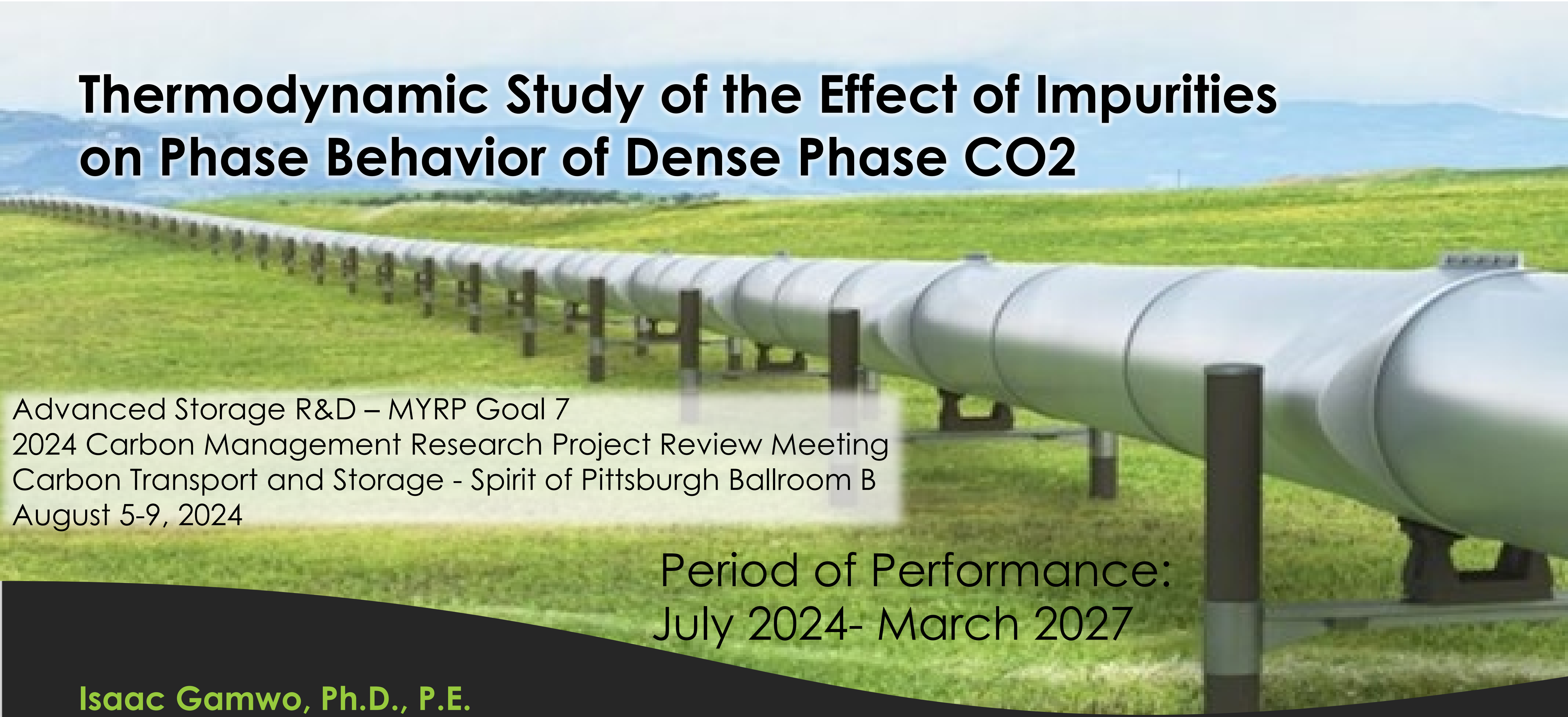


Thermodynamic Study of the Effect of Impurities on Phase Behavior of Dense Phase CO2

Advanced Storage R&D – MYRP Goal 7
2024 Carbon Management Research Project Review Meeting
Carbon Transport and Storage - Spirit of Pittsburgh Ballroom B
August 5-9, 2024

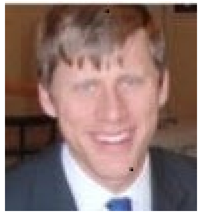
Period of Performance:
July 2024- March 2027

Isaac Gamwo, Ph.D., P.E.
U.S. Department of Energy
National Energy Technology Laboratory - PGH
gamwo@netl.doe.gov

CO2 Transport Research Team (2024)

