



Role of Nanoparticle Technology in Oil and Gas Industry Application: Small Size, Big Effects

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Agenda



- Background
- Introduction to nanoscale
- Challenges facing nanoparticle application
- Integration of nanoparticles in processes of:
 - Oil upgrading and recovery
 - Asphaltene
 - Friction reduction
 - Natural gas
 - Produced water treatment
 - Conversion of waste hydrocarbon into valuable products
- Take-home message
- Acknowledgments



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Proven Oil Reserves Worldwide



Image courtesy: Kjell Aleklett, Unconventional Oil & Gas 2012
TaiYuan 2012-09-24

FIGURE 1. DISTRIBUTION OF CANADIAN ENERGY RESOURCES



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Oil and Natural Gas Resources



- Canada ranks third, in terms of proven global crude oil reserves.
- More than 96% of Canada's oil reserves are in Alberta.
- In 2010, Alberta's total proven oil reserves were 170.8 billion barrels, or about 12% of total global oil reserves (1,469.6 billion barrels).

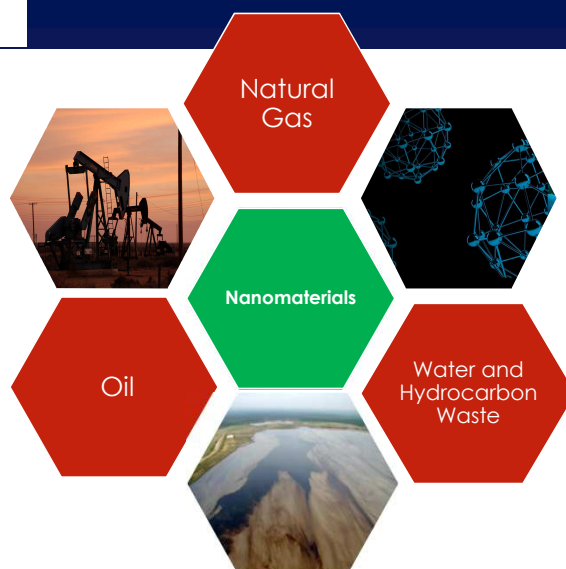


- Canada ranks fourth, in terms of proven global NG reserves
- 2020: marketed NG production in Alberta = 8,286.6 Million Cubic Metres
- In August 2021, marketable natural gas production was 9.0 billion cubic metres, up 8.4% from August 2020's production level.



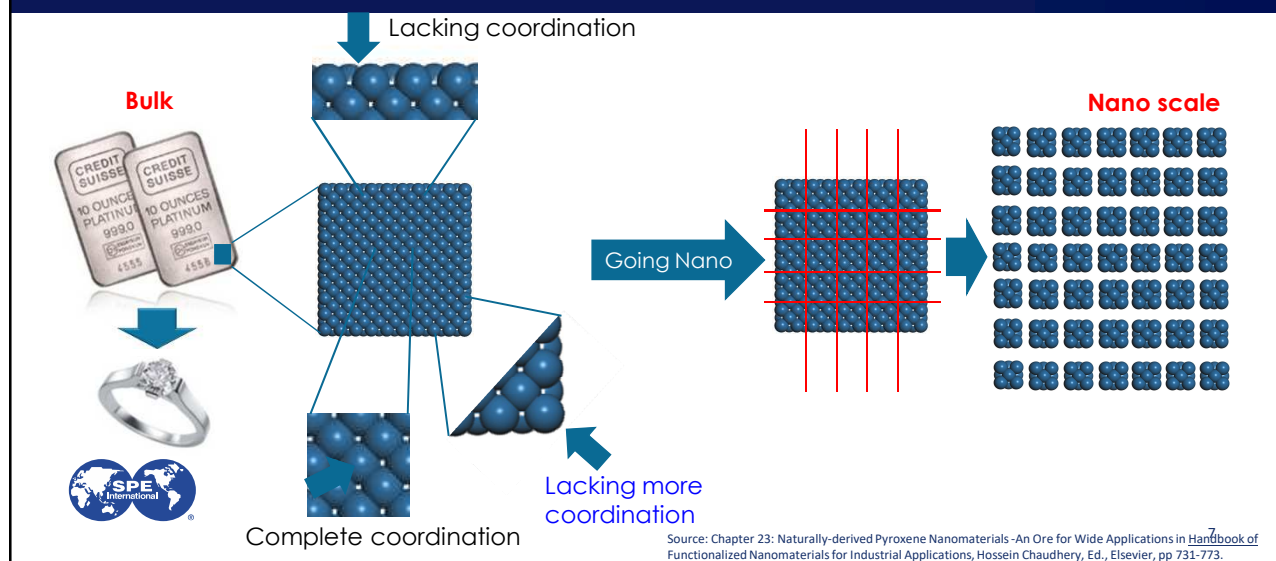
- There are 220 km² of tailing in Alberta
- 340 billion gallons of toxic sludge
- 27 billion dollars is the estimated amount needed for the cleanup using current implemented technologies
- 150 million metric tons of petroleum coke is stockpiled per annum.

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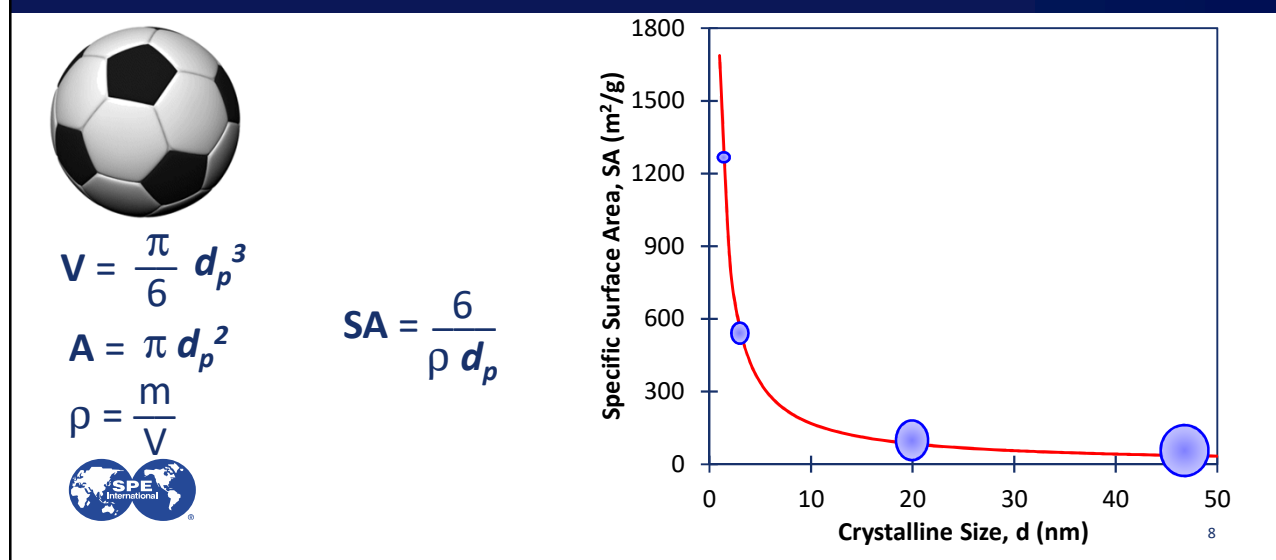


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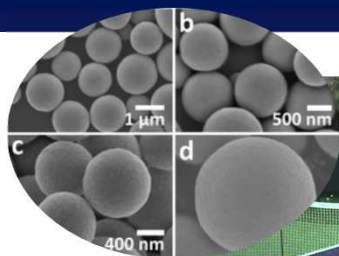
Why Nanoparticles are different?



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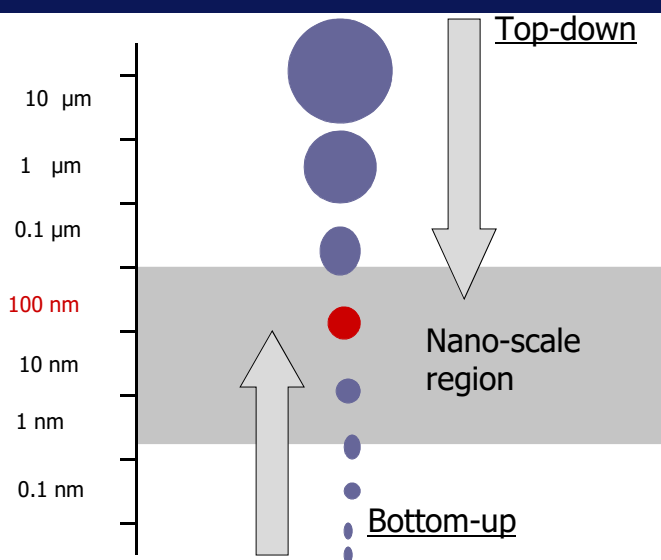


Area of one gram of nanoparticles =
1000 m² (4 tennis courts)



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Preparation of Nanoparticles?



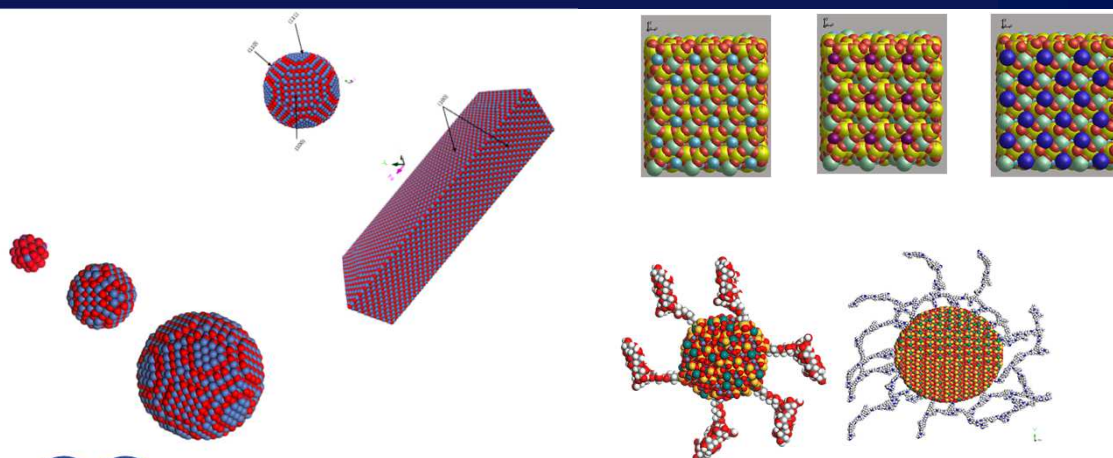
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Naturally bottom-up built materials



