Theoretical and Experimental Evaluation of Natural Gas Properties & Environmental Issues

Gas and Fuels Research Initiative
Mert Atilhan
Qatar University & TAMUQ
March 26, 2014
Houston, TX
About Qatar

- Population 2.1 Million (148th) as of July 2013
- GDP (total): ~ $182B – GDP (per capita): ~ $110,000
- 11,500 km² (4500 mi²)
- Capital: Doha
About Qatar

• Ethnicity:
  – Arabs 40%
  – Indian 18%
  – Pakistani 18%
  – Iranian 10%
  – Other 14%
Qatar Economy

- Economy
  - GDP: $ 198.7 Billion (est. 2013)
  - Real growth rate 5.5%
  - 2.5% GDP for education
  - 2% GDP for health
  - Unemployment 0.3%
  - 1.4 M labor force
Qatar Energy

• Oil
  – Crude Oil Reserves: 25.38 billion bbl (no. 12)
  – Petroleum product production: 287,500 bbl/day (no. 44)
  – Petroleum product exports: 210,000 bbl/day (no. 31)

• Natural Gas
  – Production: 133.2 billion cu m (no. 6)
  – Consumption: 19.53 billion cu m (no. 36)
  – Exports: 113.7 (no. 2)
  – Reserves: 25.2 trillion cu m (no. 3 – proven reserves)
Qatar Vision
Qatar Industry

- Recognized as a leader in providing clean fuel to the world, exporting over 77 million ton of LNG annually. (1996 – 2006)

- Portfolio is continuously expanding. LNG, GTL products, petrochemicals, power, aluminum, steel, cement...

- Three large industrial complexes
Research Investments in Qatar

• Research that support Qatar’s vision 2030 and National Priorities.

**National Priorities**

Environmental Sustainability
Reduce Green House Gas Emissions
Climate Change

**Infrastructure**

QF: Head by First Lady/Sheikha Moza
QNRF: 2.5% National Income  ~$4.8 Billion
Qatar Science and Technology Park, QSTP
QU Research Center/ CEDRA Research Center
Qatar University

- Only national state university
- About 21,000 students
- Graduate school
- MS and PHD (first ever PHD program of the country)
Qatar University
Department of Chemical Engineering

Graduates - Chemical Engineering (2008-2013)

Enrolled Statistics (2008-2013) - Chemical Engineering

Since 2006...

Accredited by ABET
Engineering Accreditation Commission

American Institute of Chemical Engineers (AIChE)
Research in ChE Department

- The Department of Chemical Engineering has grown steadily in the recent years. This has resulted in boosting research expertise and the production of high quality research. The research is driven by the needs of the Qatari Industry and is aligned with the vision and aspiration of Qatar’s leadership.
Research Status By Numbers

PEOPLE
- 14 Faculty
- 13 Postdocs
- 10 RAs
- 2 PhDs

FUNDING
- $1.9 M QSTP
- $23.1 M NPRP
- $870 K UREP
- $1.6 M Industry
- Σ (since’07) = $27.6 M

PROJECTS
- 24 NPRP
- 24 UREP
- 12 QU Internal
- 2 Industry Funded
- 1 QSTP
Outline

• PART I
  – Energy outlook and natural gas (brief recap)
  – Natural gas key properties
  – Density
  – Viscosity

• PART II
  – Phase behavior
  – Gas hydrates
  – CO$_2$ Control and mitigation
Energy Outlook
US Natural Gas vs Oil Prices

Energy spot prices
2012 dollars per million Btu

History

2012

Projections

2018

2020

2025

2030

2035

2040

Brent crude oil spot price

Henry Hub spot price

Ratio:

7.1

Oil to gas price ratio:

3.4

Ratio:

3.2

Source: EIA, Annual Energy Outlook 2014 Early Release
Shale gas leads growth in total gas production through 2040 to reach half of US output

Source: EIA, Annual Energy Outlook 2014 Early Release
Shale gas in the US is rapidly increasing as an available source of natural gas. Led by new applications of hydraulic fracturing technology and horizontal drilling, development of new sources of shale gas has offset declines in production from conventional gas reservoirs, and has led to major increases in reserves of US natural gas. Largely due to shale gas discoveries, estimated reserves of natural gas in the US in 2008 were 35% higher than in 2006.
Natural gas consumption growth is driven by electric power, industrial, and transportation use.

U.S. dry gas consumption trillion cubic feet

<table>
<thead>
<tr>
<th>Year</th>
<th>History</th>
<th>Projections</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>8.5</td>
<td>11.0</td>
</tr>
<tr>
<td>2012</td>
<td>9.1</td>
<td>11.2</td>
</tr>
<tr>
<td>2020</td>
<td>2.9</td>
<td>1.7</td>
</tr>
<tr>
<td>2025</td>
<td>4.2</td>
<td>3.6</td>
</tr>
<tr>
<td>2030</td>
<td>4.2</td>
<td>4.1</td>
</tr>
<tr>
<td>2035</td>
<td>4.2</td>
<td>4.1</td>
</tr>
<tr>
<td>2040</td>
<td>4.2</td>
<td>4.1</td>
</tr>
</tbody>
</table>

- **Electric power**
- **Industrial***
- **Transportation****
- **Commercial**
- **Residential**

*Includes combined heat-and-power and lease and plant fuel
**Includes pipeline fuel

Source: EIA, Annual Energy Outlook 2014 Early Release
Manufacturing output and natural gas use grows with low natural gas prices, particularly in the near term.

Source: EIA, Annual Energy Outlook 2014 Early Release
Natural gas use in the transportation sector grows rapidly with the largest share in freight trucks.

Source: EIA, Annual Energy Outlook 2014 Early Release
US NG gross exports exceed 5 tcf in 2025

U.S. natural gas imports and exports trillion cubic feet per year

<table>
<thead>
<tr>
<th></th>
<th>History</th>
<th>2012</th>
<th>Projections</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>2025</td>
</tr>
<tr>
<td></td>
<td>billion cubic feet per day</td>
<td>5.4 tcf of exports (14.8 bcf/day)</td>
<td>Pipeline exports to Mexico</td>
</tr>
<tr>
<td></td>
<td>Pipeline exports to Canada</td>
<td>2.0 tcf of imports (5.4 bcf/day)</td>
<td>Pipeline exports to Canada</td>
</tr>
<tr>
<td></td>
<td>Lower 48 states LNG exports</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alaska LNG exports</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LNG imports</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: EIA, Annual Energy Outlook 2014 Early Release
US Becomes a next exporter of NG

U.S. dry natural gas trillion cubic feet per year

Source: EIA, Annual Energy Outlook 2014 Early Release
Natural Gas Property Measurements

• Measurement Uncertainties
  – Mixture
    • Reservoir sampling
    • Mixture preparation
  – Temperature
  – Pressure

• Density
  – Hydrostatic balance
  – Vibrating tube

• Viscosity

• Speed of Sound

• Calorimetric properties

• Phase Equilibrium
  – Phase Envelopes
  – Gas Hydrate Equilibrium
Total Uncertainties in Gas Property Measurements

- Components in mixture
- Temperature measurements
- Pressure measurements
- Equipment specific parameters
Mixture Sampling and Preparation

• It is essential to prepare mixtures of accurately known composition, from pure components, that represent mixtures often used in industry or are of theoretical interest.

• It is difficult to underestimate how important it is that the composition of the fluid sample be representative to that of the fluid within the pore space of the reservoir rock.

• The purity of each component, always of the highest purity available, must be verified before preparing mixtures. Gas chromatographic analysis of the sample should be performed with the appropriate detectors after preliminary tests.
Mixture Preparation

• For gravimetric gas mixture preparation, to determine the mass of each component added to a mixture, an equal arm balance was used where each pan has a capacity of 25 kg, with a relative precision of $\pm 3.2 \times 10^{-7}$ (about 8 mg in 25 kg).