Dr. Gamwo

Dr. Tapriyal



Dr. Burgess

Dr. Morsi

Dr. Enick

Dr. Baled

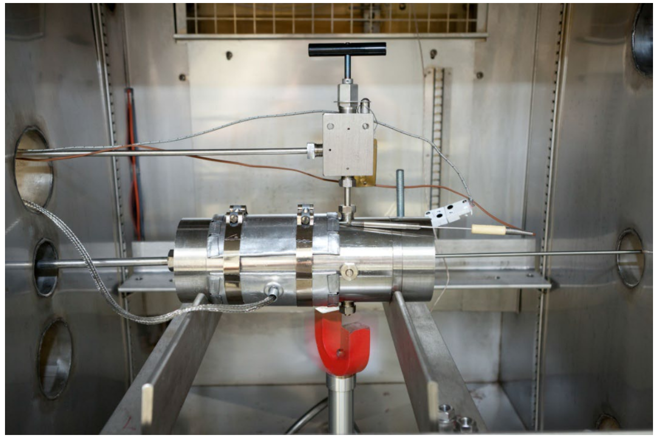
Collaborations

ExxonMobil

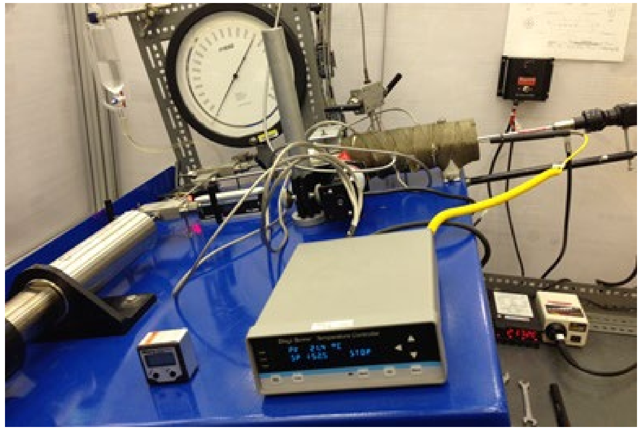
DNV

NETL's Experimental Capabilities

- **Densimeter: windowed HPHT view cell** rated to 40,000 psi (275 MPa) and 500°F (260°C).
  - ➢ System was used to generate PVT data for live crude oil
  - ➢ System can be used to generate to PVT data for CO_2 with various impurities (N_2, O_2, H_2,CH_4, SO_2, H_2S, NO_x, H_2O, etc.).
- **Viscometer: Windowed HPHT rolling-ball viscometer** rated to 40,000 psi (275 MPa) and 500°F (260°C).
  - ➢ System can be used to measure viscosity of CO_2 in presence of impurities over wide ranges of pressure and temperature conditions.
- **Solubility experimental system** to measure the solubility of scale forming mineral in simulated brine formation.
  - ➢ System can be used to study the influence of impurities on water solubility limits in dense phase/supercritical CO_2.