Source: seashells.com

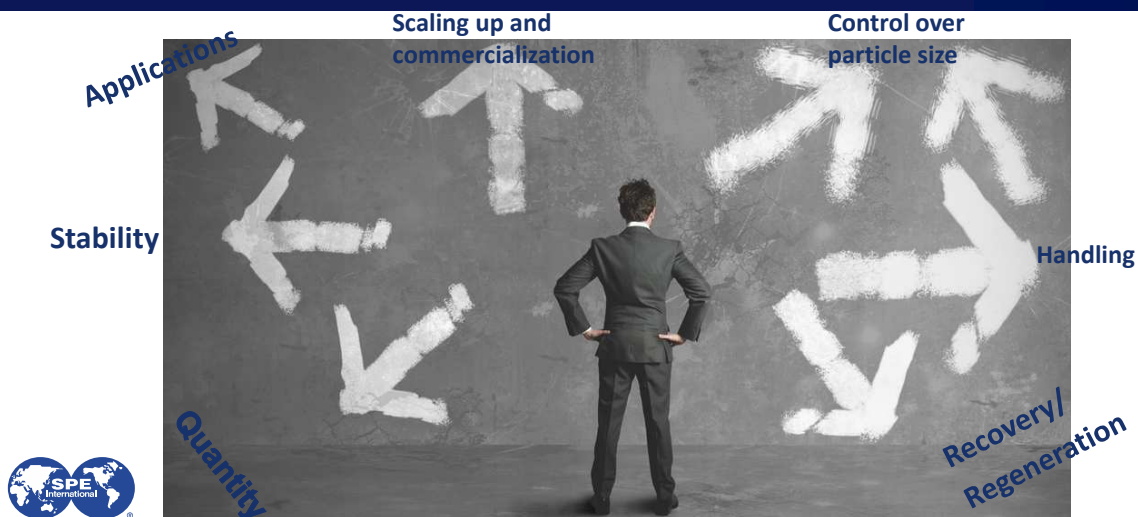
Size, Shape, Surface and Structural Modifications



ACS Applied Nano Materials, 3 [2020] 5311–5326
 Phys. Chem. Chem. Phys., 2016, 18, 6839
 RSC Adv., 2017, 7, 14021
 Journal of Colloid and Interface Science, 2016, 461, 396–408

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Nanoparticle Challenges



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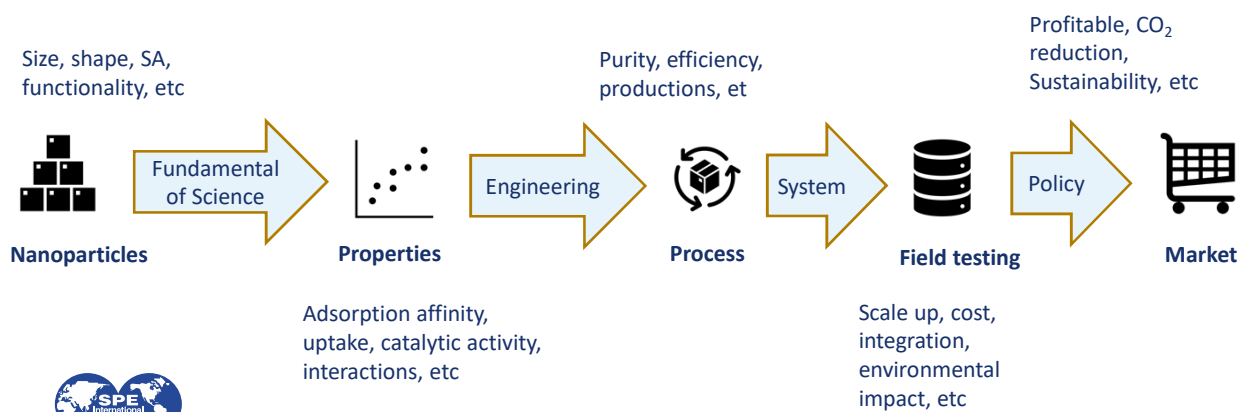
“If I have 300 ideas in a year and **just one** turns out to work, I am satisfied.”

ALFRED NOBEL
Founder of the Nobel Prize



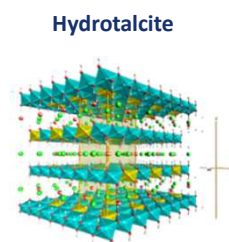
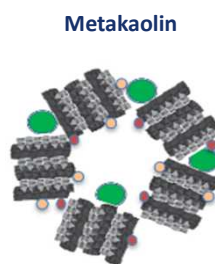
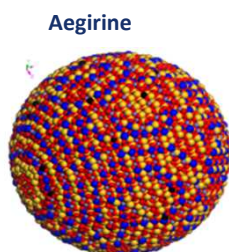
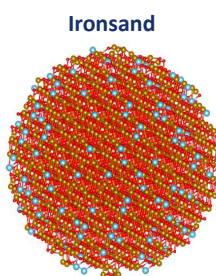
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Challenge: Nano to real application



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Materials Toolbox: Naturally-derived Nanomaterials



- Naturally-derived nanomaterials
- Prepared at mild conditions
- Tunable surface
- Most abundant elements on earth
- Could be utilized for both in-situ and ex-situ applications.



USA Patent No. US16/289,218 (pending)
 USA Patent No. US63/231,083 (pending)
 RSC Adv., 2016, 6, 64482
 RSC Adv., 2017, 7, 14021
 Journal of Colloid and Interface Science, 2016, 461, 396–408

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Process toolbox: Oil, gas, water, and solid waste



Oil



- ☐ Upgrading & recovery
- ☐ Asphaltenes
- ☐ Formation damage
- ☐ TAN
- ☐ Friction reduction (fracking)

Natural Gas



- ☐ Purification
- ☐ Transportation (LNG)
- ☐ Conversion (G2L, DME, H₂)

Wastewater



- ☐ SAGD
- ☐ MFT
- ☐ Oil spill

Solid waste

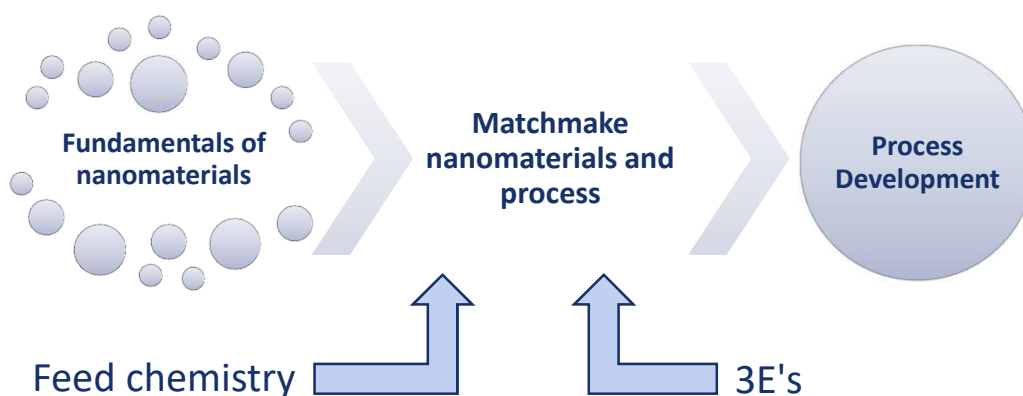


- ☐ Petroleum coke
- ☐ Asphaltenes
- ☐ Low-rank coal



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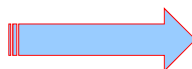
Combining Efforts



Is it a material challenge and/or a process challenge?

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Nano-catalysts: Partial upgrading of heavy oil to meet pipeline specifications!



- **Dilbit using NGC**
- Costly
- High volume capacity (~50%)
- Not readily available in large quantity
- Energy intensive

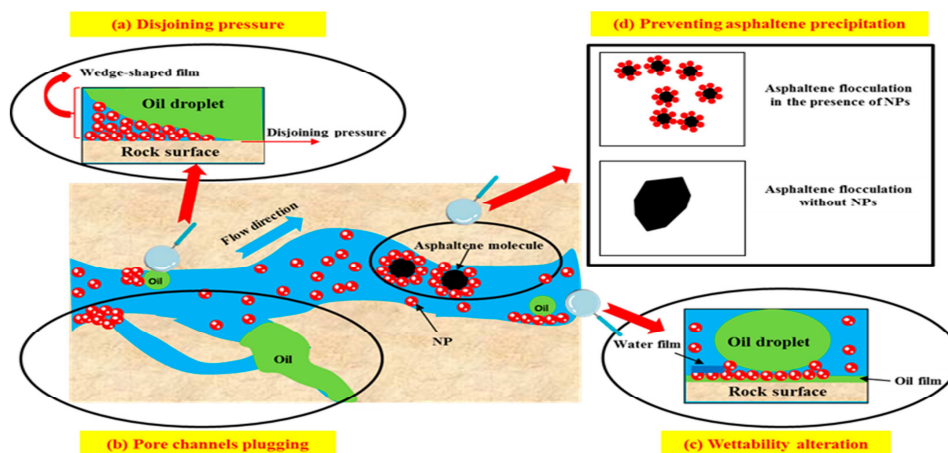


Applied Energy, 2014, 133, 374–387
Energy Fuels, 2014, 28, 1338–1350
Energy Fuels 2014, 28, 1351–1361

- **Upgrading**
- On surface
- In-situ
- **Catalytic upgrading with E-UD nanocatalysts**

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Integrating Nanoparticles with Water Flooding for EOR



Ind. Eng. Chem. Res. 2016, 55, 6122–6132
Ind. Eng. Chem. Res. 2015, 54, 8201–8211

Contents lists available at ScienceDirect
Applied Catalysis A: General
 journal homepage: www.elsevier.com/locate/apcata

Catalytic steam gasification of *n*-C₅ asphaltenes by kaolin-based catalysts in a fixed-bed reactor
 Azfar Hassan^a, Lante Carboneani-Arambarri, Nishaat N. Nassar, Gerardo Vitale, Francisco Lopez-Linares, Pedro Pereira-Almiao
^aChemical and Petroleum Engineering Department, Schulich School of Engineering, University of Calgary, Calgary, Alberta T2N 1N4, Canada

