relevance: Phase diagram for methane (C_1 gas)

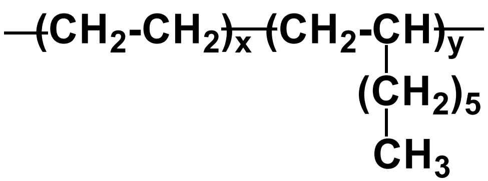


It is logical to think that, in the presence of Petrogel substrate with good affinity to NG molecules (interactive binding energy), the critical temperature will further increase toward ambient temperature.

Approach: Design and Synthesis of hydrocarbon polymers with good affinity with methane (C_1) gas

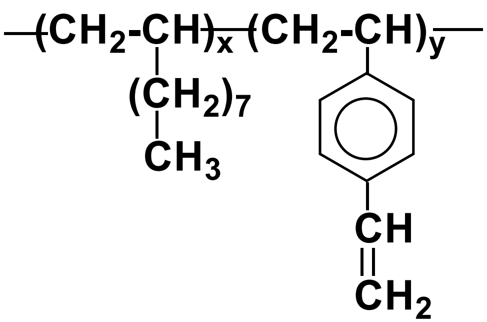
LLDPE

Poly(ethylene-co-1-octene)



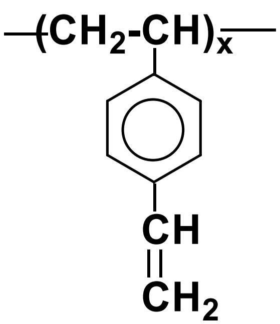
Poly(D-DVB)

Poly(1-decene-co-divinylbenzene)



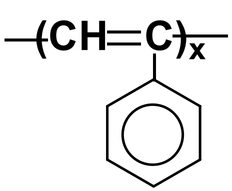
Poly(DVB)

Poly(divinylbenzene)



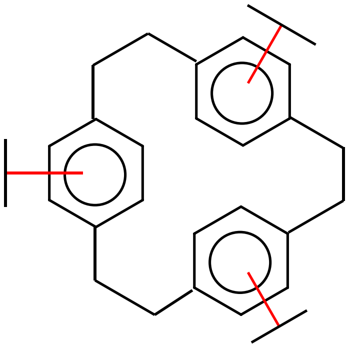
Poly(PA)

Poly(phenylacetylene)



COP-150

Covalent organic polymer



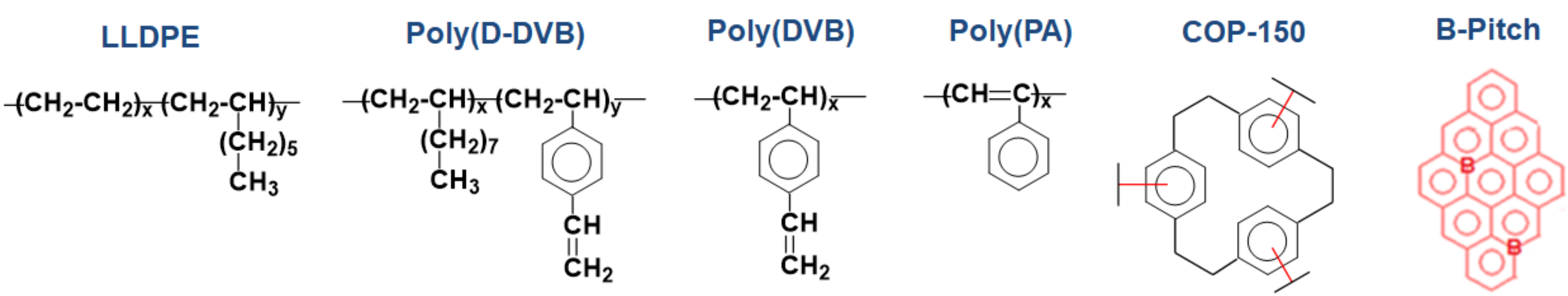
B-Pitch

Boron-substituted pitch

Accomplishments: BET surface area (as prepared)