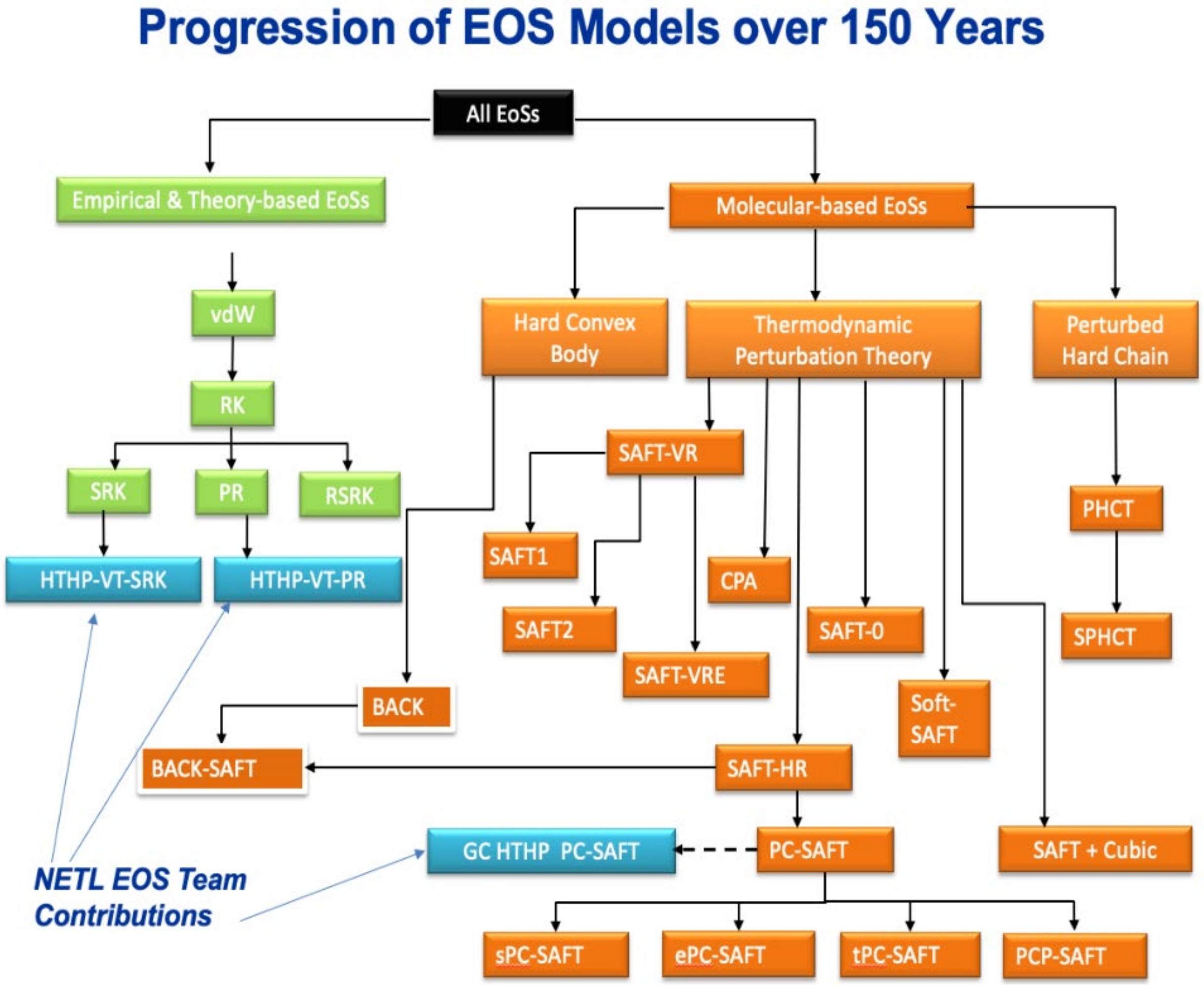


HTHP Densimeter



HTHP Viscometer

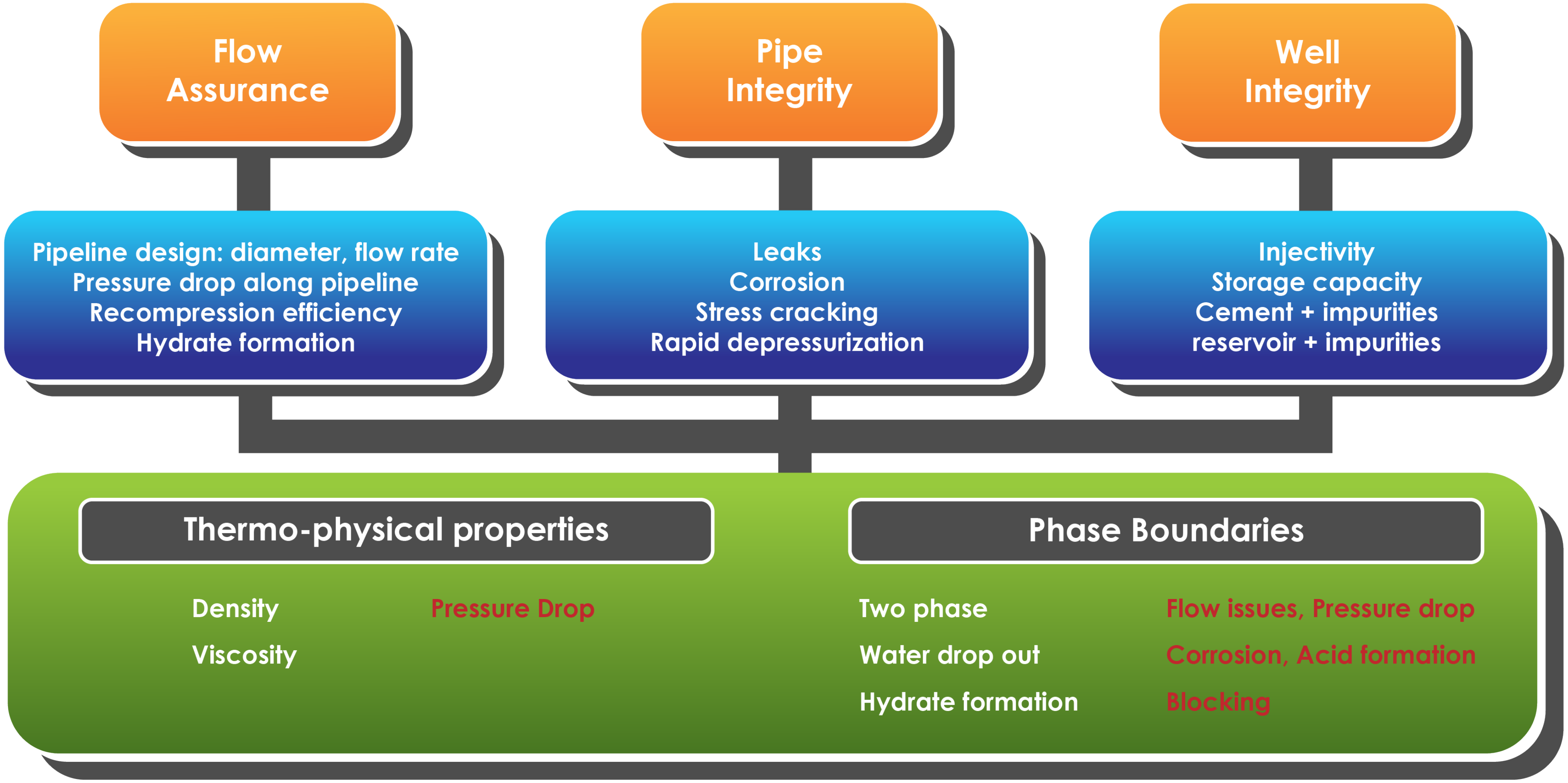
Equations of State Modeling Capabilities – Phase Transitions