Adsorbent (Clay) + **Nanoparticles** → **SORBCAT**

Asphaltenes + **Steam** → **H₂, CH₄, CO, CO₂**

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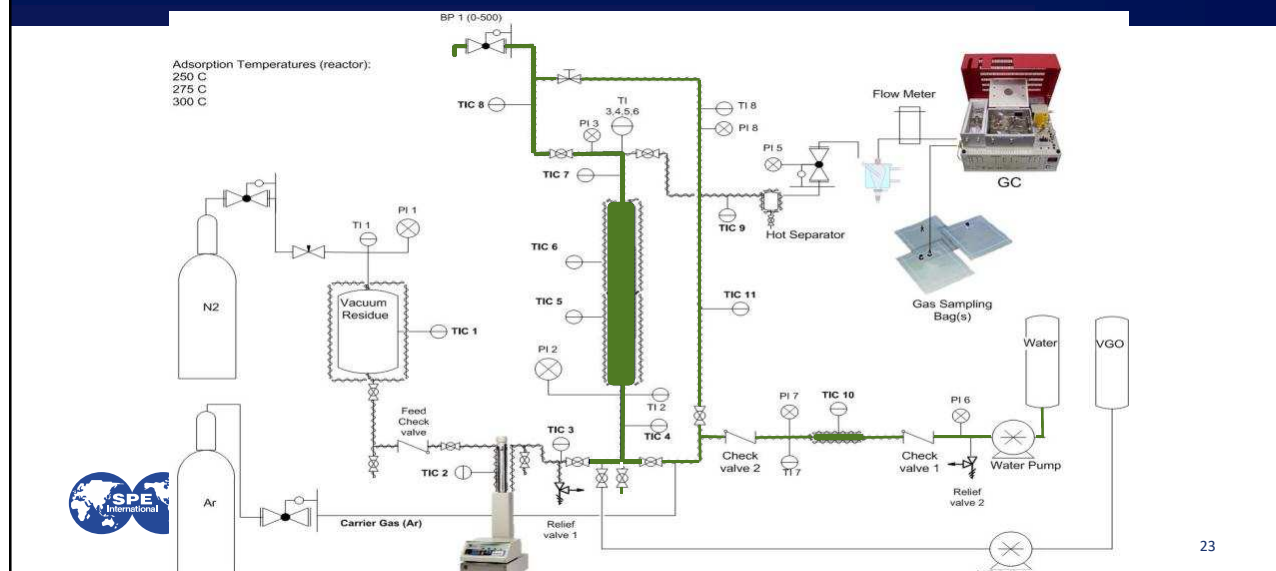
Getting Real: Adsorption and Gasification Processes

Adsorption

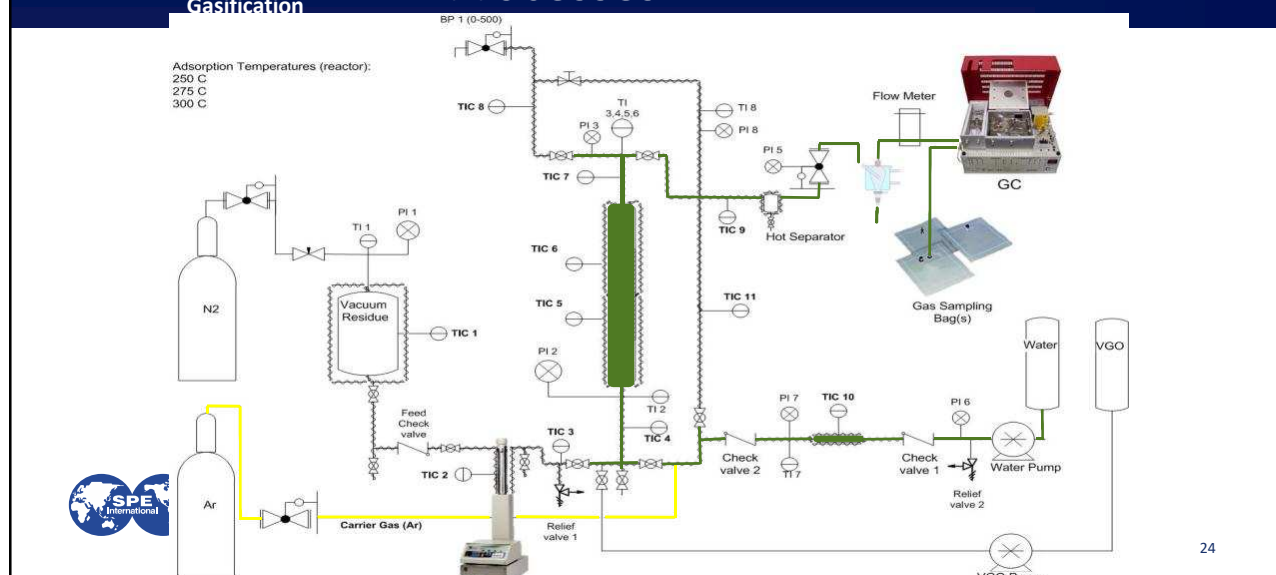
Adsorption Temperatures (reactor):
 250 C
 275 C
 300 C

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Getting Real: Adsorption and Gasification Processes



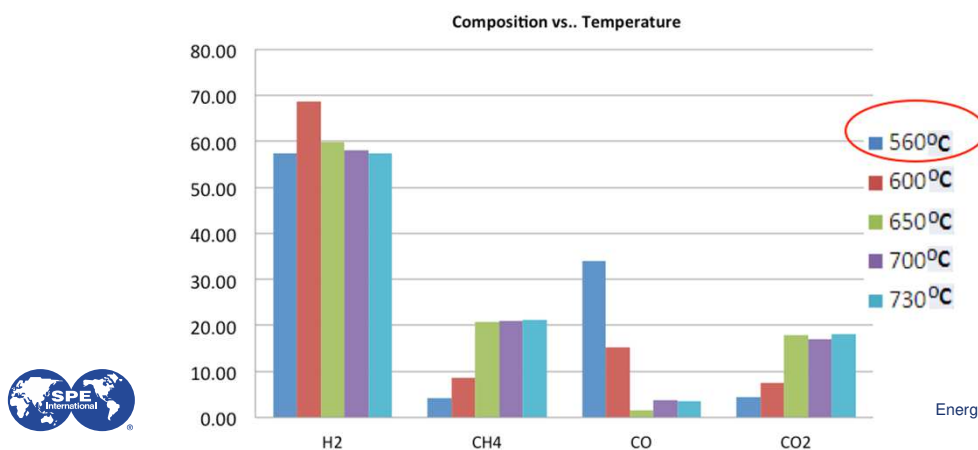
Getting Real: Adsorption and Gasification Processes



Preliminary Catalytic Steam Gasification Results



- ▶ Feed: Athabasca Vacuum Residue
- ▶ Catalyst: 3wt% NiO-Kaoline



Nano-inhibitor: prevents asphaltene deposition



energy&fuels

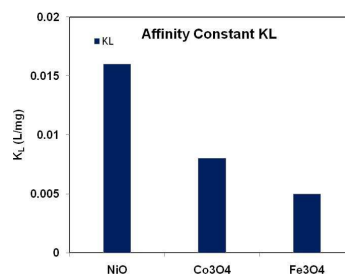
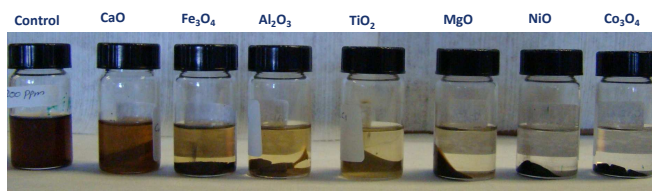
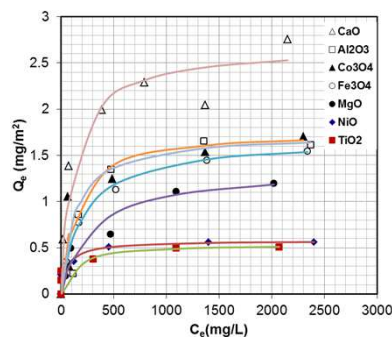
ARTICLE
pubs.rsc.org/EF

Metal Oxide Nanoparticles for Asphaltene Adsorption and Oxidation

Nasihat N. Nassar,^{1,2} Azfar Hassan,^{1,2} and Pedro Pereira-Almiao^{1,2}

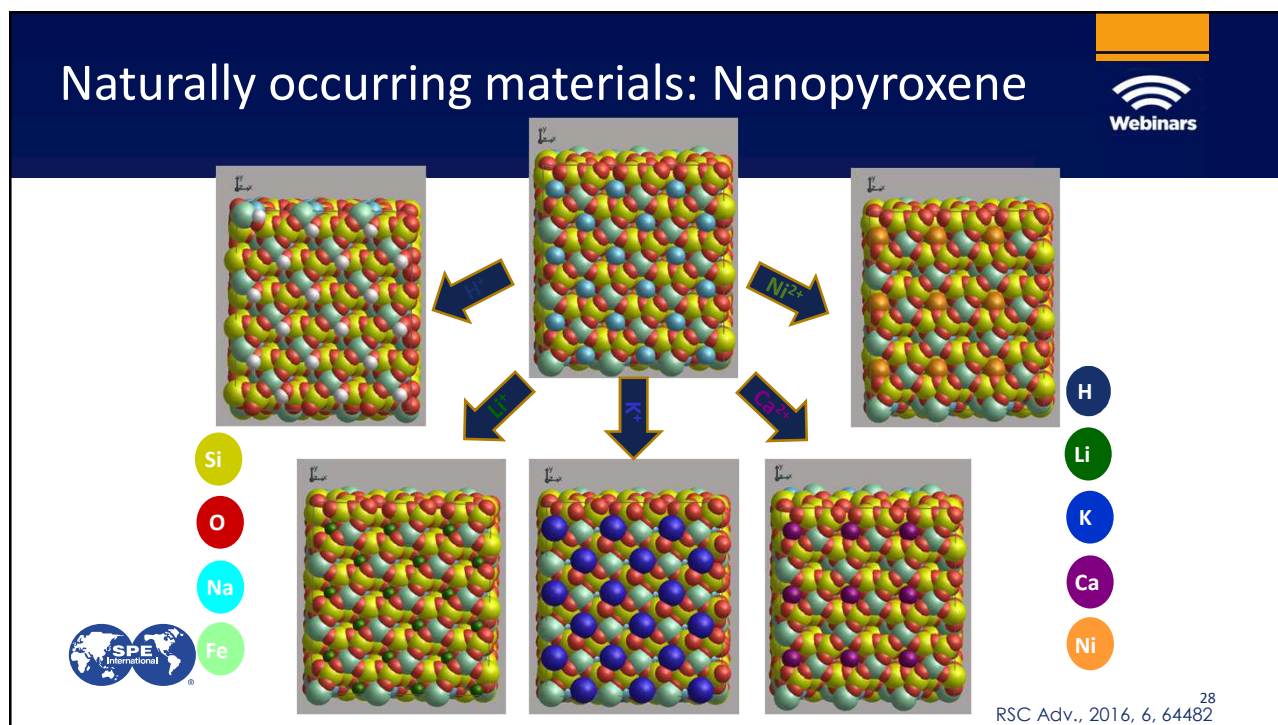
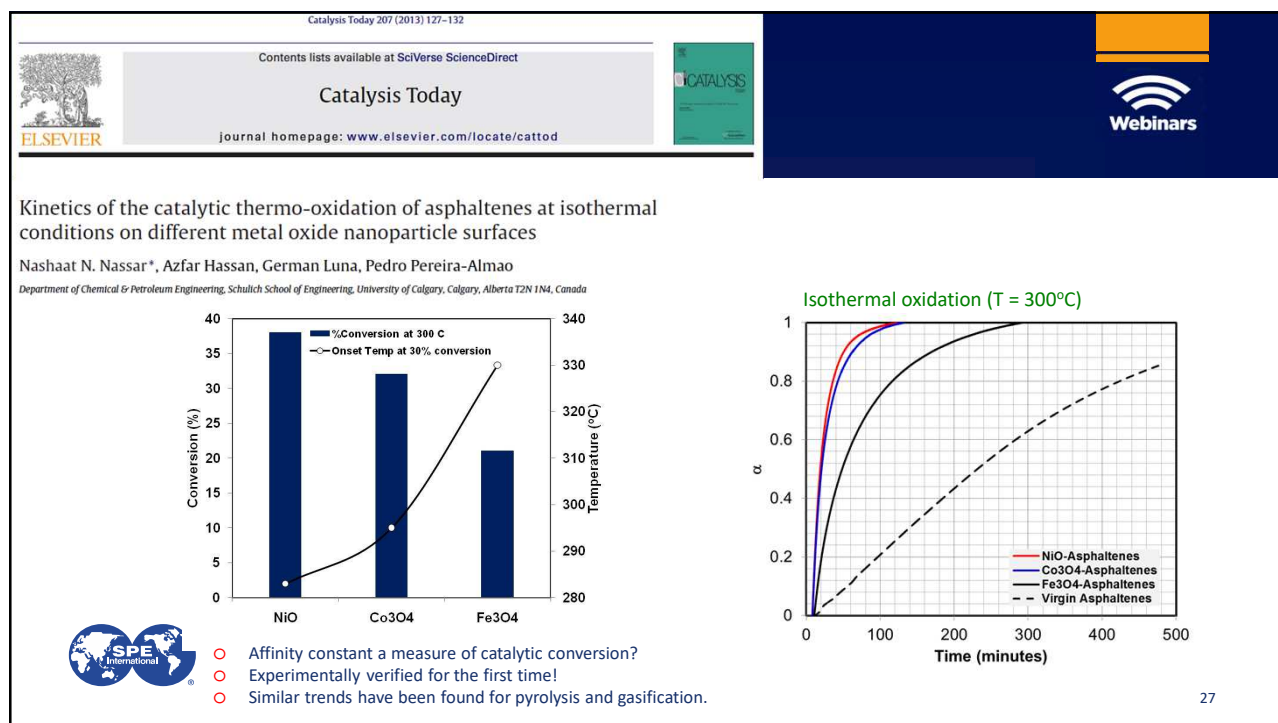
¹Alberta Ingenuity Centre for In-Situ Energy, University of Calgary, Calgary, Alberta, Canada