Sample	*Specific Surface Area* $[m^2/g]_{BET}$	*Pore Volume* $[cm^3/g]$	*Pore Size* [nm]
LLDPE	**19.93**	**0.45**	**10.1**
Poly(D-DVB)	**5.31**	**0.45**	**14.8**
Poly(DVB)	**17.5**	**0.36**	**9.5**
Poly-PA (PPA)	**26.3**	**0.87**	**12.4**
COP-150	**28.8**	**1.56**	**7.5**
B-Pitch	**4.42**	**0.48**	**11.7**

Surface Area were determined by nitrogen (N_2) sorption isotherms and calculated by the BET (Brunauer–Emmett–Teller) method over a relative pressure range of P/P0 (0.05–0.30) using ASAP 2020 Automated Surface Area and Porosimetry System.



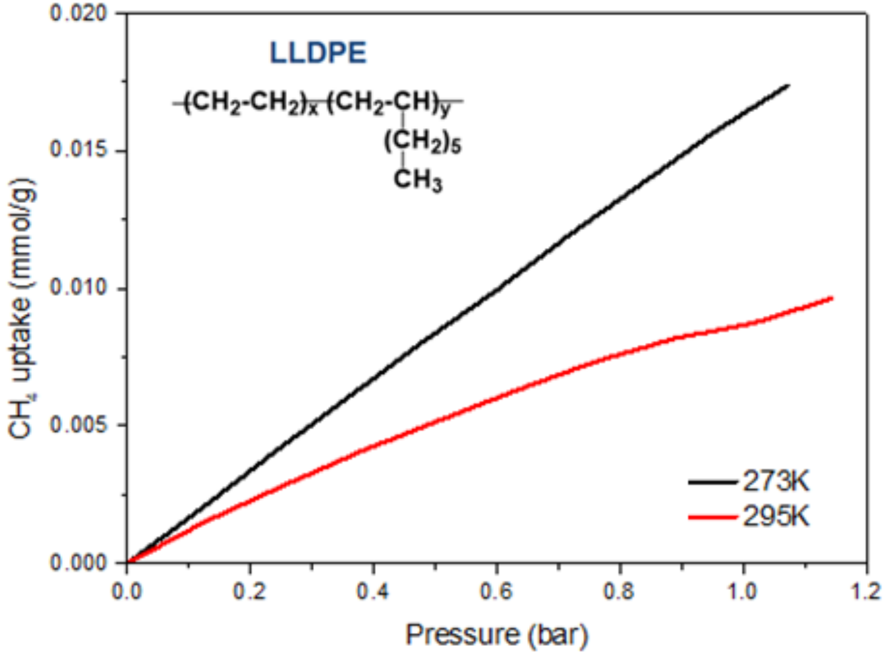
SSA: 120 m^2/g in the report

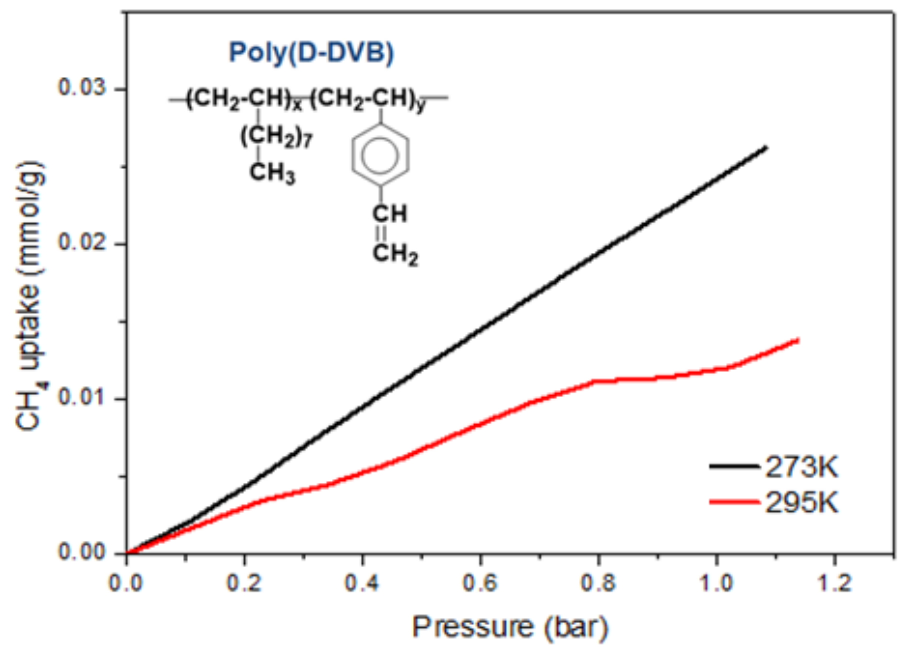
Accomplishments: Methane (C_1) binding energy