Progression of EOS Models over 150 Years

Burgess W., Bamgbade B., Gamwo* I. K., Experimental and Predictive PC-SAFT Modeling Results for Density and Isothermal Compressibility for Two Crude Oil Samples at Elevated Temperatures and Pressures, Fuel, 28, 385, 2018

CO2 Transport Technical challenges*



Flow Assurance

Pipeline design: diameter, flow rate
Pressure drop along pipeline
Recompression efficiency
Hydrate formation

Pipe Integrity

Leaks
Corrosion
Stress cracking
Rapid depressurization

Well Integrity

Injectivity
Storage capacity
Cement + impurities
reservoir + impurities

Thermo-physical properties

Density	Pressure Drop
Viscosity	

Phase Boundaries

Two phase	Flow issues, Pressure drop
Water drop out	Corrosion, Acid formation
Hydrate formation	Blocking

*DOE/FECM 2023 Workshop Findings - Workshop on Applied Research for CO2 Transport

Overall Research Plan

Thermodynamic and Transport challenges of CO2 streams with impurities.

- **Goals:** accelerate understanding/implementation of impure CO2 transport technologies enhance their efficiency, safety, and environmental sustainability.

- **Approach:**

- Review literature- Technical challenges
- Identify CO2 sources & Compositions
- Construct P-T and P-T-x diagrams
- Design experiments and models
- Risk mitigations: CO2 dispersion models; addition of tracers
- Share information with corrosion group
- Implement findings

Examples of CO_2 sources, facilities and main components - ~78% Coal & Gas

Industry	Number of Facilities	Share of 45Q-Eligible Facility Emissions	CO_2	Biogenic CO_2^*	Methane	Nitrous Oxide
Coal Power Plant	308	53.80%	1,269.6	0.3	3.0	6.2
Gas Power Plant	571	23.80%	565.4	0.7	0.4	0.4
Refineries	78	6.90%	163.3		0.6	0.4
Cement	135	3.70%	88.8	0.9	0.1	0.2
Hydrogen	57	2.70%	64.3		0.1	0.1
Steel	31	2.30%	54		0.2	
Ethanol	173	1.30%	31	9.0	0.1	0.1
Ammonia	21	1.20%	25.1	0.0	0.0	4.1
Petrochemicals	30	1.10%	26	0.1	0.4	0.1
Metals, Minerals & Other	37	0.90%	19.5		0.4	
Gas Processing	40	0.90%	19.9		0.7	
Chemicals	16	0.80%	8.7		0.0	10.4
Pulp & Paper	18	0.40%	7.8	25.5	2.4	0.1
Waste	2	0.10%	0.8	1.2	0.6	
Grand Total	1,517	100%	2,344.20	29.3	9.1	22.1

All emissions are in million metric tons [1]

- **Biogenic (CO_2) is that released due to combustion or decomposition of organic material, that is biomass and its derivatives.**

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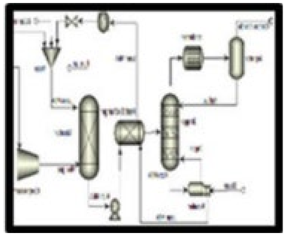
[1] https://www.betterenergy.org/wp-content/uploads/2020/06/GPI_RegionalCO2Whitepaper.pdf

Expected Impurities from different CO_2 capture technologies [4]

Impurities	Post-Combustion	Oxy-fuel Combustion	Pre-Combustion
CO_2	> 99%	> 90%	> 95.6%
O_2	< 0.1%	< 3%	trace
H_2O	0.14%	0.14%	0.14%
H_2	trace	trace	< 3%
H_2S	trace	trace	< 3.4%
CH_4	< 0.01%	-	< 0.035%
N_2	< 0.8%	< 1.4%	balance
Ar	trace	< 5%	< 0.05%
SOx	< 0.001%	< 0.25%	-
NOx	< 0.001%	< 0.25%	-

[4] European CCS Demonstration Project Network. A public report outlining the progress, lessons learnt and details of the European CCS Demonstration Project Network 2012.

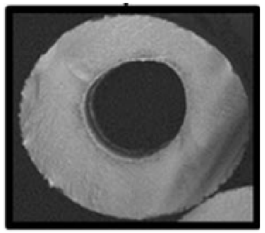
CO_2 capture technologies



Absorption

- Amine-based
- Alkaline solutions
- Ionic liquids
- Ammonia

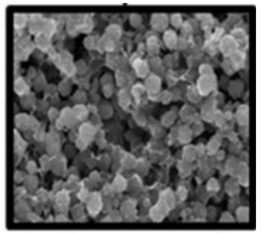
Commercial scale: Amine-based, ammonia and alkaline solutions have all been implemented at commercial level
Lab scale: ILs are implemented at lab scale so far but are close to industrial scale



Membrane

- Inorganic
- Polymeric
- Facilitated-transport
- Mixed-matrix

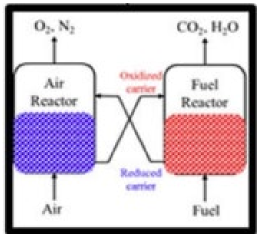
Commercial scale: Polymeric membranes have been implemented at commercial level
Lab scale: Inorganic, FTMs, and MMs have been investigated at lab scale