²Department of Chemical & Petroleum Engineering, University of Calgary, Calgary, Alberta, Canada



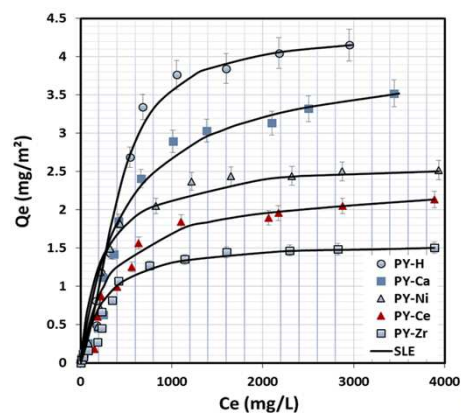
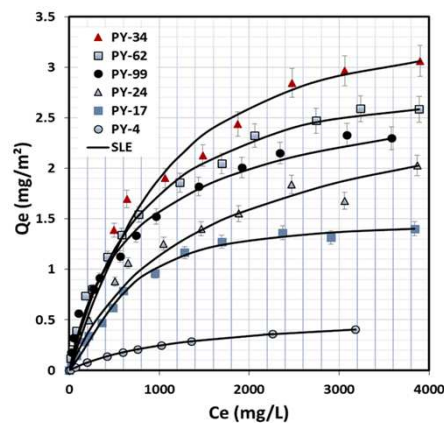
$$Q_e = Q_m \frac{K_L C_e}{1 + K_L C_e}$$

Energy Fuels 2014, 28, 4963–4975
Energy Fuels 2015, 29, 1610–1621

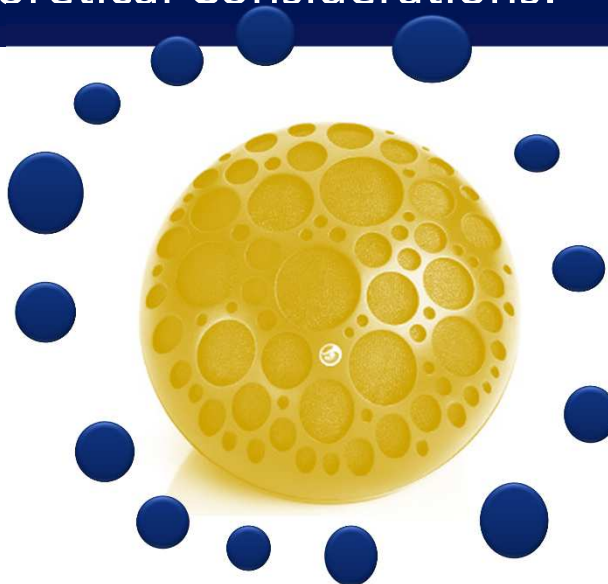


Cite this: *RSC Adv.*, 2016, 6, 64482

Effect of nanosized and surface-structural-modified nano-pyroxene on adsorption of violanthrone-79⁺

Maryam Hmoudah,^{ab} Nashaat N. Nassar,^{*a} Gerardo Vitale^a and Amjad El-Qanni^{ab}

Theoretical Considerations:



Theoretical Considerations:



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Theoretical Considerations:

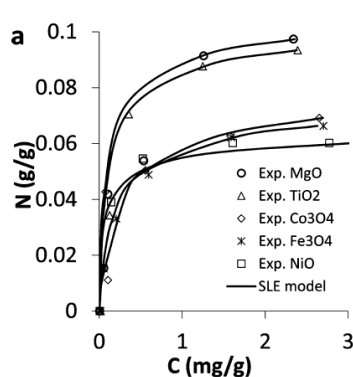


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A Novel Solid–Liquid Equilibrium Model for Describing the Adsorption of Associating Asphaltene Molecules onto Solid Surfaces Based on the “Chemical Theory”

Tatiana Montoya,[†] Diana Coral,[†] Camilo A. Franco,[‡] Nashaat N. Nassar,^{*,‡} and Farid B. Cortés^{*,†}



$$C = \frac{\psi H}{1 + K\psi} \exp\left(\frac{\psi}{N_m}\right) \quad (12)$$

This adsorption isotherm model describes the behavior of asphaltenes onto a solid surface, i.e., solid–liquid equilibrium, which is a temperature-dependent model of three parameters (i.e., N_m , H , and K).^{6,70,71} H is the measured Henry's law constant, which is only a function of temperature, and an indicator of the adsorption affinity (i.e., the strength of interactions for adsorption) of asphaltenes onto solid surface. The lower the H value (i.e., higher Henry's constant), the higher the affinity (i.e., the active sites are in locations that are easily accessible by asphaltenes). K is constant and an indicator of rapid association of asphaltenes molecules once the primary sites are occupied. N_m is the maximum adsorption capacity of asphaltenes (g/g). The other parameters are defined as follows:



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A New Model for Describing the Adsorption of Asphaltenes on Porous Media at a High Pressure and Temperature under Flow Conditions

Nashaat N. Nassar,^{*,†} Tatiana Montoya,[†] Camilo A. Franco,[‡] Farid B. Cortés^{*,‡}

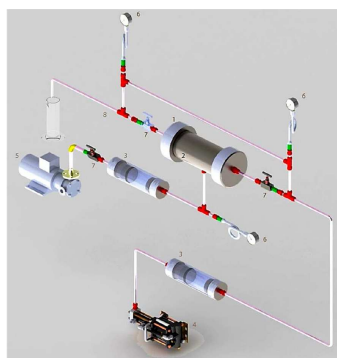


Figure 2. Schematic representation of the experimental setup. Legend: (1) the core holder, (2) the sand packed bed, (3) the displacement cylinder, (4) the displacement positive pump, (5) the mineral oil pump, (6) the pressure transducers, (7) the valves, and (8) sample output.



$$C = \frac{\Psi H}{1 + K\Psi} \exp\left(\frac{\Psi}{N_m}\right) \exp\left[-\frac{v_{as}}{RT}(\delta_{as} - \delta_T)^2\right] \quad (12)$$

where the definitions of K and Ψ are given by³³

$$K = \frac{K_T RT}{SA} \quad (13)$$

$$\Psi = \frac{-1 + \sqrt{1 + 4K\xi}}{2K} \quad (14)$$

where ξ is a constant (defined as $\xi = NN_m/(N_m - N)$), N is the amount adsorbed (in units of g/g), N_m is the maximum adsorption capacity, K_T is the reaction constant for dimer formation, SA is the specific surface area of the adsorbent (in units of cm^2/g), v_{as} is the asphaltene molar volume (in units of cm^3/mol), δ_{as} is the solubility parameter for asphaltenes (in units of $\text{MPa}^{1/2}$), and δ_T is the solubility parameter (in units of $\text{MPa}^{1/2}$) for the dissolvent reported in the literature.⁶⁵ Equation 12 represents the new adsorption model that considers the effects of the temperature and pressure.

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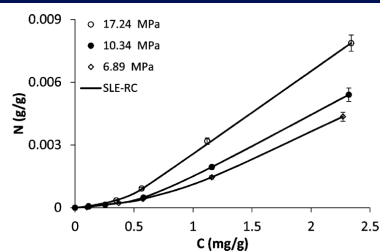


Figure 4. Adsorption isotherms of n -C₇ asphaltenes at different test pressures and temperature of 313 K. The symbols represent the experimental data and the solid curves are from SLE-RC model (see eq 12).

Table 2. Estimated Parameters of the Solid–Liquid Model under Reservoir Conditions in the SLE-RC Model for Different Test Pressures at 313 K

parameter	Value		
	6.89 MPa	10.34 MPa	17.24 MPa
H (mg/g)	8086.42	7030.61	3321.65
K (g/g)	1259.76	1440.82	1473.52
N_m (g/g)	0.00668	0.00708	0.00879
δ_{as} (MPa ^{1/2})	16.56	16.64	16.80
v_{as} (cm ³ /mol)	1040.4	1025.28	743.74
RMSE%	1.70	0.04	0.63



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Importance of the Adsorption Method Used for Obtaining the Nanoparticle Dosage for Asphaltene-Related Treatments

Juan D. Guzmán,[†] Stefania Betancur,[‡] Francisco Carrasco-Marín,[‡] Camilo A. Franco,^{†,⊥}
Nashaat N. Nassar,^{*,§} and Farid B. Cortés,^{*,†,⊥}

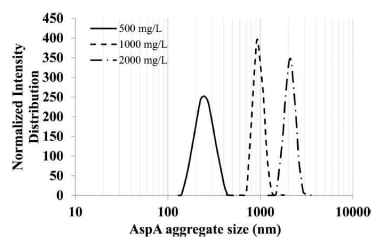


Figure 2. AspA aggregate size distribution in Heptol 60 solutions at different asphaltene initial concentrations of 500, 1000, and 2000 mg/L and 298 K.