C_1 binding energy was measured by C1 sorption isotherms at 273 and 295 K, respectively, using ASAP 2020 System and calculated by Clausius-Clapeyron equation.

Clausius–Clapeyron relation

$$\ln \frac{P_2}{P_1} = -\frac{L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$



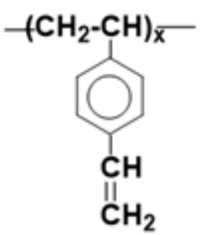


Uptake (mmol/g)	P_1, 273K (mmHg)	P_2, 295K (mmHg)	Q (KJ/mol)
0.0041	183.8919	290.5912	**13.93**
0.008	303.1524	483.3765	**14.20**

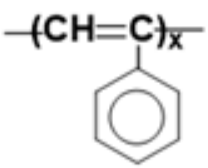
Uptake (mmol/g)	P_1, 273K (mmHg)	P_2, 295K (mmHg)	Q (KJ/mol)
0.006	208.9259	345.2355	**15.3**
0.010	328.7666	561.3276	**16.3**

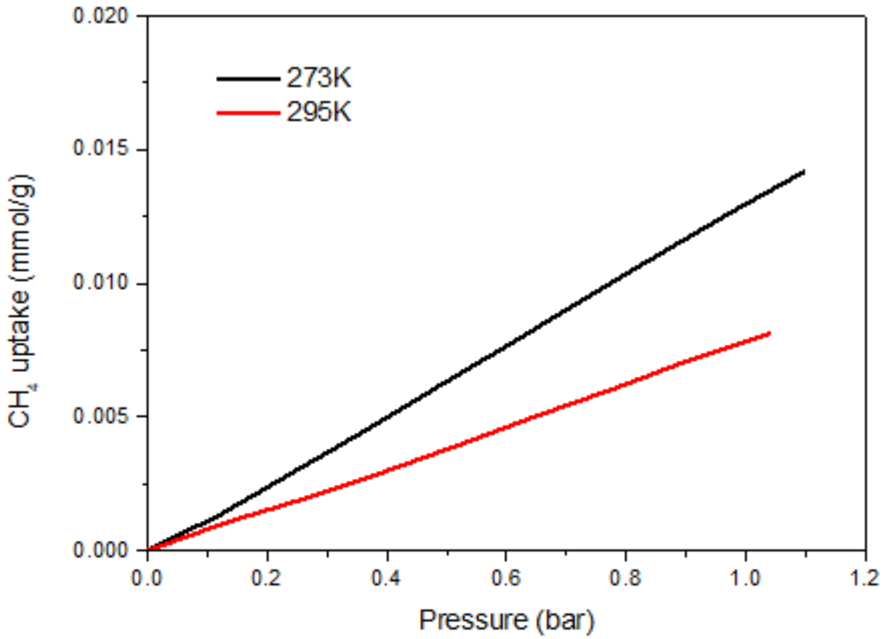
Accomplishments: Methane (C_1) binding energy