Adsorption

- Zeolites
- Carbon-based
- MOFs/PPNs
- Metal oxides
- Supported amines

Commercial scale: Not implemented yet
Lab scale: Most of current CO_2 adsorption have been investigated at lab scale



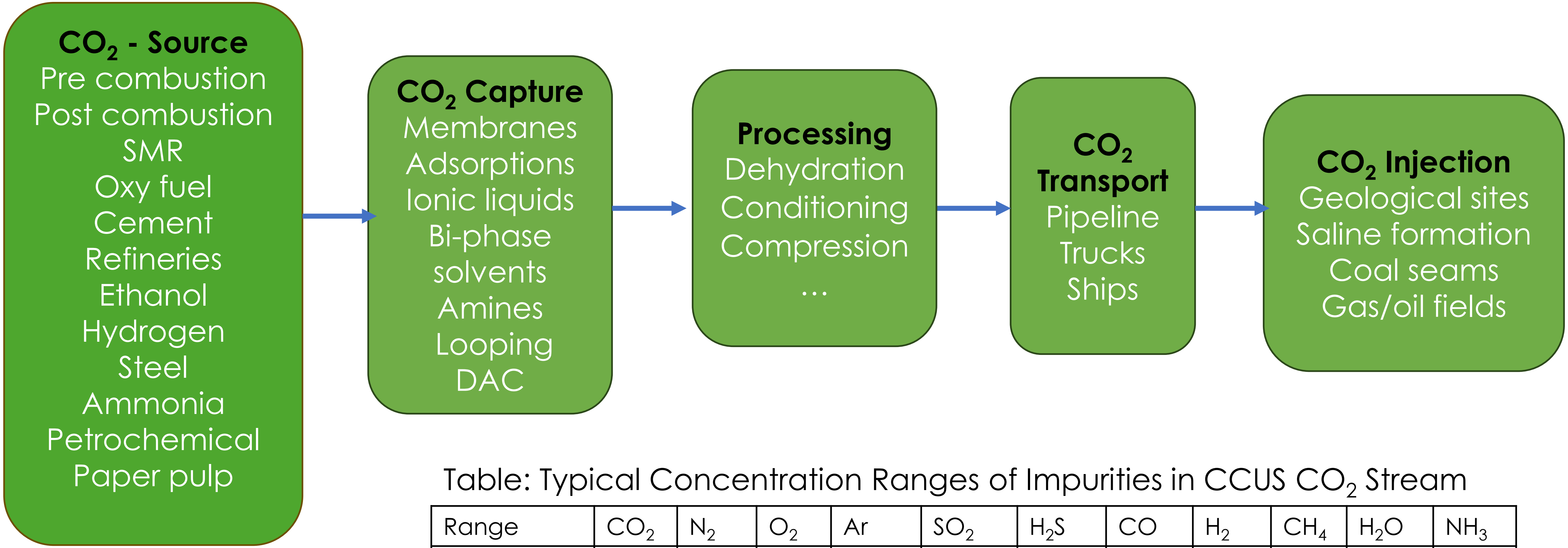
Chemical Looping

- Combustion
- Reforming

Commercial scale: Not implemented yet, but there are a few pilot-scale demonstrations
Lab scale: Most of current chemical looping have been investigated at lab scale

2. Carbon Capture and Utilization Update, Energy Technol. 2017, 5, 1 – 17

Where is CO_2 transport in the CCTS system?



CO_2 - Source
Pre combustion
Post combustion
SMR
Oxy fuel
Cement
Refineries
Ethanol
Hydrogen
Steel
Ammonia
Petrochemical
Paper pulp

CO_2 Capture
Membranes
Adsorptions
Ionic liquids
Bi-phase solvents
Amines
Looping
DAC

Processing
Dehydration
Conditioning
Compression
…

CO_2 Transport
Pipeline
Trucks
Ships

CO_2 Injection
Geological sites
Saline formation
Coal seams
Gas/oil fields

Table: Typical Concentration Ranges of Impurities in CCUS CO_2 Stream

Range	CO_2	N_2	O_2	Ar	SO_2	H_2S	CO	H_2	CH_4	H_2O	NH_3
Min (mol %)	75	0.02	0.04	0.005	$<10^{-3}$	<0.01	$<10^{-3}$	0.06	0.7	0.005	$<10^{-3}$
Max (mol %)	99.95	10	5	3.5	1.5	1.5	0.2	4	4	6.5	3

Quality specifications for CO_2 pipelines

01 **Product**
Contain at least 95 mol% of CO_2

02 **Water**
Contain no free water, and not more than thirty (30) pounds of water per MMcf in the vapor phase.

03 **Hydrogen Sulfide**
Contain no more than 20 ppmv of H_2S.

04 **Total Sulfur**
Contain no more than 35 ppm.

05 **Nitrogen**
Contain no more than 4 mol%..

06 **Hydrocarbons**
Contain no more than 5% mol% and Dew point no more than -20 °F.

07 **Oxygen**
Contain no more than 10 ppm.

08 **Other**
Contain no liquid glycol or no more than 0.3 gallons of glycol per MMcf.