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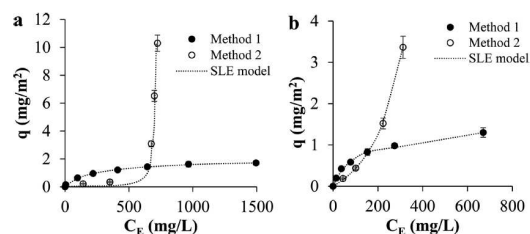


Figure 6. Adsorption isotherms for AspB adsorption onto (a) SS and (b) CM nanoparticles constructed through methods 1 ($M = 10$ g/L) and 2 ($C_i = 1000$ mg/L) at 298 K.

Development of a Population Balance Model to Describe the Influence of Shear and Nanoparticles on the Aggregation and Fragmentation of Asphaltene Aggregates

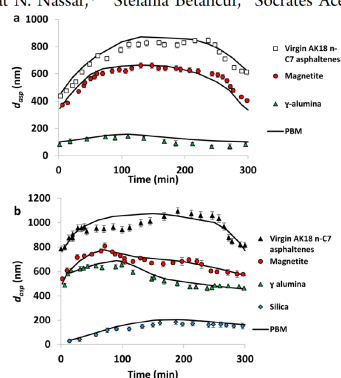
 Nashaat N. Nassar,^{*,†} Stefania Betancur,^{*} Sócrates Acevedo,[§] Camilo A. Franco,[‡] and Farid B. Cortés^{*,†}


Figure 5. Kinetics of asphaltenes aggregation-fragmentation in the presence of nanoparticles for (a) heptol 20 and (b) heptol 40 at 293 K. The symbols are experimental data, and the solid lines are from the PBM model (see eq 3).

$$\frac{dn_i}{dt} = \frac{1}{2} \sum_{j+k=i} \alpha \beta_{jk}(V_j, V_k) n_j n_k - n_i \sum_{k=1}^{n_{\max}} \alpha \beta_{ik}(V_i, V_k) n_k - B_i n_i + \sum_{j=i+1}^{n_{\max}} \gamma_{ij} B_j n_j - \frac{dq}{dt} \quad (3)$$

where n_i is the number concentration of aggregates with size i that contains i primary particles and $n_{\max}$ is the maximum size of the particles that will form fragments of size i before fragmentation. In eq 3 from right to left, the first term defines the adsorption kinetics on the nanoparticle, the second and fifth terms define the formation of i -sized particles, and the third and fourth terms account for the disappearance of particles of size i . β_{jk} is the collision frequency between particles of volume V_j and V_k due to Brownian motion and fluid shear, as expressed in eq 4:^{16,76,77}

$$B_{jk} = \frac{2}{3} \frac{K_B T}{\mu} \left(\frac{d_i - d_j}{d_i d_j} \right)^2 + \frac{G}{6} (d_i + d_j)^3 \quad (4)$$



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Nanoparticles for Inhibition of Asphaltenes Damage: Adsorption Study and Displacement Test on Porous Media

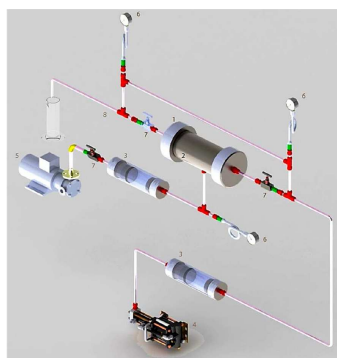
 Camilo A. Franco,[†] Nashaat N. Nassar,^{‡,§} Marco A. Ruiz,[†] Pedro Pereira-Almao,[‡] and Farid B. Cortés^{*,†}


Figure 2. Schematic representation of the experimental setup. Legend: (1) the core holder, (2) the sand packed bed, (3) the displacement cylinder, (4) the displacement positive pump, (5) the mineral oil pump, (6) the pressure transducers, (7) the valves, and (8) sample output.

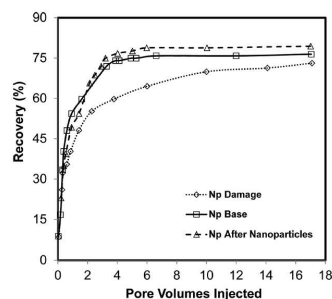
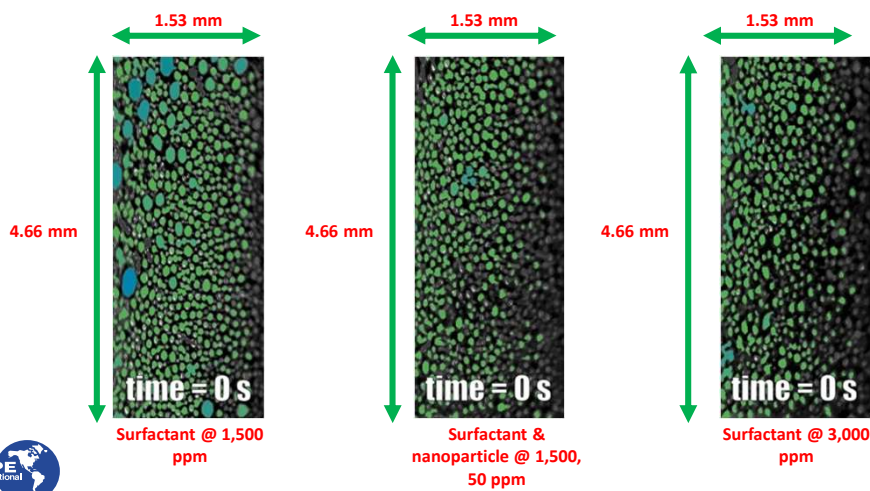


Figure 5. Recovery curves for (1) the base system; (2) the system after nanoparticle injection (where 0.5 PV of nanofluids was injected simultaneously with crude oil, followed by injection of 0.5 PV of n -heptane); and (3) the damaged system (where 0.5 PV of n -heptane was injected without the presence of nanoparticles to generate damage). Other experimental conditions include porosity, 33%; pressure, 6.9 MPa; and temperature, 323 K.



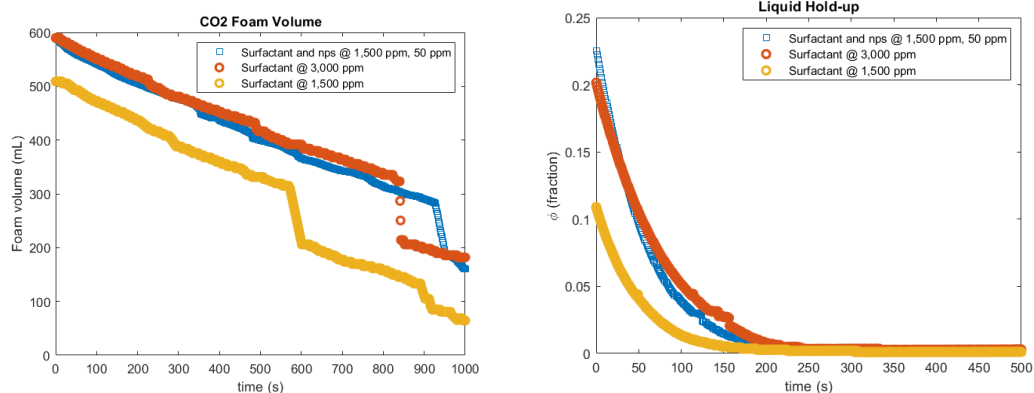
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Foamability and Foam Stability for CO₂-EOR



Unpublished work
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Foamability and Foam Stability for CO₂-EOR



Unpublished work
40

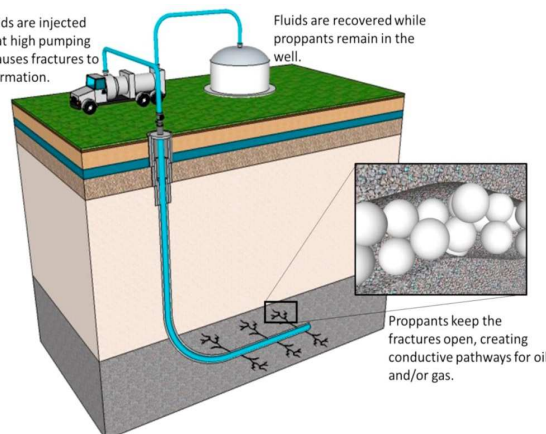
Hydraulic Fracturing



- The high flow rates (>100bbl/min) and high pressure in hydraulic fracturing results in high energy consumption and pumping power
- To mitigate these concerns, dilute concentrations of polymers (friction reducers) reduce the energy consumption, and pumping power in hydraulic fracturing by up to 80%



Fracturing fluids are injected into the well at high pumping rates which causes fractures to form in the formation.