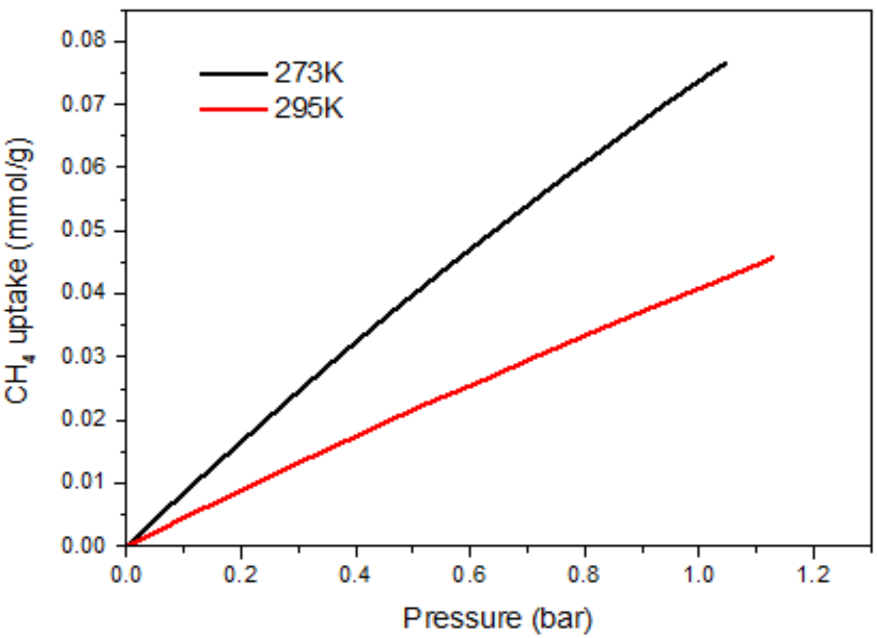
Poly(DVB)



Poly(PA)





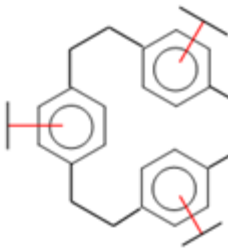


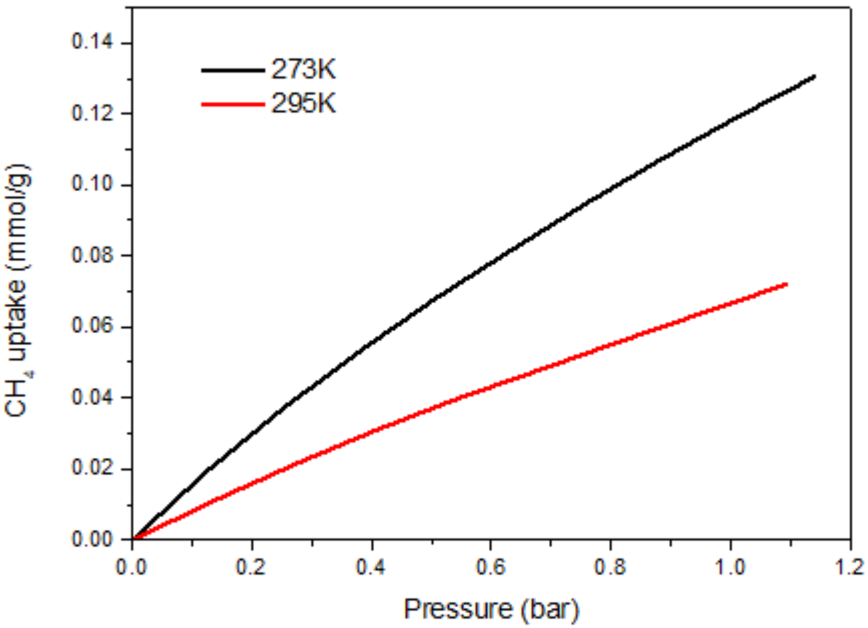
Uptake (mmol/g)	P_1, 273K (mmHg)	P_2, 295K (mmHg)	Q (KJ/mol)
0.003	185.9036	297.5944	**14.32**
0.006	360.5659	586.4830	**14.80**

Uptake (mmol/g)	P_1, 273K (mmHg)	P_2, 295K (mmHg)	Q (KJ/mol)
0.018	163.2155	310.6684	**19.59**
0.038	360.2359	701.2571	**20.30**