• The balance is constructed without a center post and capable of weighing objects at least 1m high, which is sufficient for a 15.7 L aluminum gas cylinder fitted with a valve and valve protector handle.

• The capacity of the balance and the conservative estimate of precision is optimum for a wide range of mixture needs. The weight set was calibrated against mass transfer standards certified by the NIST Gaithersburg laboratory responsible for maintaining those standards.
Temperature Measurements

- **ITS-90** covers the temperature range from 0.65K up to the highest temperature practicably measurable in terms of the Planck radiation law.

- The official text for the ITS-90 is published by the Bureau International des Poids et Mesures (BIPM), and an English version is included in the Supplementary Information for ITS-90

\[ W(T_{90}) = \frac{R(T_{90})}{R(273.16 \text{ K})} \]

An outline of the main features of ITS-90.
Temperature Measurements

2-Wire: The simplest resistance thermometer configuration uses two wires. It is only used when high accuracy is not required.

3-Wire: In order to minimize the effects of the lead resistances, a three-wire configuration can be used.

4-Wire: The four-wire resistance thermometer configuration increases the accuracy and reliability of the resistance being measured: the resistance error due to lead wire resistance is zero.
Temperature Measurements

Commercial PRT

Thermal emf

Cross section of PRT

Triple point of water cell
Pressure Measurements

- **Electronic Pressure Gauges**
  - Physical Principle of Resistive Strain Gauge Pressure Transducer
  - *Silicon Piezoresistive Micromachined Pressure Transducer*
  - Resonant Pressure Sensors Based on Mechanical Vibrations
  - Pressure Sensors Based on Capacitance
  - Silicon Capacitive Pressure Transducers
  - *Performances of Piezoresistive and Capacitive Pressure Sensors*

- **Piston Gauges**
  - Simple Piston-Cylinder Mounting Systems
  - Digital Piston Gauges

- **Pressure Measurements in a Diamond-Anvil Cell**
  - XRAY
  - Optical Sensors
Pressure Measurements

Schematic of a piston gauge combined with a reference pressure gauge, which measures the pressure generated by the piston gauge, to determine pressure \( p \).

Schematic of a two piston gauge configuration, for measurement of pressures up to 10 kPa.
Pressure Measurements

Ruska Dead Weight Gauge
Reservoir Types

**GEOLOGICAL TRAPS**

- **Conventional Gas**
  - Reservoir rock
  - Conventional reservoir

- **Shale Gas**
  - Reservoir rock
  - Conventional reservoir

- **Coalbed Methane**
  - Mature source rock with remaining gas not migrated
  - Tight traditional reservoir
  - Traditional permeable reservoir

- **Tight Gas**
  - Reservoir rock
  - Unconventional reservoir

Gas migration over geological times

Large, well connected pores

Small, poorly connected pores

Very small, hardly connected pores
New/Recent Reservoirs

- Ultra-deep gas have completely different characteristics which effects the PVT behavior of the gas.
- Need of PVT data for such gases in order to check EOS performance and loop condition to avoid condensation.
Qatar North Field

Qatar natural gas flows, 2003-2012

Qatar’s natural gas production rate & Qatar’s proven reservoirs.
Density
DENSITY

• The density is required for the fundamental development of equations of state, custody transfer of fluids, and industrial process design and implementation.

• Several methods are used to obtain density experimentally and numerous equations are used to estimate theoretically.

• Why exactly?
Why Density?

\[
\frac{\$}{\text{day}} = \left( \frac{m^3}{\text{day}} \right) \left( \frac{\text{kg}}{m^3} \right) \left( \frac{j}{\text{kg}} \right) \left( \frac{\$}{j} \right)
\]

<table>
<thead>
<tr>
<th>Accuracy (% Deviation)</th>
<th>Density [kg/m³]</th>
<th>Economic impact of inaccurate density measurements [$/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Lower Boundary]</td>
<td>[Upper Boundary]</td>
<td>[True Value]</td>
</tr>
<tr>
<td>0.03</td>
<td>0.9343</td>
<td>0.9349</td>
</tr>
<tr>
<td>0.50</td>
<td>0.9299</td>
<td>0.9392</td>
</tr>
<tr>
<td>3.00</td>
<td>0.9065</td>
<td>0.9626</td>
</tr>
</tbody>
</table>

- **Producer ➔ Loss**
- **Buyer ➔ Profit**

- **Cost of gas (from market)**
- **Heat capacity (from composition)**
- **On-site determined Orifice meters**

- **Why Density?**

- **Department of Chemical Engineering**

- **Qatar University**
Impact of the Density Measurement Project

System with unknown thermophysical properties

**Density**

**Viscosity**

**Phase Envelope**

**Computational Techniques**

Thermodynamics Tools

High accuracy PVT data

Process Calculations
- math. modeling,
- simulation,
- optimization

Database
- High-accuracy data used in calibration

Custody
- Transfer of NG knowledge for NG industry, management decision making
Equation of State (EOS)

- Boyle’s Law (1662)
- Charles’s Law (1787)
- Dalton’s Law (1801)
- Ideal Gas Law - Clapeyron (1834)
- Van der Waals (1873)
- Redlich-Kwong (1949)
- Soave-Redlich-Kwong (1972)
- Peng-Robinson (1976)
- ...
Cubic Equation of State

- Cubic equations of state are the **most common** option in the chemical and gas industries to model complex phase behavior and to design chemical processes,\(^1,2\) due to their simplicity. They are widely used for the prediction of phase envelopes\(^3\) in academia and industry via **commercial software** available for process design.

- These kind of EOS have showed good capabilities for correlating properties of complex reservoirs fluids.

\[
\left( p + \frac{a}{V_m^2} \right) (V_m - b) = RT
\]

\[
a = \frac{27(RT_c)^2}{64p_c}
\]

\[
b = \frac{RT_c}{8p_c}.
\]


Cubic Equation of State

• Cubic EOS are modifications of the original basic van der Waals EOS, proposed more than one century ago, and they are termed as cubic because they take a cubic form in terms of compressibility. In these EOS, two contributions are considered to the total pressure, a repulsive (usually hard-spheres) and an attractive term to describe the intermolecular interactions.

• Most of the different modifications to the original EOS have centered on the attractive term whilst less attention have been paid to the repulsive term because most of the proposed variations of the repulsive term give rise to non-cubic EOS with the subsequent loss of simplicity.
Cubic Equation of State

• Between all the modifications of the attractive term of the original equation, the proposal by Redlich–Kwong (RK), is probably the most important as it was the starting point of many modified EOS. The RK EOS did not have a strong theoretical background but their inspired EOS gave good results for many different systems.

\[ P = \frac{RT}{v - b - aTv} + b(\sqrt{T}v(v + b)) \]

In this equation, the force constant, so-called co-pressure, takes account of the attractive interactions whereas the \( b \) constant, so-called co-volume, takes account of repulsive forces.
Molecular Based EOS

• The **advances in statistical mechanics and computational capabilities** have allowed the development of equations of state based on molecular principles, so–called molecular based EOS, with strong theoretical basis. They are accurate for pure fluids as well as multi–component mixtures and have shown appreciable performance in predicting volumetric properties and phase equilibria in wide temperature and pressure ranges.

• **These EOS allow separating and quantifying the effects of molecular structure and interactions on bulk properties and phase behavior.** Despite the advances in this field, impact and practical use of these EOS for industrial purposes has been very **limited since their intrinsic algebraic complexity that causes demanding computational power and time.**
Molecular Based EOS

- The Wertheim’s thermodynamic perturbation theory of first order constitutes one of the most successful starting points to develop molecular based EOS.
- Based in this approach Chapman et al.\textsuperscript{1,2} developed the so-called Statistical Associating Fluid Theory (SAFT).
- SAFT describes the residual Helmholtz free energy, $A$, of a mixture of non–associating fluids as a sum of different contributions

\[
\frac{A}{RT} = \frac{A^{seg}}{RT} + \frac{A^{chain}}{RT} = \bar{m} \left( \frac{A^{hs}}{RT} + \frac{A^{disp}}{RT} \right) + \frac{A^{chain}}{RT}
\]

where $A^{seg}$, $A^{chain}$, $A^{hs}$ and $A^{disp}$ and are the segment, chain, hard–sphere and dispersive contributions respectively to the total Helmholtz free energy and is the segment number

Benchmark EOS for Natural Gas

• Thermodynamic properties of the natural gas main component methane and of natural gases have frequently been investigated because of their industrial importance.