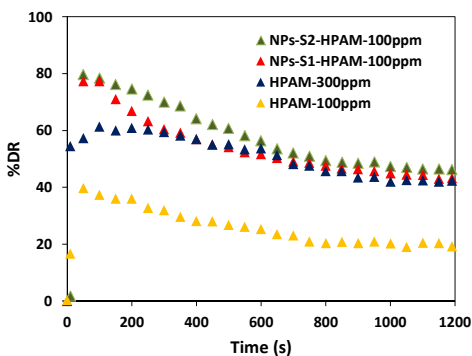


Schematic of hydraulic fracturing¹

¹ Polymers for proppants used in hydraulic fracturing, Pangilinan et al (2016); copyright © 2016 Elsevier B.V

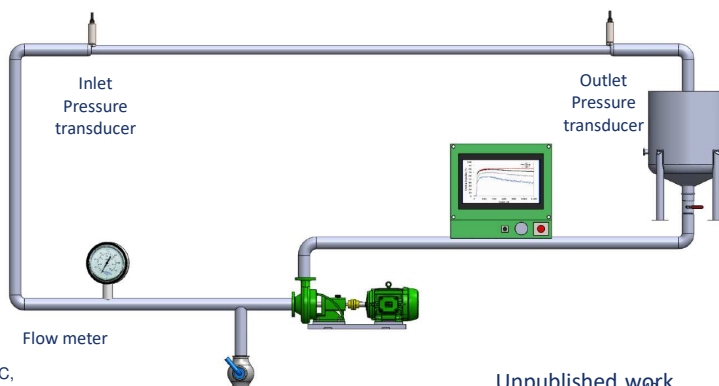
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Drag Reduction



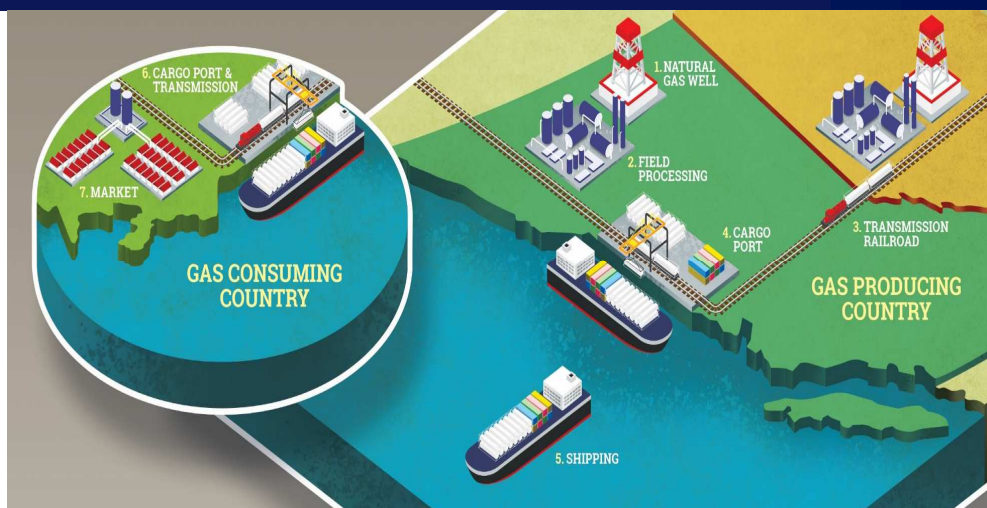
* All flow loop experiments were performed at ~25°C, 80L/min (Re=~105538), and a 0.709" ID pipe

$$FR\% = \left(\frac{f_0 - f_1}{f_0} \right) \times 100 = \left(\frac{\Delta P_0 - \Delta P_1}{\Delta P_0} \right) \times 100$$



Unpublished work

Small Scale LNG Value Chain

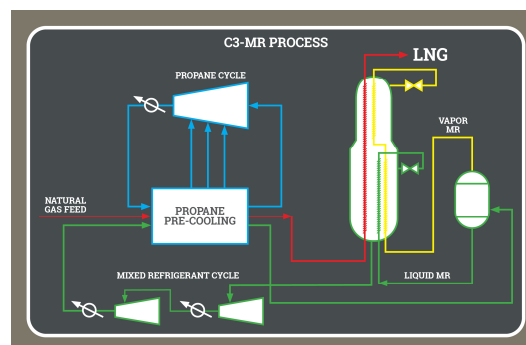
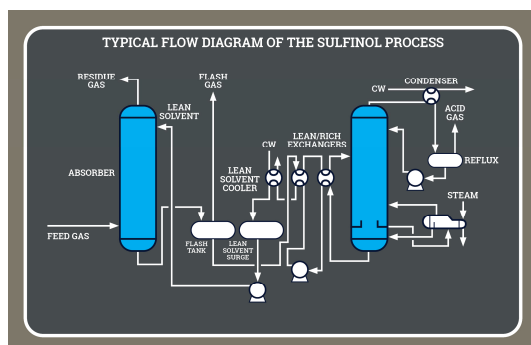


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LNG Production Unit

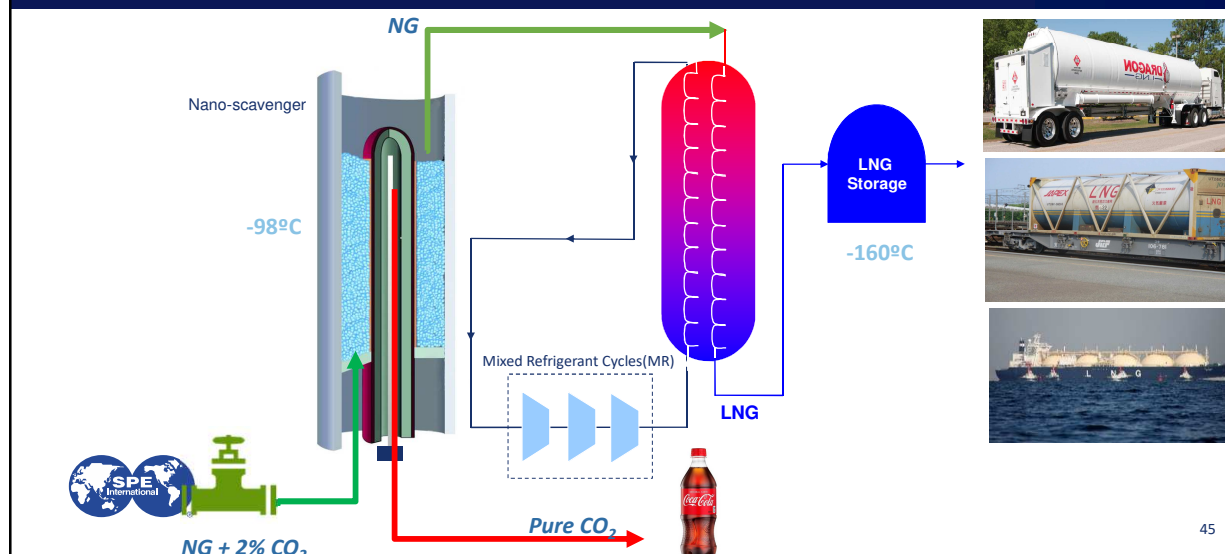


- Any LNG production plant comprised two main sections;
 - Natural Gas Purification
 - Natural Gas Liquefaction



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NG to LNG

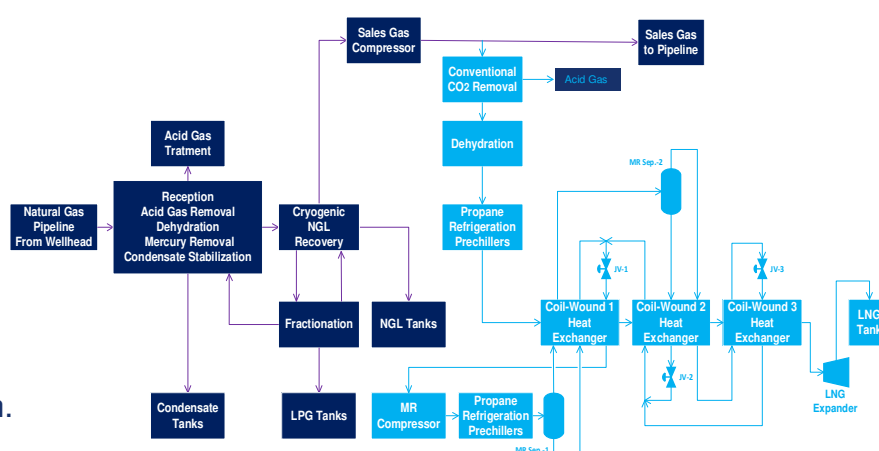


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Conventional Technology – Non-Integrated LNG Production Unit



- The blue process blocks are representation of a conventional LNG production, classical Amine Treating and Dehydration process in purification section and C3-MR process in liquefaction section.

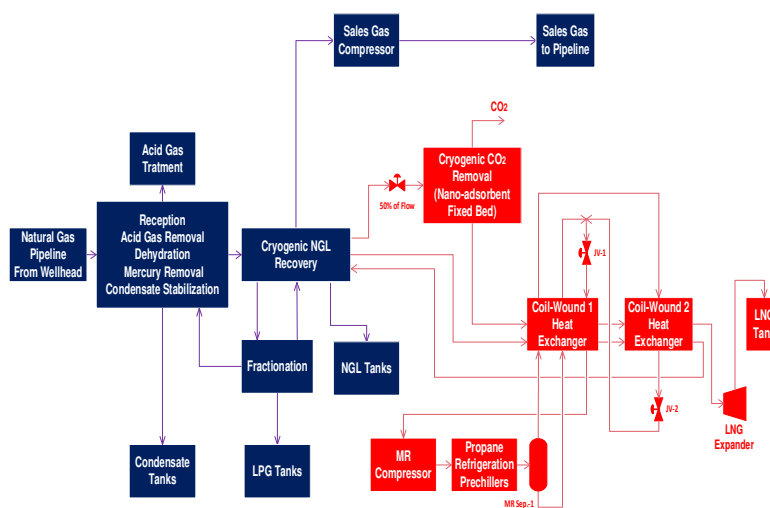


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Split Flow Integrated LNG Production Unit (SFI-LNG)

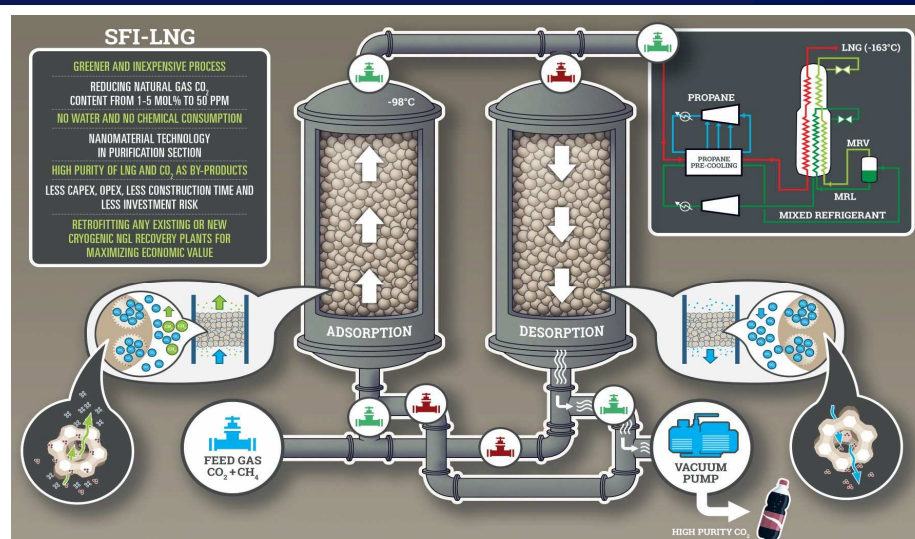


- Red process boxes represent the SFI-LNG process, a new Cryogenic CO₂ Removal process in purification section and Semi-C3-MR process in liquefaction section.