Accomplishments: Methane (C_1) binding energy

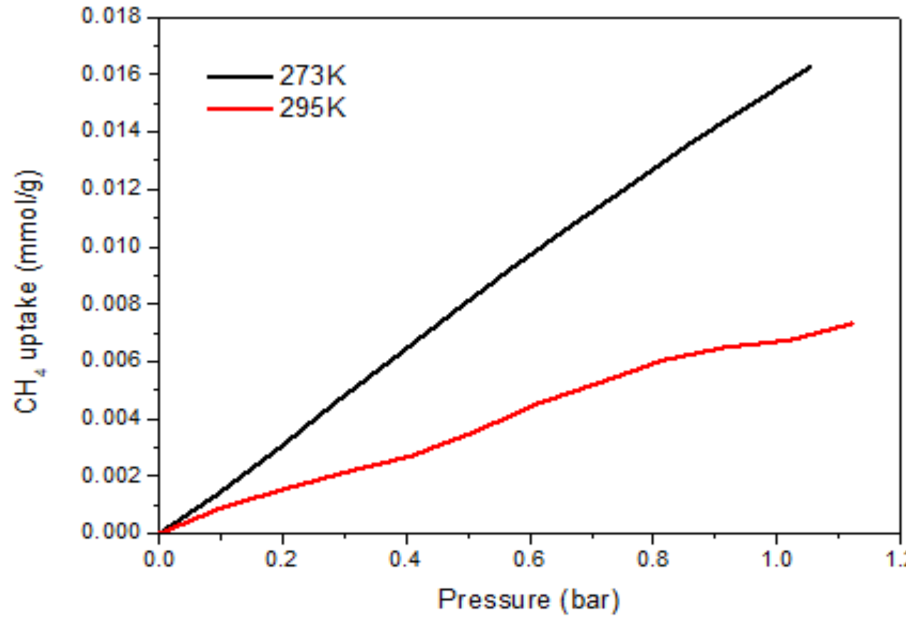
COP-150





Uptake (mmol/g)	P_1, 273K (mmHg)	P_2, 295K (mmHg)	Q (KJ/mol)
0.020	95.88716	193.7826	**21.41**
0.0399	206.2534	414.1797	**21.22**

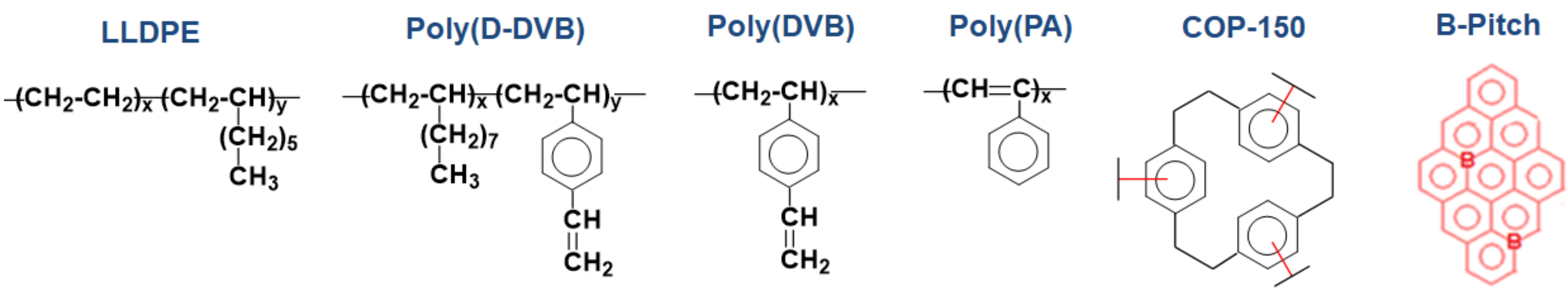
B-Pitch



Uptake (mmol/g)	P_1, 273K (mmHg)	P_2, 295K (mmHg)	Q (KJ/mol)
0.0027	147.4259	309.5945	**22.58**
0.0046	218.9051	464.6055	**22.90**