• The most recent equations of state for thermodynamic properties were reported for methane by Wagner and de Reuck\textsuperscript{1} and for natural gases by Jaeschke et al.\textsuperscript{2,3} (GERG\textsuperscript{88} equation) and by Starling and Savidge\textsuperscript{4} (AGA\textsuperscript{8-DC92} equation), respectively. These equations for natural gases are now routinely applied in energy billing.

• Specifically with the help of these equations the volume metered under varying, actual field conditions are converted to well defined reference conditions.

• AGA8-DC92 is the current industry standard EOS.
• Complex, multi component EOS.

Table 1. Ranges of Gas Mixture Characteristics

<table>
<thead>
<tr>
<th>Components</th>
<th>Normal Range</th>
<th>Expanded Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Composition [% mol]</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>0 - 50</td>
<td>0 – 100</td>
</tr>
<tr>
<td>CO2</td>
<td>0 – 30</td>
<td>0 – 100</td>
</tr>
<tr>
<td>CH4</td>
<td>45 - 100</td>
<td>0 – 100</td>
</tr>
<tr>
<td>C2H6</td>
<td>0 - 10</td>
<td>0 – 100</td>
</tr>
<tr>
<td>C3H8</td>
<td>0 - 4</td>
<td>0 – 12</td>
</tr>
<tr>
<td>C4</td>
<td>0 - 1</td>
<td>0 – 6</td>
</tr>
<tr>
<td>C5</td>
<td>0 – 0.3</td>
<td>0 – 4</td>
</tr>
<tr>
<td>C6+</td>
<td>0 – 0.2</td>
<td>0 – dew point</td>
</tr>
</tbody>
</table>

Table 2. Accuracy of AGA8-DC92

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.12</td>
<td>265-340</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>2</td>
<td>12-17</td>
<td>211-394</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>3</td>
<td>17-70</td>
<td>144-477</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>4</td>
<td>70-140</td>
<td>144-477</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

None of the sample mixtures that are used invalidation of AGA8 are in extended region of the EOS.
• Standard EOS for custody transfer: AGA8

### AGA8 EOS

![Graph showing Range 1, R2, Range 3, and Expanded Range with P [MPa] on the x-axis and % Dev on the y-axis.]

<table>
<thead>
<tr>
<th>Component</th>
<th>% mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0 - 50</td>
</tr>
<tr>
<td>CO₂</td>
<td>0 – 30</td>
</tr>
<tr>
<td>CH₄</td>
<td>45 - 100</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0 - 10</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0 - 4</td>
</tr>
<tr>
<td>C₄~</td>
<td>0 - 1</td>
</tr>
<tr>
<td>C₅~</td>
<td>0 – 0.3</td>
</tr>
<tr>
<td>C₅₃~</td>
<td>0 – 0.2</td>
</tr>
</tbody>
</table>
AGA8 EOS
GERG EOS

• GERG-2004 and GERG-2008 EOS are wide-range equation of state for natural gases and other mixtures that meets the requirements of standard and advanced natural gas applications.

• GERG project was supported by the European natural-gas
GERG EOS

• This equation of state covers mixtures consisting of up to **18 components** that are listed in the table; originally, n-nonane, n-decane and hydrogen sulfide did not belong to these components. In contrast to the AGA8-DC92 equation, there are basically **no limitations in the concentration range**.

Components, which were taken into account in the development of the equations of state GERG-2004 EOS (without the components n-nonane, n-decane and hydrogen sulfide) and GERG-2008 EOS (all of the listed components).

**Yellow:** natural gas main components  
**Red:** further hydrocarbons  
**Blue:** further components
• The two EOS, GERG-2004 & 2008 have the same form; only difference is that the summations. They are performed up to $N = 18$ for GERG-2004 and up to $N = 21$ for GERG-2008.

• EOS are based on a **multi-fluid mixture model, which is explicit in the reduced Helmholtz free energy** \( \alpha = \alpha^o/(RT) \) as a function of the density, the temperature and the mole fractions of the mixture.
REFPROP
REFPROP
Industry Rule of Thumb Methods

• Compressibility method is a know technique used in quick estimations in industry.


• Hall, K. R. and Yarborough, L., Oil Gas J. 71, No. 25, 82 (June 18, 1973).

• Hall, K. R. and Yarborough, L., Oil Gas J. 72, No. 7, 86 (Feb. 18, 1974).
Compressibility Factors for Natural Gas
Compressibility Factors for Natural Gas
Specific Gravity of Petroleum Fluids

Identification
A. 8 mol % C6H16—92 mol % C18H38 (370-739 lpsk)
B. 50.25 wt. % C6H14—49.75 wt. % n-C18H38
C. 19.2 wt. % CH4—80.8 wt. % C18H38 (2410-2506 lpsk)
D. 7.15 wt. % CH4—92.85 wt. % n-C18H38 (854-1043 lpsk)
E. National Standard Petroleum Oil Tables

F. 7.15 wt. % CH4—92.85 wt. % n-C18H38 (at 3000 lpsk)
G. 9.78 wt. % C6H14—90.22 wt. % n-C18H38
H. 75.45 mol % C6H14—24.55 % n-C18H38 (ref. 4)
I. 65.77 mol % C6H14—34.23 % n-C18H38 (ref. 3)

(Note: Reference for streams A-G see ref. 19)
Natural Gas Density Measurements

Two major density measuring devices are:

1) Hydrostatic Balance Densimeters with Magnetic Suspension Couplings
2) Measurement of Density with Vibrating Bodies

MAGNETIC SUSPENSION DENSIMETER
Archimedes’ Principle ~ buoyancy

VIBRATING TUBE DENSIMETER
Measures the fluid density of interest by determining the oscillation frequency of the vibrating element in the fluid.
Hydrostatic Balance Densimeter

• Basis: Archimedes’ Principle (or buoyancy)
  “A solid body (sinker) suspended in a fluid experiences a buoyant force exerted by the mass of a volume of fluid displaced by the solid body.”

\[ m_v \text{ or } m_a \]

Balance Pan

\[ m_v = \text{true mass of sinker (in vacuum)} \]
\[ m_a = \text{apparent mass of sinker (in fluid)} \]
\[ m_f = \text{mass of fluid displaced by sinker} \]

\[ f = \frac{m_v}{m_a} \]

\[ V_s \]
Conventional Devices vs. Magnetic Suspension Devices

- The main difficulty when using conventional gravimetric instruments is the direct contact between the measuring cell (sample atmosphere) and the weighing instrument. The balance can be damaged or disturbed by the measuring atmosphere and the measuring atmosphere can be adversely affected by flushing gases and pollution. These limitations considerably reduce the field of application of conventional measuring devices.
Magnetic Suspension Densimeter

These reliable suspension balances make it possible to weigh samples contactlessly under nearly all environments. Instead of hanging directly at the balance the sample to be investigated is linked to a so-called suspension magnet which consists of a permanent magnet, a sensor core and a device for decoupling the measuring load (sample). An electromagnet, which is attached to the underfloor weighing hook of a balance, maintains a freely suspended state of the suspension magnet via an electronic control unit. Using this magnetic suspension coupling the measuring force is transmitted contactlessly from the measuring chamber to the microbalance, which is located outside the chamber under ambient atmospheric conditions. Consequently, this arrangement eliminates almost all restrictions which are inherent to conventional gravimetric measuring instruments.
Magnetic Suspension Densimeter
Why MSD?