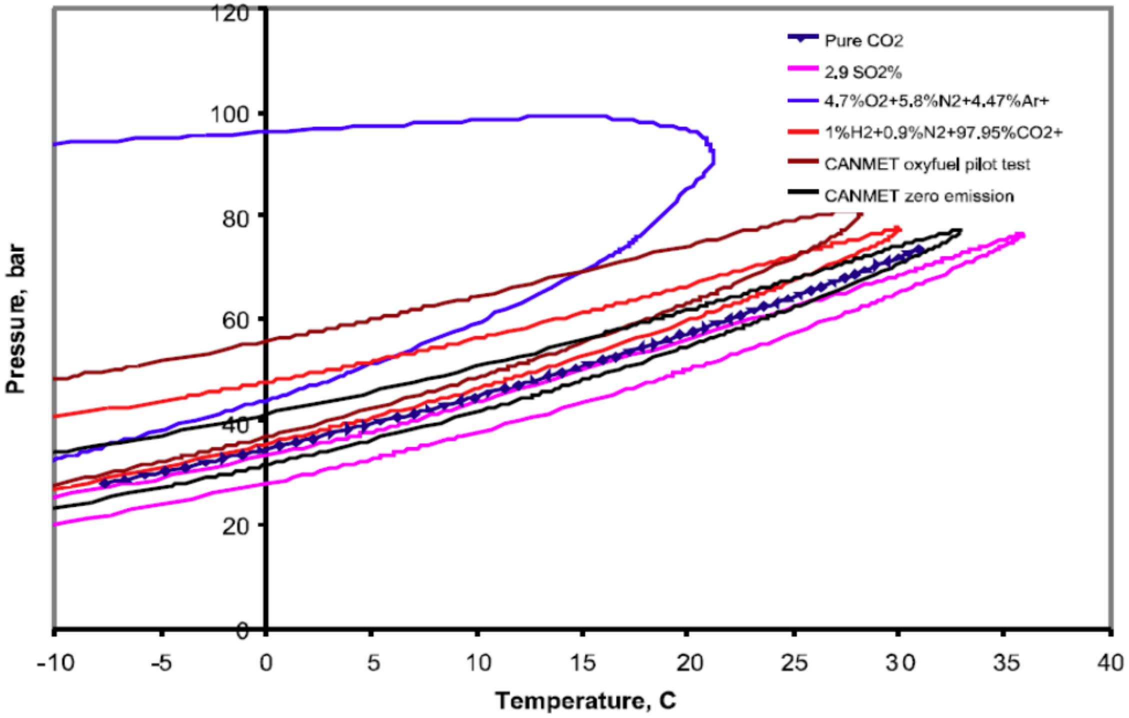
09 **Temperature**
Shall not exceed 120 °F.

CO_2 pipeline conditions (Received from ExxonMobil)

Operation condition: temperature 4 - 50°C, pressure: 70 - 100 bar

Element	Range	Note (potential reaction)
H_2O	10-3000 ppmv	Interaction with SOx / NOx / H_2S / O_2 that influence phase behavior and trigger water drop out
SOx	0 – 500 ppmv	Potential formation of strong acid H_2SO_4 (sulfuric acid)
NOx	0 – 500 ppmv	Potential formation of strong acid HNO_3 (nitric acid)
H_2S	0 – 500 ppmv	Sour service cracking
CO	0 – 3000 ppmv	Stress corrosion cracking (SCC)
H_2	0 – 3 vol.%	Embrittlement
O_2	0 – 500 ppmv	Harmful effect with CO, SOx, H_2S
Glycol	TBD	

Phase envelopes for pure CO_2 and CO_2 mixtures [7]



The presence of impurities alters the critical pressure of the CO_2 stream due to the differences in the vapor pressure of various constituent species, and thus affects the repressurization distance along the CO_2 transport pipeline. To alleviate the impact of impurities on the possibility of two-phase flow, the operating pressure of the CO_2 transport pipeline needs to be increased and suitable points of repressurization need to be identified