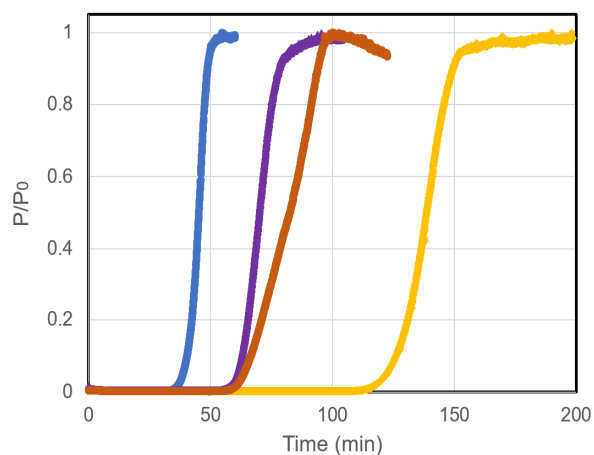
USA Patent, No. 62/636,385 (Pending) 7

SFI-LNG Cryogenic CO₂ Removal

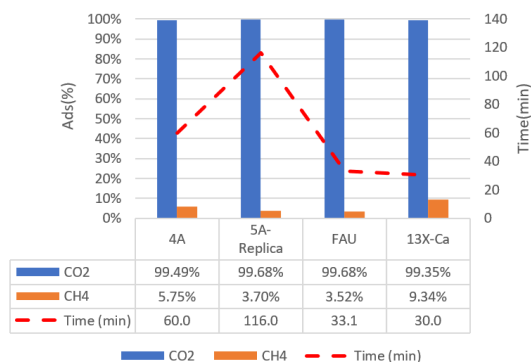


48

Results – Lead Adsorbent



— FAU CO₂ Adsorption at Low Pressure - (95mol%) CH₄+(5 mol%) CO₂
 — SA CO₂ Adsorption at Low Pressure - (95mol%) CH₄+(5 mol%) CO₂ (Replica)
 — 4A CO₂ Adsorption at Low Pressure - (95mol%) CH₄+(5 mol%) CO₂
 — 13X-Ca CO₂ Adsorption at Low Pressure - (95mol%) CH₄+(5 mol%) CO₂ (Replica)

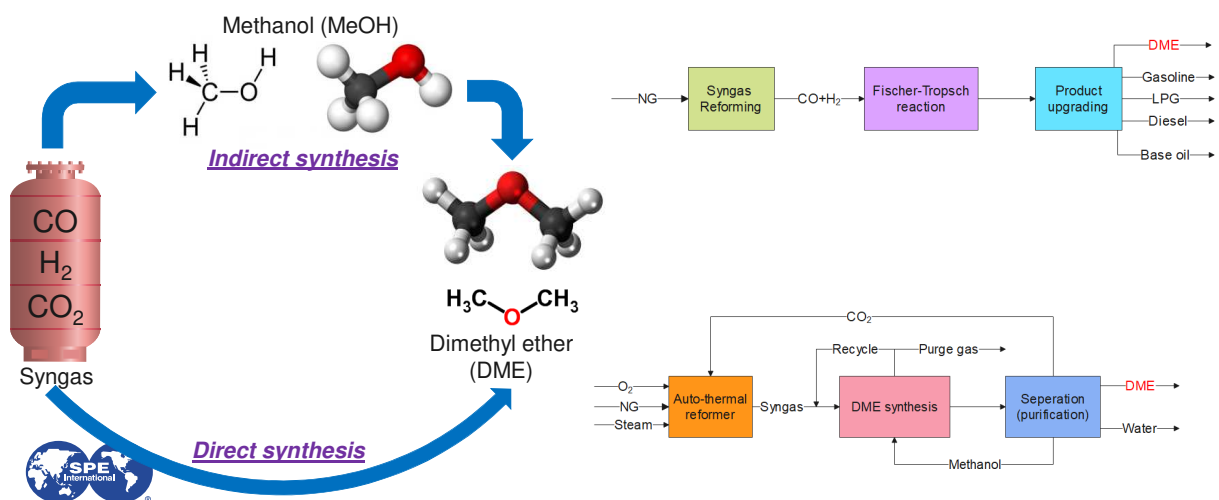


Adsorption % at break point on 4A, 5A, FAU, 13X-Ca at Low-Pressure and High-Concentration

Unpublished work

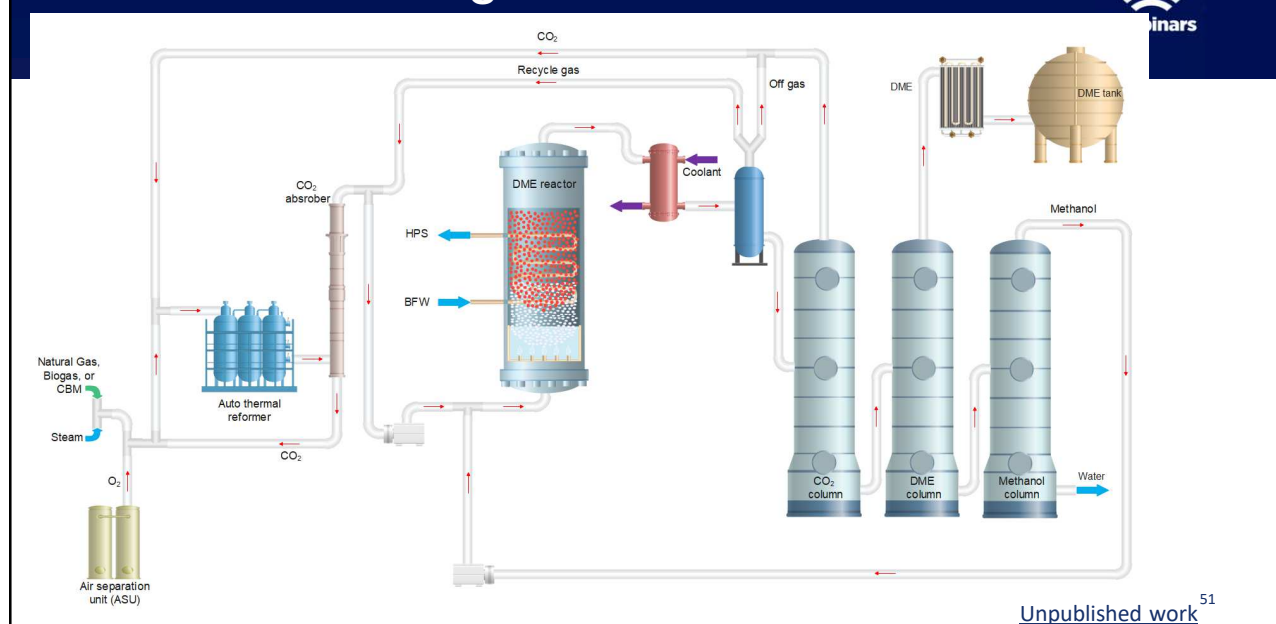
51

NG to DME

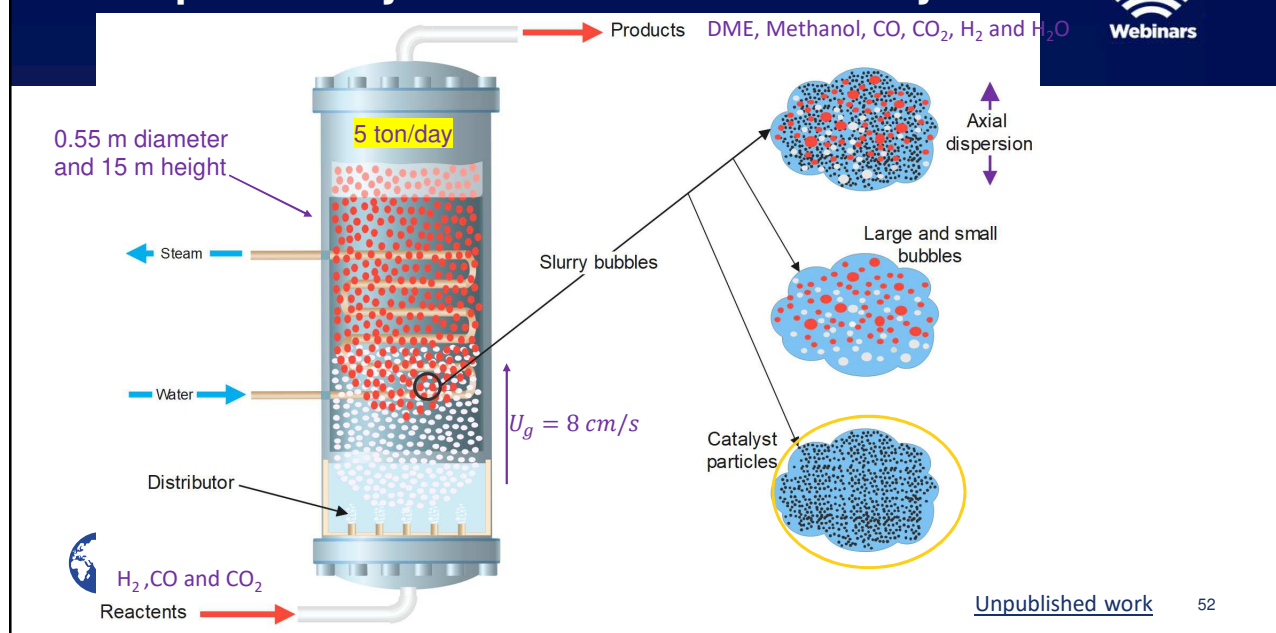


50

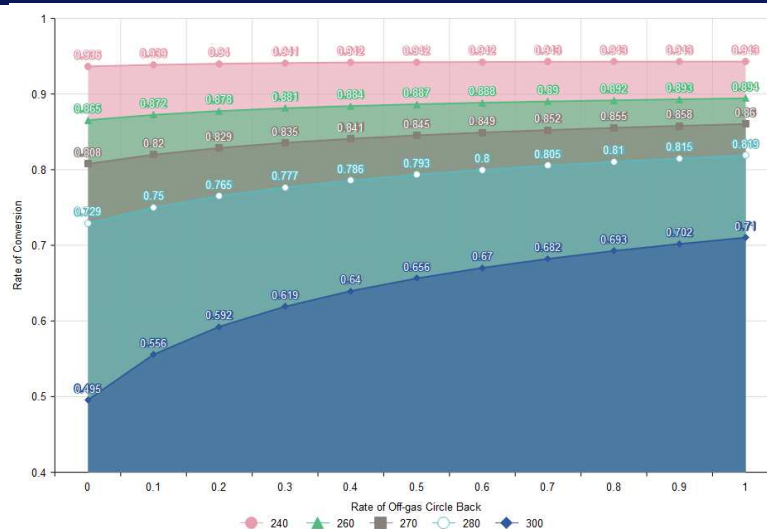
Process Flow Diagram – 5 metric ton/d DME