• Contact free weighing of all kinds of samples in hermetically closed reactors with patented magnetic suspension.

• Hermetic separation of measurement area (sample) and weighing area (balance) to avoid any damage, destruction or interference from the process media (e.g. corrosive gases, vapors), pressure or temperature.

• The reactor of the magnetic suspension balance is completely metal sealed, even highly aggressive or corrosive atmospheres can be used for measurements over a wide pressure and temperature range.

• Excellent long term stability. The sample can be automatically disconnected from the balance at any time to re-tare and/or calibrate the balance. After that it is reconnected and lifted up to measuring position to continue the measurement. High precision long term measurements without baseline drift are performable without limit in measuring time.

• The density of the measuring atmosphere in the reactor is determined highly accurate by applying Archimedes’ principle. A sinker is weighed by the balance additionally and simultaneously to the sample, so determining the buoyancy effect acting on it.

• Modular construction: The magnetic suspension balance can flexibly be adapted to all kinds of applications by combining different modular parts of the instrument.
High Pressure MSD
Vibrating Tube Densimeter (VTD)

• VTD consist of an assembly that includes two thin walled metallic or glass tubes bent in Y or V shapes.

• A permanent magnet and drive coil reside between these two tubes. A drive coil and a permanent magnet are placed in the middle of the two tubes and mounted on the opposite legs. Each coil and magnet on the side leg forms a pick-off circuit.

• Attractive and repulsive magnetic fields between the coils and magnets are provided by sending alternating current to the drive coil.
Vibrating Tube Densimeter (VTD)

- A sine wave generated by the two pick-up circuits represents the motion of one tube relative to the other. The density of the fluid is:

\[
\rho = A \tau^2 - B
\]

\[
A = \frac{c}{4\pi^2V}
\]

\[
B = \frac{m_0}{V}
\]

- Where \( A \) and \( B \) are calibration constants that should be determined.
- \( A \) is related with the spring constant of the oscillator, \( c \), with the inner volume of the vibrating tube, \( V \), and \( B \) is related with the mass of the empty tube, \( m_0 \), and also with the inner volume.
- These \( A \) and \( B \) calibration constant are pressure and temperature dependent, and thus, they should be determined very carefully to be able of obtaining the low limits of uncertainty for the measurement of gases densities.
Vibrating Tube Densimeter (VTD)
Density Measurements

• Pure gas components
  – $N_2$
  – $CO_2$
  – $CH_4$

• Multicomponent gas mixtures that represent natural gas
  – Gulf of Mexico samples
  – Lean natural gas samples
  – Qatar gas samples
Pure Gas Density Measurements – $N_2$

**Figure 1.** Percent deviation of experimental data using Span et al.\textsuperscript{1} as the reference. ▲, this work; ○, Klimeck et al.;\textsuperscript{7} ◇, Michels et al.;\textsuperscript{8} □, Wiebe and Gaddy.\textsuperscript{9}
Pure Gas Density Measurements – CO₂

Figure 1. Percent deviation of experimental data compared to Span and Wagner equation of state. ▲, This work; ○, Klimeck;¹⁰ ◇, Michels;⁸ □, Juza;⁹ ×, Gokmenoglu.¹¹
Pure Gas Density Measurements – CH$_4$

**Figure 1.** Percentage deviation of the experimental $PpT$ data from values calculated using the Setzmann and Wagner$^1$ equation of state. This work: ◆, 298 K; ⋄, 305 K; ▲, 338 K; ■, 400 K; ▼, 450 K; ref 2, Δ, (273.25 to 423.25) K; ref 4, ○, 310 K; ref 5, ×, 298.15 K.
Pure Gas Density Measurements – $C_2H_6$

Figure 1. Percentage deviation of the experimental $PpT$ data from values calculated using the Bücker and Wagner\(^1\) equation of state. This work: ●, 298.150 K; ▲, 350.000 K; ■, 400.000 K; ★, 450.000 K. Ref 2, ○, (290 to 345) K; ref 3, △, (255 to 270) K.
Multicomponent Mixture Experiments

- Gulf of Mexico Mixtures
- Lean natural gas mixtures
- Qatar natural gas mixtures
Gulf of Mexico

Deep Discovery

Drilling in waters up to two miles deep, oil companies are making some very large discoveries. The first test of whether oil would flow from these ultra-deep wells, at Chevron’s Jack well, was successful.

<table>
<thead>
<tr>
<th>Operator</th>
<th>Prospect Name</th>
<th>Water Depth (feet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrobras/Devon</td>
<td>Cascade</td>
<td>8,143</td>
</tr>
<tr>
<td>Petrobras</td>
<td>Chinook</td>
<td>8,831</td>
</tr>
<tr>
<td>BP</td>
<td>Kaskida</td>
<td>5,860</td>
</tr>
<tr>
<td>Chevron</td>
<td>Trident</td>
<td>9,743</td>
</tr>
<tr>
<td></td>
<td>Tobago</td>
<td>9,627</td>
</tr>
<tr>
<td></td>
<td>Silvertip</td>
<td>9,226</td>
</tr>
<tr>
<td></td>
<td>Tiger</td>
<td>9,004</td>
</tr>
<tr>
<td></td>
<td>St. Malo</td>
<td>7,036</td>
</tr>
<tr>
<td></td>
<td>Jack</td>
<td>6,965</td>
</tr>
<tr>
<td>Shell</td>
<td>Stones</td>
<td>9,556</td>
</tr>
<tr>
<td></td>
<td>Great White</td>
<td>8,717</td>
</tr>
</tbody>
</table>

Source: Minerals Management Service
GoM Mixtures

- Part of series of measurements for Gulf of Mexico natural gas type mixtures.
- Deep water source includes heavy components which includes $C_{6+}$ more than 0.2%.
- AGA8 EOS normal range was designed to predict up to 0.2% total $C_6+$ fractions.
- AGA8 cannot predict phase boundaries. It works only in the single phase region.

<table>
<thead>
<tr>
<th>Component</th>
<th>Sample 1 [%]</th>
<th>Sample 2 [%]</th>
<th>Sample 3 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>94.045</td>
<td>88.023</td>
<td>77.762</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>1.867</td>
<td>5.824</td>
<td>10.623</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>1.802</td>
<td>3.292</td>
<td>5.993</td>
</tr>
<tr>
<td>iC$<em>4$H$</em>{10}$</td>
<td>0.356</td>
<td>0.537</td>
<td>1.731</td>
</tr>
<tr>
<td>nC$<em>4$H$</em>{10}$</td>
<td>0.706</td>
<td>0.936</td>
<td>1.013</td>
</tr>
<tr>
<td>iC$<em>5$H$</em>{12}$</td>
<td>0.201</td>
<td>0.249</td>
<td>0.460</td>
</tr>
<tr>
<td>nC$<em>5$H$</em>{12}$</td>
<td>0.252</td>
<td>0.236</td>
<td>0.436</td>
</tr>
<tr>
<td>nC$<em>6$H$</em>{14}$</td>
<td>0.199</td>
<td>0.089</td>
<td>0.219</td>
</tr>
<tr>
<td>nC$<em>6$H$</em>{18}$</td>
<td>0.100</td>
<td>0.189</td>
<td>0.130</td>
</tr>
<tr>
<td>nC$<em>7$H$</em>{18}$</td>
<td>0.052</td>
<td>0.098</td>
<td>0.053</td>
</tr>
<tr>
<td>nC$<em>8$H$</em>{20}$</td>
<td>0.025</td>
<td>0.036</td>
<td>0.029</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>-</td>
<td>0.045</td>
<td>0.135</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>-</td>
<td>0.015</td>
<td>0.132</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>0.006</td>
<td>-</td>
<td>0.007</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>-</td>
<td>-</td>
<td>0.020</td>
</tr>
<tr>
<td>2,3 Dimethylhexane</td>
<td>-</td>
<td>-</td>
<td>0.052</td>
</tr>
<tr>
<td>3 Methylhexane</td>
<td>-</td>
<td>-</td>
<td>0.051</td>
</tr>
<tr>
<td>2,2,4 Trimethylpentane</td>
<td>-</td>
<td>-</td>
<td>0.029</td>
</tr>
<tr>
<td>Toluene</td>
<td>-</td>
<td>-</td>
<td>0.033</td>
</tr>
<tr>
<td>Benzene</td>
<td>-</td>
<td>-</td>
<td>0.028</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.143</td>
<td>0.169</td>
<td>0.404</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.246</td>
<td>0.262</td>
<td>0.660</td>
</tr>
</tbody>
</table>
94% Mixture