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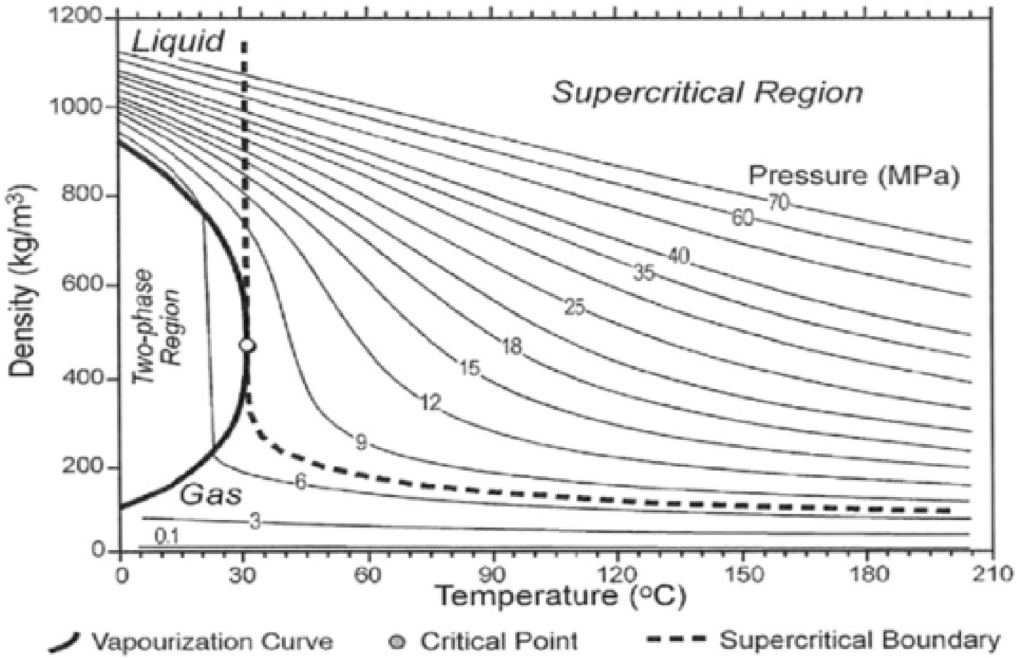
7. Onyebuchi, V.E., Kolios, A., Hanak, D.P., Biliyok, C. and Manovic, V., 2018. A systematic review of key challenges of CO_2 transport via pipelines. *Renewable and Sustainable Energy Reviews*, *81*, pp.2563-2583.

Variation of CO_2 density with temperature [7]



A small alteration in the working conditions close to the CO_2 critical point can result in a significant change in CO_2 density. For example, the density will double for a decrease of about 10 °C from the critical temperature. This has both technical and cost implications on the hydraulic system of CCS pipeline systems. To keep the CO_2 stream at the supercritical phase throughout the CO2transport pipeline, a pump-based system is recommended for flow repressurization

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[7] Onyebuchi, V.E., Kolios, A., Hanak, D.P., Biliyok, C. and Manovic, V., 2018. A systematic review of key challenges of CO_2 transport via pipelines. *Renewable and Sustainable Energy Reviews*, *81*, pp.2563-2583.

Effect of impurities and temperature on CO_2 stream viscosity at 100 bar [7]

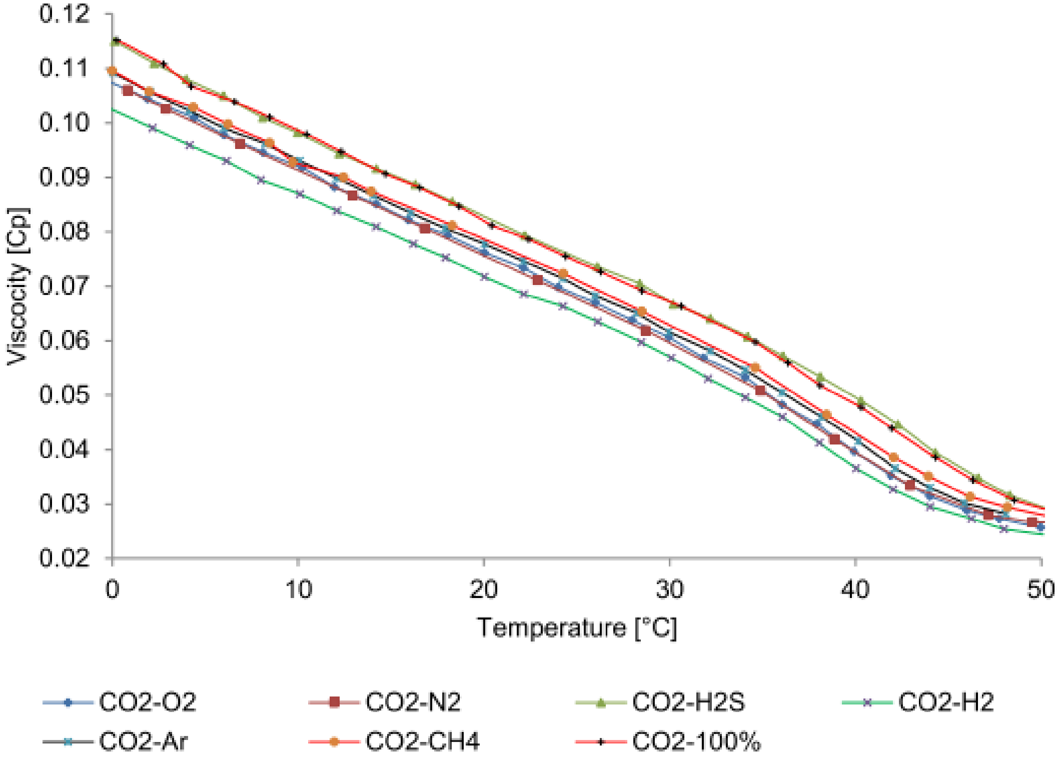

Figure shows that the viscosity of pure CO_2 decreases with increase in temperature and reduces further with the presence of impurities. Importantly, the reduction in CO_2 viscosity increases the efficiency of transport along the pipeline, as the pressure losses throughout the pipeline are reduced

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7. Onyebuchi, V.E., Kolios, A., Hanak, D.P., Biliyok, C. and Manovic, V., 2018. A systematic review of key challenges of CO_2 transport via pipelines. *Renewable and Sustainable Energy Reviews*, *81*, pp.2563-2583.