Concept of slurry reactor for direct DME synthesis

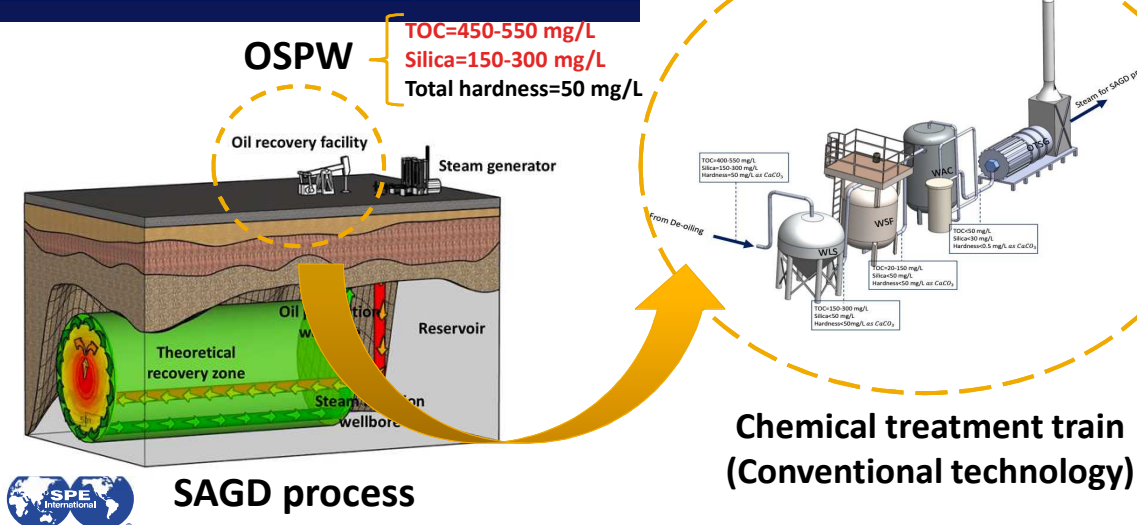


Rate of Conversion of CO at 50bar



Unpublished work 53

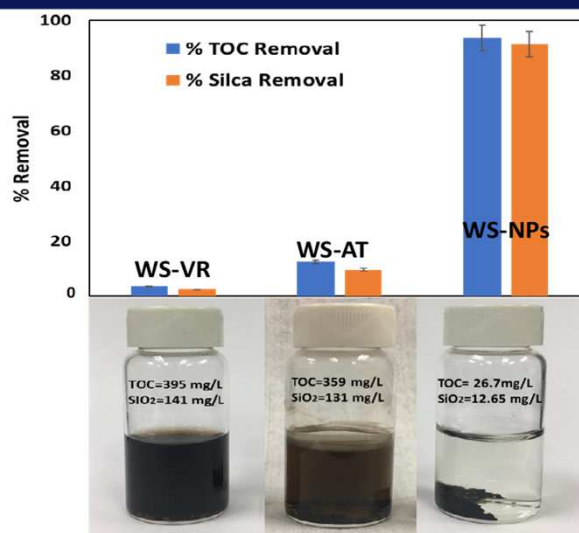
SAGD Produced Water Treatment



Hethnawi et al (2021). Journal of Water Process Engineering, 43, 102016.

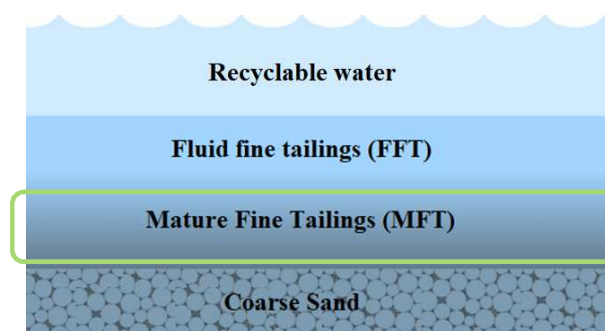
54

SAGD produced water Treatment



Patent No PCT/CA2021/050255 (Pending)
55

Oil Sands Tailings



- Tailings ponds currently cover over 220 km² of land in Alberta.
- Tailings contain toxic materials such as naphthenic acids, phenolic compounds and ammonia.

Mature Fine Tailing (MFT):

- Water: ~ 60%
- Solid content: 35 - 40%
- Residual bitumen: 1- 3%



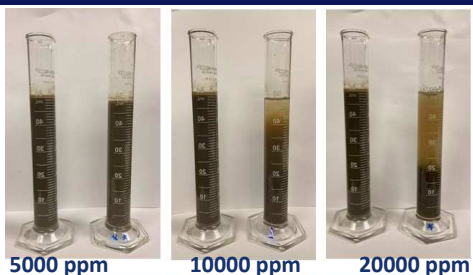
Image courtesy: <https://www.oilsandsmagazine.com>

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Enhanced Settling and Dewatering of MFT



Commercially anionic PAM
(CAP)

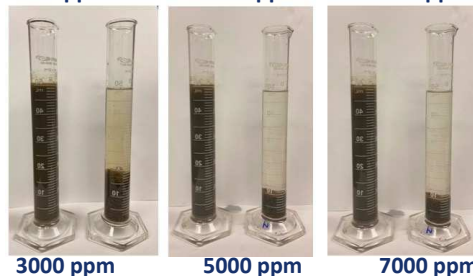


5000 ppm

10000 ppm

20000 ppm

Nanoflocculant



3000 ppm

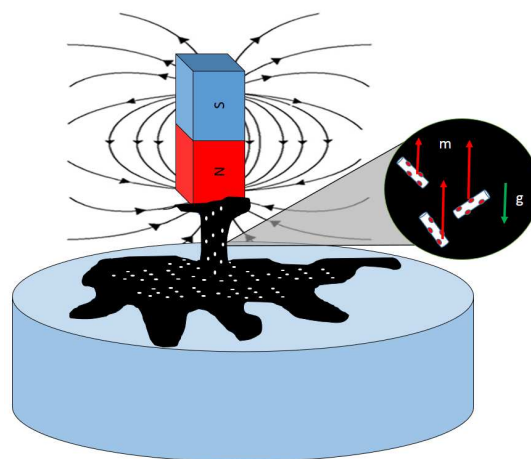
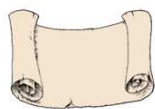
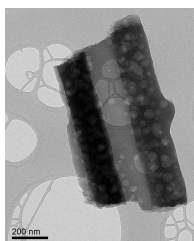
5000 ppm

7000 ppm

Patent No. 63/231,083 (Pending)

57

Nano-scrolls: Oil spill cleanup



Material	Oil absorption capacity (own weight ratio g/g)
Magnetic particles 100% (Bulk)	15
Magnetic nanoparticles 100% (5 nm)	20
Magnetic hydrophobic scrolls	53
• Nano-Magnetite 5%	
• Hydrophobic scrolls 95%	

ACS Appl. Nano Mater. 2018, 1, 4491–4501
Ind. Eng. Chem. Res. 2018, 57, 13065–13076

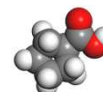
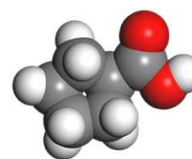
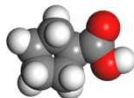
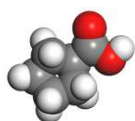
58

β -CD Grafted nanopyroxenes for industrial wastewater treatment

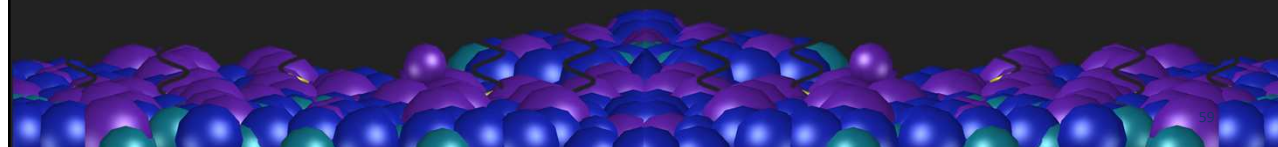


Oil & Gas Industry

Pharmaceuticals Industry



ACS Appl. Mater. Interfaces 2017, 9, 42393–42407



NanoSoln Inc.: Increasing process efficiency for industrial wastewater treatment.



NanoSoln Inc



NanoFlocculant

Key Benefits:

1. >50% Chemical Savings
2. >35% Cost Savings
3. <30 mins for particle settling & dewatering vs 1-2 days
4. Environmentally Friendly

NanoSorbent

Key Benefits:

1. >60% Chemical Savings
2. >57% Cost Savings
3. Area of Implementation:
 - Textile wastewater
 - Tanneries wastewater
 - Carpet Manufacturer

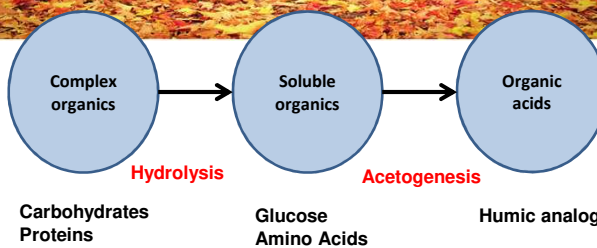
NanoFilters

Key Benefits:

1. >50% Chemical Savings
2. >35% Cost Savings
3. Area of Implementation:
 - O&G: Disposal Water
 - O&G: Produced Water
 - Mining: Lithium Brine



Oxy-Cracking: A new technique for converting waste hydrocarbon into valuable product



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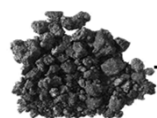
Oxy-Cracking a new technique for converting waste hydrocarbon into valuable product



- The global production is 150 million metric tons per annum.
- 70% in North America alone.
- 100 MT was stockpiled in Alberta 2016.



Minerals Recovery



Solid phase

+

O₂

Oxy-cracked products

Liquid phase



Humic Acids
(Fertilizer)

- Increased Nutrient Uptake
- Decreased Toxins
- Increased Water Retention



USA Patent No. S 10,883,060 B2
React. Chem. Eng., 2017, 703-719
Fuel, 2018, 215, 865-878

Carbon OxyTech Inc.

A scientific-based technology that provides highly effective and sustainable solution to convert carbon-based materials into valuable products.

Dedicated to providing more convenient, flexible, and cost-effective solution in the fields of agriculture and the environment.



Carbon OxyTech



Take-home message



- Nanoparticle is an enabling technology 🤝 not a stand alone one
- Success = Nanomaterials + Process integration 🖱️ = 🧬 🤝 👤♀
- Naturally-derived nanomaterials can be the best choice for oncethrough process ✓
- Process modeling and scale up provide great ideas 💡 for field testing and commercialization
- Process and cost limits exist
- Nanoparticles are 🔑 for process improvement



65

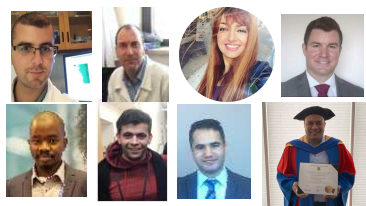
Acknowledgements



Grad students



RA/PDFs



HQPs