**Figure.** Density deviations compared to predictions from: (a) AGA8-DC92 and (b) GERG2008 EOS, for M94C1 mixture

Symbols: (◇) 270 K, (□) 280 K, (△) 290 K, (×) 305 K, (⋆) 320 K, (○) 340 K
88% Mixture

Figure. Density deviations compared to predictions from (a) AGA8-DC92 and (b) GERG2008 EOS, for M88C1 mixture. Symbols: (◇) 270 K, (△) 290 K, (□) 305 K, (○) 340 K
78% Mixture

- Total 28 density points measured.
  - 3/3 points out in region 1
  - 4/8 points out in region 2
  - 4/17 points out in region 3
do not agree with the AGA8 prediction capabilities depending on the prediction regions determined in the original AGA report.
Lean Gas Mixtures - SNG

<table>
<thead>
<tr>
<th>Component</th>
<th>SNG-1</th>
<th>SNG-2</th>
<th>SNG-3</th>
<th>SNG-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.89982</td>
<td>0.89990</td>
<td>0.89975</td>
<td>0.90001</td>
</tr>
<tr>
<td>ethane</td>
<td>0.03009</td>
<td>0.03150</td>
<td>0.02855</td>
<td>0.04565</td>
</tr>
<tr>
<td>propane</td>
<td>0.01506</td>
<td>0.01583</td>
<td>0.01427</td>
<td>0.02243</td>
</tr>
<tr>
<td>2-methylpropane</td>
<td>0.00752</td>
<td>0.00781</td>
<td>0.00709</td>
<td>0.01140</td>
</tr>
<tr>
<td>butane</td>
<td>0.00753</td>
<td>0.00790</td>
<td>0.00722</td>
<td>0.01151</td>
</tr>
<tr>
<td>2-methylbutane</td>
<td>0.00300</td>
<td>0.00150</td>
<td>0.00450</td>
<td>0.00450</td>
</tr>
<tr>
<td>pentane</td>
<td>0.00300</td>
<td>0.00150</td>
<td>0.00450</td>
<td>0.00450</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.01697</td>
<td>0.01699</td>
<td>0.01713</td>
<td>-</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>0.01701</td>
<td>0.01707</td>
<td>0.01699</td>
<td>-</td>
</tr>
</tbody>
</table>

Four synthetic natural gas samples were prepared gravimetrically by Accurate Gas Products, LLC in Lafayette, LA. The samples that are used in this work are named SNG-1, SNG-2, SNG-3, and SNG-4.
Relative deviations of density data from single-sinker and two-sinker densimeters with respect to the AGA8 equation on a log-linear scale (symbols: △ single-sinker data at 250 K, □ single-sinker data at 350 K, ○ single-sinker data at 450 K, ▲ two-single-sinker data at 250 K, ■ two-single-sinker data at 350 K, ● two-single-sinker data at 450 K); from left to right: solid line box is AGA uncertainty region 1, long dashed-line is AGA uncertainty region 2, fine dashed-line is AGA uncertainty region 3.

Relative deviations of density data from single-sinker and two-sinker densimeters with respect to GERG equation in log-linear scale (symbols: △ single-sinker data at 250 K, □ single-sinker data at 350 K, ○ single-sinker data at 450 K); fine dashed-line is GERG uncertainty region, between (265 to 335) K and at pressures up to 12 MPa it is +/- 0.3%.
SNG-2 Mixture

Experimental density deviations w.r.t. AGA8 EOS
(○ 250K; △ 350K; □ 450K)

Experimental density deviations w.r.t. GERG EOS
(○ 250K; △ 350K; □ 450K)
SNG-3 Mixture

Experimental density deviations w.r.t. AGA8 EOS
(○ 250K; △ 350K; □ 450K)

Experimental density deviations w.r.t. GERG EOS
(○ 250K; △ 350K; □ 450K)
SNG-4 Mixture

Experimental density deviations w.r.t. AGA8 EOS
(○ 250K; △ 350K; □ 450K)

Experimental density deviations w.r.t. GERG EOS
(○ 250K; △ 350K; □ 450K)
# Qatar Gas Mixtures - QNG

<table>
<thead>
<tr>
<th>Component</th>
<th>QNG-S1&lt;sup&gt;b&lt;/sup&gt;</th>
<th>QNG-S2&lt;sup&gt;c&lt;/sup&gt;</th>
<th>QNG-S3&lt;sup&gt;d&lt;/sup&gt;</th>
<th>QNG-S4&lt;sup&gt;e&lt;/sup&gt;</th>
<th>QNG-S5&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Methane</td>
<td>0.84990</td>
<td>0.90260</td>
<td>0.80340</td>
<td>0.84700</td>
<td>0.85094</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.05529</td>
<td>0.05828</td>
<td>0.05189</td>
<td>0.05584</td>
<td>0.05529</td>
</tr>
<tr>
<td>Propane</td>
<td>0.02008</td>
<td>0.02106</td>
<td>0.01878</td>
<td>0.01962</td>
<td>0.02009</td>
</tr>
<tr>
<td>2-methylpropane</td>
<td>0.00401</td>
<td>0.00412</td>
<td>0.00384</td>
<td>0.00416</td>
<td>0.00401</td>
</tr>
<tr>
<td>Butane</td>
<td>0.00585</td>
<td>0.00641</td>
<td>0.00573</td>
<td>0.00553</td>
<td>0.00612</td>
</tr>
<tr>
<td>2-methylbutane</td>
<td>0.00169</td>
<td>0.00214</td>
<td>0.00188</td>
<td>0.00214</td>
<td>0.00171</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.00147</td>
<td>0.00162</td>
<td>0.00140</td>
<td>0.00155</td>
<td>0.00141</td>
</tr>
<tr>
<td>Octane</td>
<td>0.00152</td>
<td>0.00161</td>
<td>0.00145</td>
<td>0.00150</td>
<td>0.00152</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.00090</td>
<td>0.00110</td>
<td>0.00092</td>
<td>0.00092</td>
<td>0.00098</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>0.00102</td>
<td>0.00111</td>
<td>0.00092</td>
<td></td>
<td>0.00099</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.03496</td>
<td>0.06596</td>
<td>0.03711</td>
<td>0.03496</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.02331</td>
<td>0.04380</td>
<td>0.02457</td>
<td>0.02296</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Relative uncertainty for samples: methane 0.2%, C₂ to C₄ 2.0%, C₅ plus higher 5%, N₂ and CO₂ 2%.

<sup>b</sup> x (C₅⁺) = 0.00344.

<sup>c</sup> x (C₅⁺) = 0.00382.

<sup>d</sup> x (C₅⁺) = 0.00329.

<sup>e</sup> x (C₅⁺) = 0.00248.

<sup>f</sup> x (C₅⁺) = 0.00251.