Accomplishments: Summary of polymer Properties

Sample	*Pore Volume [cm³/g]*	*Pore Size [nm]*	*SSA_{BET} [m²/g]*	*C_1 Binding Energy [KJ/mol]*
LLDPE	**0.45**	**10.1**	**19.93**	**14.1**
Poly(D-DVB)	**0.45**	**14.8**	**5.31**	**15.8**
Poly(DVB)	**0.36**	**9.5**	**17.5**	**14.1**
Poly-PA (PPA)	**0.87**	**12.4**	**26.3**	**19.9**
COP-150	**1.56**	**7.5**	**28.8**	**21.3**
B-Pitch	**0.48**	**11.7**	**4.42**	**22.8**



Milestone Summary Table

Recipient Name: T. C. Mike Chung

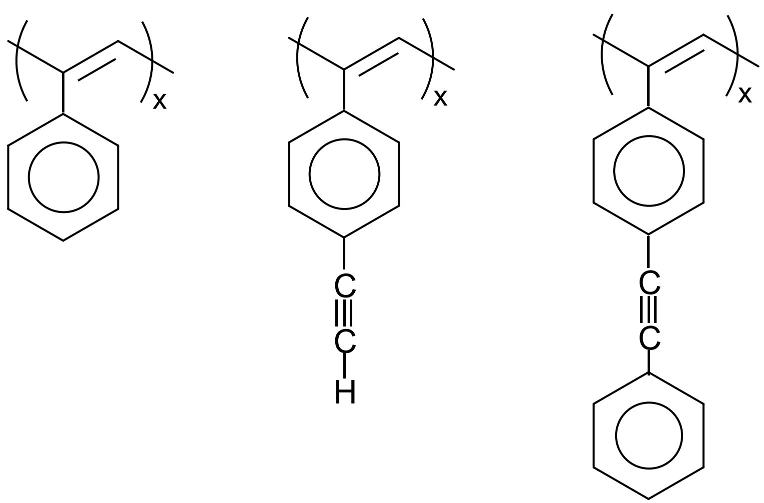
Project Title: Developing A New Natural Gas Super-Absorbent Polymer (NG-SAP) for A Practical NG Storage System with Low Pressure, Ambient Temperature, and High Energy Density