Preliminary thermodynamic results: CO_2 stream from Longview post-combustion power plant

Longview power plant post-combustion CO_2 capture and sequestration

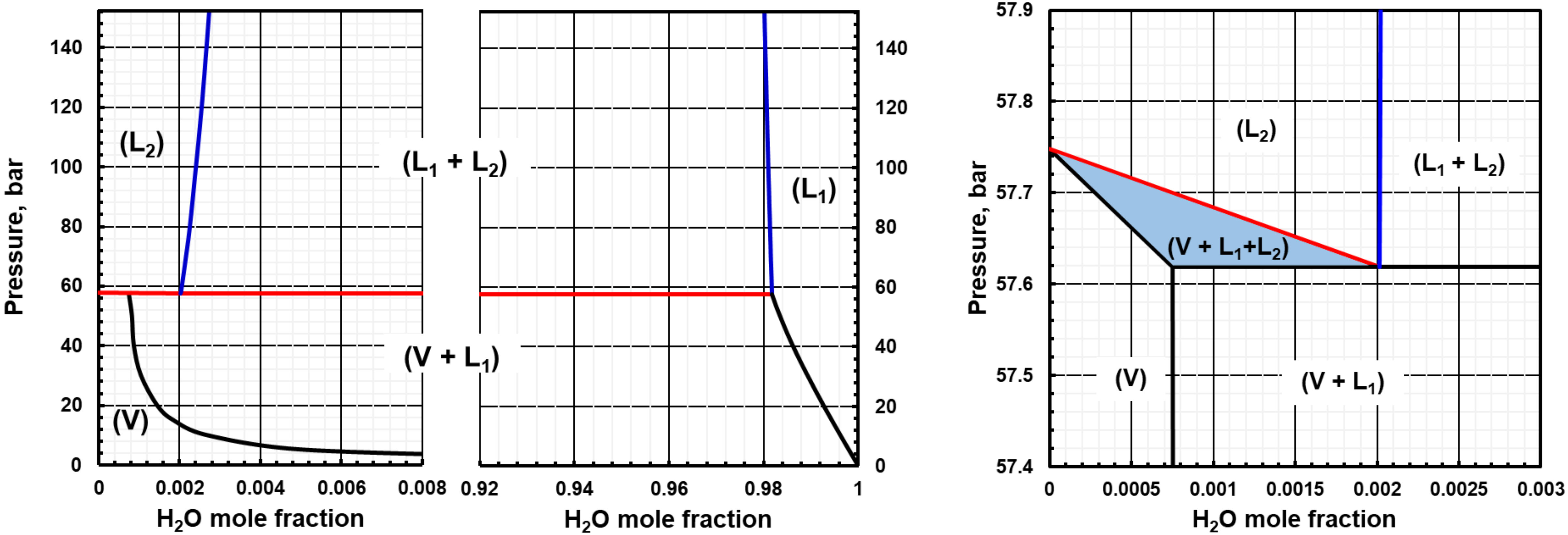
Flue gas from the Longview power plant		
Temperature, °F	125	
Pressure, bar	1	
Components	**mol %**	**mass %**
CO_2	12.022	17.668
O_2	4.79	5.12
N_2	79.198	74.086
H_2O	3.00	1.80
Ar	0.98	1.31
CO	0.003	0.003
SO_2	0.003	0.007
NO_2	0.004	0.005

CO_2 stream captured from the Longview power plant contains 500 ppm H_2O

Conditions and composition		
Temperature, °C	20	
Pressure, bar	152.7	
Components	**mol%**	**mass%**
CO_2	99.877	99.95
H_2O	0.123	0.05

CO_2 stream phase diagram at 20 °C

Predicted using PC-SAFT Equation of State (EOS) in Aspen Plus v12.1



At H_2O mole fraction 0.0012, the pressure in the pipeline should be maintained above 57.67 bar to avoid the formation of three-phase (V +L1 + L2) flow

Thermodynamic to address some of these issues

- Literature review focused on the challenges of the transport of CO2 streams and impurities, chemical compositions of impure CO2 streams, speciation of impure CO2 streams, and the thermodynamic phase behavior of impure CO2 streams.

- Identify thermodynamic experimental and modeling research challenges to accelerate the implementation of impure CO2 transport technologies.

- Develop preliminary experimental design and modeling activities to fill literature gaps on effects of impure CO2 transport streams.

Disclaimer and Acknowledgement

- **Disclaimer:** This project was funded by the United States Department of Energy, National Energy Technology Laboratory, in part, through a site support contract. Neither the United States Government nor any agency thereof, nor any of their employees, nor the support contractor, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

- **Acknowledgement:** This work was performed in support of the U.S. Department of Energy's (DOE) Office of Fossil Energy and Carbon Management's Advanced Storage R&D Program.

THANK YOU FOR YOUR ATTENTION

QUESTIONS?

Isaac.gamwo@netl.doe.gov