- 5 natural gas like mixtures are purchased from LINDE® in Spain.
- Mixtures resembles Qatari type natural gas.
QNG Experiments

Experimental PVT measurements were performed with Anton Paar DMA 512P high-pressure cell, which contains a stainless steel vibrating U-shaped tube and the electronics to excite the tube and measure the oscillating period. The cell temperature was controlled by a Julabo LH50 circulating bath; the temperature was measured to ±1 \(10^{-2}\)K by using a calibrating Pt100 platinum sensor placed in the measuring cell. A Teledyne Isco 100DM syringe pump controls the sample pressure measured within ±0.01 MPa by a pressure transducer.
Pre-QNG / Pure Components

Relative density deviation plots between the data obtained in this work for calibration purposes and those from Refprop 9.0 (used as reference data): (a) CH4 and (b) N2
FIGURE 3. Relative density deviation plots with respect to AGA8-DC92 EOS and GERG-2008 EOS and the experimental density data obtained for QNG-S1 (a) AGA8-DC92 EOS and (b) GERG-2008 EOS (Istoherms; ⊙ 250 K, □ 300 K, △ 350 K, ◇ 400 K, and + 450 K).
FIGURE 4. Relative density deviation plots with respect to AGA8-DC92 EOS and GERG-2008 EOS and the experimental density data obtained for QNG-S2 (a) AGA8-DC92 EOS and (b) GERG-2008 EOS (Isentropes; ○ 250 K, □ 300 K, △ 350 K, ◊ 400 K, and + 450 K).
FIGURE 5. Relative density deviation plots with respect to AGA8-DC92 EOS and GERG-2008 EOS and the experimental density data obtained for QNG-S3 (a) AGA8-DC92 EOS and (b) GERG-2008 EOS (Isotherms; ○ 250 K, □ 300 K, △ 350 K, ◇ 400 K, and + 450 K).
Figure 6. Relative density deviation plots with respect to AGA8-DC92 EOS and GERG-2008 EOS and the experimental density data obtained for QNG-S4 (a) AGA8-DC92 EOS and (b) GERG-2008 EOS (Isotherms: ○ 250 K, □ 300 K, △ 350 K, ◊ 400 K, and + 450 K).
FIGURE 7. Relative density deviation plots with respect to AGA8-DC92 EOS and GERG-2008 EOS and the experimental density data obtained for QNG-S5 (a) AGA8-DC92 EOS and (b) GERG-2008 EOS (isotherms; ○ 250 K, □ 300 K, △ 350 K, ◆ 400 K, and + 450 K).
Viscosity
Evaluation of Predictive Models for High-Pressure Natural Gas Viscosity

René D. Elms, Bryan Research & Engineering, Inc.
Mert Atilhan, Qatar University
Santiago Aparicio, University of Burgos
Carl Fitz, S-CON, Inc.
Mahmoud El-Halwagi, Texas A&M University
Background

• Production and utilization of natural gas is expected to continue to increase. Importance of accurate knowledge of natural gas thermophysical properties
• For production, transmission, and processing, etc...
• **Importance of viscosity as it is a important transport property: pumping!**
• 1% error in viscosity produces at least a % error in...

• High Pressure and High Temperature applications are of increasing interest
  * Deeper drilling
  * Higher wellhead pressures
  * Discover of new reservoirs with such conditions
  * Qatar reserves
  * Emergence of Shale Gas
  * etc..

• **High quality viscosity data in this range of pressures and temperatures has been limited.**
Previous Work

2010: High quality viscosity data for 5 synthetic natural gas samples collected and reported


Viscometer
Viscometer

- **Two coils move the piston back and forth magnetically at a constant force.** Proprietary circuitry analyzes the piston's two-way travel time to measure absolute viscosity.

- A set of six calibrated pistons to cover viscosity ranging from **0.01 cP to 10,000 cP**

- Temperature range: up to 190°C

- Pressure range: up to 15,000 psi
Viscosity Data

**Figure.** Oscillation of the vibrating tube, $\tau$, (PVT behavior) for QNG – S3 synthetic natural gas – like sample in the 10 – 65 MPa pressure range and 250 – 450 K temperature range (10 K step from bottom, 250 K, to top, 450 K) measured with the high pressure vibrating tube densimeter. Symbols: experimental points, lines: reported for guiding purposes. Raw data are reported, corrections according to mechanical equations of the cell are under development.

**Figure.** Dynamic viscosity, $\eta$, (P$\eta$T behavior) for QNG – S3 synthetic natural gas – like simple in the 1 – 70 MPa pressure range and 250 – 450 K temperature range (20 K step from top, 250 K, to bottom, 450 K) measured with the electromagnetic viscometer. Symbols: experimental points, lines: reported for guiding purposes.
Viscosity Data

Percentage deviations between experimental, $\eta_{\text{exp}}$, and predicted, $\eta_{\text{mod}}$, viscosity values. Symbols, circles: values for 250 K, squares: values for 350 K and triangles: values for 450 K; filled symbols: values for QNG-S1, empty symbols: values for QNG-S2. Panels: (a) NBS, (b) CLS, (c) LBC and (d) PFT models. (Uncertainties of experimental values reported in this work are ± 2.5 % for $P < 30 \text{MPa}$ and ± 4.0 % for $P > 30 \text{MPa}$.)

NBS: Nilpotent-Bazhanov-Stroganov (AKA TRAPP)
CLS: Chung, Lee, and Starling
LBC: Lohrenz, Bray, and Clark
PFTC: Pedersen, Fredenslund, Thomassen, and Christensen
Purpose

Extension of previous work: Provides additional evaluation of viscosity predictions for the given samples – SRK and PR

SRK and PR:

- Utilized heavily in day-to-day natural gas process design, etc...
- Often utilized by process design simulators
- Here: Comparing ProMax process design simulator SRK and PR packages
  - Bryan Research & Engineering, Inc., Bryan, TX
  - Used extensively worldwide in the natural gas industry
- Begin to provide insight into the accuracy in this context of current modeling methods for design, etc... in the natural gas industry
- Inaccuracies have the potential to create a ‘ripple’ effect throughout the design
Approach

- Utilized ProMax version 3.2 to calculate viscosity for the 5 samples
  - PR and SRK property packages. Viscosity models based on EOS.

- Viscosities were calculated for:
  - Temperature: 250 K to 450 K (-10 F to 350 F) in 10 K increments
  - Pressure: 10 – 65 MPa (1450 psia to 9400 psia) in 5 MPa increments
  - Compositional differences: CO₂, N₂, aromatic and cyclic compounds

- Comparisons
  - SRK and PR – more detail
  - SRK and PR with the previous 4 models
# Natural Gas Sample Compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>QNG-S1</th>
<th>QNG-S2</th>
<th>QNG-S3</th>
<th>QNG-S4</th>
<th>QNG-S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>0.8499</td>
<td>0.9026</td>
<td>0.8034</td>
<td>0.847</td>
<td>0.85094</td>
</tr>
<tr>
<td>ethane</td>
<td>0.05529</td>
<td>0.05828</td>
<td>0.05189</td>
<td>0.05584</td>
<td>0.05529</td>
</tr>
<tr>
<td>propane</td>
<td>0.02008</td>
<td>0.02106</td>
<td>0.01878</td>
<td>0.01962</td>
<td>0.02009</td>
</tr>
<tr>
<td>isobutane</td>
<td>0.00401</td>
<td>0.00412</td>
<td>0.00384</td>
<td>0.00416</td>
<td>0.00401</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.00585</td>
<td>0.00641</td>
<td>0.00573</td>
<td>0.00553</td>
<td>0.00612</td>
</tr>
<tr>
<td>isopentane</td>
<td>0.00169</td>
<td>0.00214</td>
<td>0.00188</td>
<td>0.00214</td>
<td>0.00171</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.00147</td>
<td>0.00162</td>
<td>0.0014</td>
<td>0.00155</td>
<td>0.00141</td>
</tr>
<tr>
<td>n-octane</td>
<td>0.00152</td>
<td>0.00161</td>
<td>0.00145</td>
<td>0.0015</td>
<td>0.00152</td>
</tr>
<tr>
<td>toluene</td>
<td>0.0009</td>
<td>0.0011</td>
<td>0.00092</td>
<td>0.00098</td>
<td>0</td>
</tr>
<tr>
<td>methylcyclopentane</td>
<td>0.00102</td>
<td>0.00111</td>
<td>0.00092</td>
<td>0</td>
<td>0.00099</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.03496</td>
<td>0</td>
<td>0.06596</td>
<td>0.03711</td>
<td>0.03496</td>
</tr>
<tr>
<td>CO2</td>
<td>0.02331</td>
<td>0</td>
<td>0.0438</td>
<td>0.02457</td>
<td>0.02296</td>
</tr>
</tbody>
</table>
Results: Viscosity Comparison for QNG-S1