Task	Task Title	Milestone Description	Milestone Verification Process	Quarter
1.1	Polymer Synthesis	Synthesis of D-DVB Copolymers	^{1}H and ^{13}NMR spectra and GPC measurement	1
1.2	Fabrication IPN structure	Fabrication of Petrogel (A) IPN Structure	solid-state NMR, HR-TEM and FE-SEM micrographs, and Solubility test	1
2.1	Morphology Study	Study of Free Volume, Surface Area, and Morphology of Petrogel (A)	BET surface analysis using N2 and CO2 gases at 77 and 273 K	2
2.2	Absorption Isotherm	Study of NG Absorption Isotherm with Petrogel (A) absorbents	Absorption isotherms at 77 and 87 K with low NG pressure and apply Clausius–Clapeyron to estimate heat of sorption	2-3
2.3	Absorption Capacity	Study of NG Absorption Capacity with Petrogel (A) absorbents	NG absorption-desorption (volumetric and gravimetric) profiles under various pressures and temperatures	3-4
2.4	Kinetic Study	Kinetics Study of NG Charge-Discharge Cycles with Petrogel (A) absorbents	Volumetric NG absorption-desorption capacity vs time under various conditions	4
Go/No Go Decision Point		Demonstrate a Petrogel absorbent with reversible total volumetric capacity exceeding that of CNG systems (263 cm^3/cm^3) at 100 bars and room temperature.	Send 10 slides to HyMARC/DOE summarizing all experimental results and provide samples to NREL for verification.	4
3.1	Polymer Synthesis	Synthesis of D-DVB Copolymers	^{1}H and ^{13}NMR spectra and GPC measurement	5
3.2	Fabrication IPN	Fabrication of Petrogel (B) IPN Structure	NMR, HR-TEM and FE-SEM micrographs, and Solubility test	6
4.1	Morphology Study	Study of Free Volume, Surface Area, and Morphology of Petrogel (B)	BET surface analysis using N2 and CO2 gases at 77 and 273 K	6
4.2	Absorption Isotherm	Study of NG Absorption Isotherm with Petrogel (B) absorbents	Absorption isotherms at 77 and 87 K with low NG pressure and apply Clausius–Clapeyron to estimate heat of sorption	7
4.3	Absorption Capacity	Study of NG Absorption Capacity with Petrogel (B) absorbents	NG absorption-desorption (volumetric and gravimetric) profiles under various pressures and temperatures	7-8
4.4	Kinetic Study	Kinetics Study of NG Charge-Discharge Cycles with Petrogel (A) absorbents	Volumetric NG absorption-desorption capacity vs time under various conditions	8
Go/No Go Decision Point		Demonstrate a Petrogel absorbent with reversible total volumetric capacity >390 cm^3/cm^3 (50% higher than that of CNG systems) at <65 bar and room temperature.	Send 10 slides to HyMARC/DOE summarizing all experimental results and provide samples to NREL for verification.	8
5.1	Polymer Synthesis	Milestone Synthesis of D-DVB Copolymers	^{1}H and ^{13}NMR spectra and GPC measurement	9-10
5.2	Fabrication IPN	Fabrication of Petrogel (C) IPN Structure	NMR, HR-TEM and FE-SEM micrographs, and Solubility test	10
6.1	Morphology Study	Study of Free Volume, Surface Area, and Morphology of Petrogel (C)	BET surface analysis using N2 and CO2 gases at 77 and 273 K	10-11
6.2	Absorption Isotherm	Study of NG Absorption Isotherm with Petrogel (C) absorbents	Absorption isotherms at 77 and 87 K with low NG pressure and apply Clausius–Clapeyron to estimate heat of sorption	11
6.3	Absorption Capacity	Study of NG Absorption Capacity with Petrogel (C) absorbents	NG absorption-desorption (volumetric and gravimetric) profiles under various pressures and temperatures	11-12
6.4	Kinetic Study	Kinetics Study of NG Charge-Discharge Cycles with Petrogel (C)	Examine volumetric NG absorption-desorption capacity vs time under various conditions.	12
Final Project Objective		Demonstrate a Petrogel absorbent with reversible total volumetric capacity >500 cm^3/cm^3 (about double that of CNG systems) at <65 bar and room temperature.	Provide samples to NREL for verification.	12

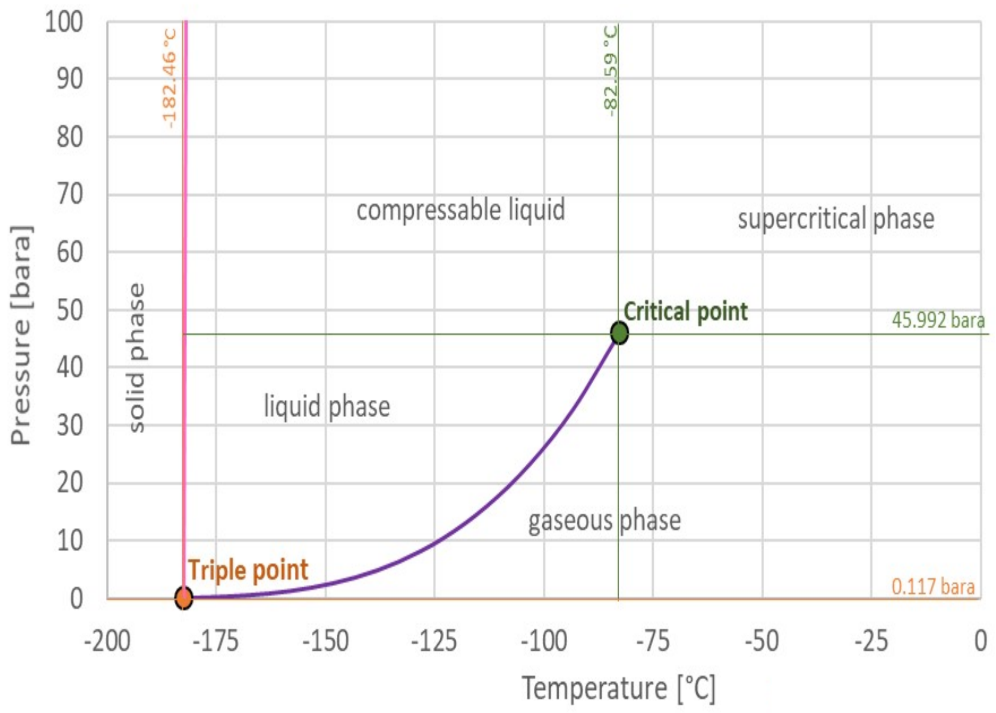
Future: Expanding polymer composition based on PPA backbone