**QNG-S1 at -10 F (250 K)**
- **Experimental**
- **PR**
- **SRK**

**QNG-S1 at 80 F (300 K)**
- **Experimental**
- **PR**
- **SRK**

**QNG-S1 at 170 F (350 K)**
- **Experimental**
- **PR**
- **SRK**

**QNG-S1 at 260 F (400 K)**
- **Experimental**
- **PR**
- **SRK**
Results: Viscosity Comparison for QNG-S1 (cont.)

![Graph showing viscosities at 350 F (450 K) for QNG-S1]

- Experimental
- PR
- SRK
Results – Overall

Average Percentage of Absolute Difference from Empirical Viscosity Values

<table>
<thead>
<tr>
<th>Sample</th>
<th>QNG-S1</th>
<th>QNG-S2</th>
<th>QNG-S3</th>
<th>QNG-S4</th>
<th>QNG-S5</th>
<th>Average of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>ProMax SRK</td>
<td>2.98</td>
<td>3.52</td>
<td>2.03</td>
<td>3.01</td>
<td>2.89</td>
<td>2.89</td>
</tr>
<tr>
<td>ProMax PR</td>
<td>6.24</td>
<td>7.92</td>
<td>7.32</td>
<td>6.15</td>
<td>6.18</td>
<td>6.76</td>
</tr>
</tbody>
</table>

- SRK has lower average % deviation than PR for all samples
- But, the level of accuracy is dependent upon the T and P
ProMax SRK and PR

Both PR and SRK: Low P viscosity is calculated by the Chapman-Enskog relation.

Both PR and SRK: Pressure correction calculated by Dean-Stiel method.

The viscosity difference is due to the compressibility difference between the two.

The compressibility is utilized to obtain the density that is used in the Dean-Stiel pressure correction.

Viscosity of Natural Gas QNG-S1 at 170 F (350 K)

- Measured
- PR
- SRK
- no pressure correction
- Z-PR
- Z-SRK

Pressure, psia vs. Compressibility Factor vs. Viscosity, µPa-s
# Natural Gas Sample Compositions

<table>
<thead>
<tr>
<th>Component</th>
<th>QNG-S1</th>
<th>QNG-S2</th>
<th>QNG-S3</th>
<th>QNG-S4</th>
<th>QNG-S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>0.8499</td>
<td>0.9026</td>
<td>0.8034</td>
<td>0.847</td>
<td>0.85094</td>
</tr>
<tr>
<td>ethane</td>
<td>0.05529</td>
<td>0.05828</td>
<td>0.05189</td>
<td>0.05584</td>
<td>0.05529</td>
</tr>
<tr>
<td>propane</td>
<td>0.02008</td>
<td>0.02106</td>
<td>0.01878</td>
<td>0.01962</td>
<td>0.02009</td>
</tr>
<tr>
<td>isobutane</td>
<td>0.00401</td>
<td>0.00412</td>
<td>0.00384</td>
<td>0.00416</td>
<td>0.00401</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.00585</td>
<td>0.00641</td>
<td>0.00573</td>
<td>0.00553</td>
<td>0.00612</td>
</tr>
<tr>
<td>isopentane</td>
<td>0.00169</td>
<td>0.00214</td>
<td>0.00188</td>
<td>0.00214</td>
<td>0.00171</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.00147</td>
<td>0.00162</td>
<td>0.0014</td>
<td>0.00155</td>
<td>0.00141</td>
</tr>
<tr>
<td>n-octane</td>
<td>0.00152</td>
<td>0.00161</td>
<td>0.00145</td>
<td>0.0015</td>
<td>0.00152</td>
</tr>
<tr>
<td>toluene</td>
<td>0.0009</td>
<td>0.0011</td>
<td>0.00092</td>
<td>0.00098</td>
<td>0</td>
</tr>
<tr>
<td>methylcyclopentane</td>
<td>0.00102</td>
<td>0.00111</td>
<td>0.00092</td>
<td>0</td>
<td>0.00099</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.03496</td>
<td>0</td>
<td>0.06596</td>
<td>0.03711</td>
<td>0.03496</td>
</tr>
<tr>
<td>CO2</td>
<td>0.02331</td>
<td>0</td>
<td>0.0438</td>
<td>0.02457</td>
<td>0.02296</td>
</tr>
</tbody>
</table>
Aromatics and cyclic compounds

Previously,

- Observed the same effect on mixture viscosity for a fixed concentration with the inclusion of:
  - only toluene
  - only methylcyclopentane
  - both
- Concluded that aromatics and cyclic compounds should have the same effect on a mixture’s viscosity

### Average Percentage of Absolute Difference from Empirical Viscosity Values

<table>
<thead>
<tr>
<th>Sample</th>
<th>QNG-S1</th>
<th>QNG-S2</th>
<th>QNG-S3</th>
<th>QNG-S4</th>
<th>QNG-S5</th>
</tr>
</thead>
<tbody>
<tr>
<td>ProMax SRK</td>
<td>2.98</td>
<td>3.52</td>
<td>2.03</td>
<td>3.01</td>
<td>2.89</td>
</tr>
<tr>
<td>ProMax PR</td>
<td>6.24</td>
<td>7.92</td>
<td>7.32</td>
<td>6.15</td>
<td>6.18</td>
</tr>
</tbody>
</table>

- Appears SRK and PR appropriately predicts the analogous effect of the inclusion of toluene, methylcyclopentane, or both
Comparison with Previous Models (cont.)

Average Percentage of Absolute Difference from Empirical Viscosity Values

<table>
<thead>
<tr>
<th>Sample</th>
<th>PFCT</th>
<th>ProMax SRK</th>
<th>LBC</th>
<th>CLS</th>
<th>NBS</th>
<th>ProMax PR</th>
<th>Average of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>QNG-S1</td>
<td>2.5</td>
<td>2.98</td>
<td>3.6</td>
<td>4.68</td>
<td>5.86</td>
<td>6.24</td>
<td>2.36</td>
</tr>
<tr>
<td>QNG-S2</td>
<td>1.59</td>
<td>3.52</td>
<td>3.58</td>
<td>3.46</td>
<td>3.92</td>
<td>7.92</td>
<td>2.89</td>
</tr>
<tr>
<td>QNG-S3</td>
<td>2.89</td>
<td>2.03</td>
<td>4.13</td>
<td>5.4</td>
<td>6.7</td>
<td>7.32</td>
<td>3.672</td>
</tr>
<tr>
<td>QNG-S4</td>
<td>2.32</td>
<td>3.01</td>
<td>3.4</td>
<td>4.21</td>
<td>5.57</td>
<td>6.15</td>
<td>4.494</td>
</tr>
<tr>
<td>QNG-S5</td>
<td>2.5</td>
<td>2.89</td>
<td>3.65</td>
<td>4.72</td>
<td>5.96</td>
<td>6.18</td>
<td>5.602</td>
</tr>
</tbody>
</table>

- Inclusion of aromatic and cyclic compounds
- CO2 and N2: Effects on predictive capability

The effect of increasing CO2 and N2 concentrations on the mixture viscosity is more properly described by SRK, leading to lower deviations as CO2 and N2 concentrations increase. This was the opposite for the previous 4 models assessed – where instead, increasing CO2 and N2 concentrations were not well described, leading to higher deviations.
Conclusions About Viscosity

- Overall, SRK performs better than PR, and second best for all 6 models considered.

- Among the 6 models considered, had the largest deviations between experimental and predicted values for all samples.