PPA Derivatives

PPA PPA-A PPA-PA



Phase Diagram for methane (C_1)



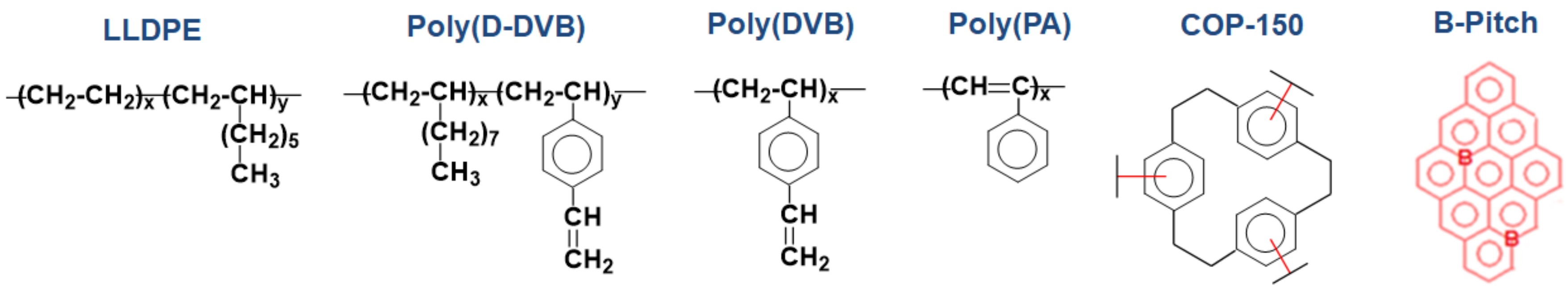
Substrate with good affinity with NG molecules (suitable binding energy 20-25 KJ/mol) shall increase the supercritical temperature or/and reduce C_1 pressure.

Collaborations

Partner	Project Roles
Penn State University Dr. Wei Zhu Mr. Houxiang Li Mr. Vandy Sengeh	Design and Synthesis of New Polymers and Study of C_1 Gas Binding Energy. Fabrication of Petrogel IPN structures and evaluation their C_1 gas sorption-desorption capacity.
HyMARC Consortium National Renewable Energy Lab.	Assisting us on NG binding energy and sorption-desorption measurements. Verification of our experimental results.

Summary

- In this early stage of research program, we have systematically prepared a series of hydrocarbon polymers (below). They are grouped into two classes, including PE-based (saturated) polymers with various side groups and polyaromatic-based (unsaturated) polymers, as well as B-Pitch material.



- Methane (C_1) gas binding energy to PE-based polymers ~15 KJ/mol.
  Methane (C_1) gas binding energy to polyaromatic-based polymers ~20 KJ/mol
  Methane (C_1) gas binding energy to B-Pitch surface ~23 KJ/mol.

Future Research:

- Expanding hydrocarbon polymer compositions and their methane (C_1) gas binding energy to the range up to 30 KJ/mol.
- Fabricating Petrogel IPN structures with the selected polymers with suitable C_1 binding energy and studying their NG sorption-desorption cycles.