  Deviations between experimental and predicted results of the models

  PFCT < SRK < LBC < CLS < NBS < PR

- Accuracy of predictions by PR is improved as the temperature increases.

- It appears that SRK and PR appropriately predicts the analogous effect of the inclusion of toluene, methylcyclopentane, or both.

- It appears that the presence of CO\textsubscript{2} and N\textsubscript{2} has an effect on the predictive capability of PR and SRK.
  - The relationship is more clear with SRK - increased CO\textsubscript{2} and N\textsubscript{2} in the ranges used improves accuracy.
  - This is opposite of the previous 4 models assessed – increased CO\textsubscript{2} and N\textsubscript{2} in the ranges used worsens the predictions.
Phase Envelopes
Isochoric Experiments

- Phase boundary measurements are important for process equipment design, i.e. compressors.
- Process performance check with the new measured data.
Isochoric Apparatus

Schematic of isochoric apparatus.

Schematic of isochoric cell.
Isochoric Experiments

\[
\frac{V(T, P)}{V_o(T_o, P_o)} = 1 + (P - P_o) + (T - T_o)
\]
78% Phase Loops

(a) Isochoric experimental data
(b) Experimental phase envelope and EOS for M78C1 (symbols: + PR; Δ SRK; □ experimental).
88% and 94% Mixture Experimental

Figure. Isochoric apparatus data and experimental phase envelope for (a) 88% and (b) 94%
(a) Symbols: (○) isochore 1, (□) isochore 2, (△) isochore 3, (×) isochore 4, (※) isochore 5
 (+) isochore 6, (-) isochore 7, (−) isochore 8, (■) isochore 9, (▲) isochore 10,
 and (●) experimental phase envelope.
88% and 94% Experimental vs EOS

**Figure.** Experimental phase envelopes in comparison with EOS predictions.
## Cricondentherm and Cricondenbar

### TABLE. Experimental cricondentherm and cricondenbar in comparison with EOS predictions. Deviations between experimental and EOS data are reported parenthesized for comparison purposes.

<table>
<thead>
<tr>
<th></th>
<th>Cricondentherm</th>
<th>Cricondenbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T / K</td>
<td>P / MPa</td>
</tr>
<tr>
<td><strong>M88C1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>experimental</td>
<td>312.9</td>
<td>5.3</td>
</tr>
<tr>
<td>SRK</td>
<td>309.5 (-3.4)</td>
<td>4.6 (-0.7)</td>
</tr>
<tr>
<td>TRK</td>
<td>309.6 (-3.3)</td>
<td>4.7 (-0.6)</td>
</tr>
<tr>
<td>PR</td>
<td>306.7 (-6.2)</td>
<td>4.3 (-1.0)</td>
</tr>
<tr>
<td>TPR</td>
<td>307.6 (-5.3)</td>
<td>4.3 (-1.0)</td>
</tr>
<tr>
<td>PT</td>
<td>306.5 (-6.4)</td>
<td>4.2 (-1.1)</td>
</tr>
<tr>
<td>SW</td>
<td>306.7 (-6.2)</td>
<td>4.3 (-1.0)</td>
</tr>
<tr>
<td>MMM</td>
<td>309.3 (-3.6)</td>
<td>4.7 (-0.6)</td>
</tr>
<tr>
<td>GD</td>
<td>307.8 (-5.1)</td>
<td>4.4 (-0.9)</td>
</tr>
<tr>
<td>SAFT</td>
<td>309.7 (-3.2)</td>
<td>5.4 (0.1)</td>
</tr>
<tr>
<td>PC-SAFT</td>
<td>309.2 (-3.7)</td>
<td>4.3 (-1.0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Cricondentherm</th>
<th>Cricondenbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T / K</td>
<td>P / MPa</td>
</tr>
<tr>
<td><strong>M94C1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>experimental</td>
<td>306.6</td>
<td>4.6</td>
</tr>
<tr>
<td>SRK</td>
<td>299.2 (-7.4)</td>
<td>4.4 (-0.2)</td>
</tr>
<tr>
<td>TRK</td>
<td>299.3 (-7.3)</td>
<td>4.5 (-0.1)</td>
</tr>
<tr>
<td>PR</td>
<td>296.4 (-10.2)</td>
<td>4.1 (-0.5)</td>
</tr>
<tr>
<td>TPR</td>
<td>297.5 (-9.1)</td>
<td>4.1 (-0.5)</td>
</tr>
<tr>
<td>PT</td>
<td>296.5 (-10.1)</td>
<td>4.0 (-0.6)</td>
</tr>
<tr>
<td>SW</td>
<td>296.7 (-9.9)</td>
<td>4.1 (-0.5)</td>
</tr>
<tr>
<td>MMM</td>
<td>299.1 (-7.5)</td>
<td>4.5 (-0.1)</td>
</tr>
<tr>
<td>GD</td>
<td>297.6 (-9.0)</td>
<td>4.2 (-0.4)</td>
</tr>
<tr>
<td>SAFT</td>
<td>296.4 (-10.2)</td>
<td>4.7 (0.1)</td>
</tr>
<tr>
<td>PC-SAFT</td>
<td>298.7 (-7.9)</td>
<td>4.1 (-0.5)</td>
</tr>
</tbody>
</table>
SNG-1-2-3-4 Phase Envelopes

![Graph showing phase envelopes for SNG Project with temperature on the x-axis and pressure on the y-axis.](image)

<table>
<thead>
<tr>
<th>Component</th>
<th>SNG-1</th>
<th>SNG-2</th>
<th>SNG-3</th>
<th>SNG-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.89982</td>
<td>0.89990</td>
<td>0.89975</td>
<td>0.90001</td>
</tr>
<tr>
<td>ethane</td>
<td>0.03009</td>
<td>0.03150</td>
<td>0.02855</td>
<td>0.04565</td>
</tr>
<tr>
<td>propane</td>
<td>0.01506</td>
<td>0.01583</td>
<td>0.01427</td>
<td>0.02243</td>
</tr>
<tr>
<td>2-methylpropane</td>
<td>0.00752</td>
<td>0.00781</td>
<td>0.00709</td>
<td>0.01140</td>
</tr>
<tr>
<td>butane</td>
<td>0.00753</td>
<td>0.00790</td>
<td>0.00722</td>
<td>0.01151</td>
</tr>
<tr>
<td>2-methylbutane</td>
<td>0.00300</td>
<td>0.00150</td>
<td>0.00450</td>
<td>0.00450</td>
</tr>
<tr>
<td>pentane</td>
<td>0.00300</td>
<td>0.00150</td>
<td>0.00450</td>
<td>0.00450</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.01697</td>
<td>0.01699</td>
<td>0.01713</td>
<td>-</td>
</tr>
<tr>
<td>carbon dioxide</td>
<td>0.01701</td>
<td>0.01707</td>
<td>0.01699</td>
<td>-</td>
</tr>
</tbody>
</table>
Facilities – Qatar University

Pressures up to 5000 psi
Temperatures 250 K ~ 450 K
Facilities – University of Burgos

- Pump temp. control
- Heated tubing
- Tubing temperatures (thermocouples)
- Pirani gauge (vacuum reading)
- ISCO 100DX Syringe pump
- Anton Para DMA512 High P. vibrating tube
- Edwards RV3 rotary vane vacuum pump
Facilities – Texas A&M University

Magnetic Suspension Densimeter Data Acquisition (Temperature)

Low P
High P
Isochoric Apparatus
Natural Gas Hydrates
Motivation

Qatar holds the world’s third-largest reserves of natural gas at 890 trillion cubic feet according to proven reserves in the latest report of Oil and Gas Journal in 2013.
Hydrate was first discovered by Sir. Humphrey Davy in 1810.

Hammershmidt defined hydrate as an irritant for the natural gas industry in 1934.

QU & TAMUQ Research Team started studying the hydrate of Qatar Natural Gas.

Hydrate were found to plug large offshore pipelines in the 1970s.

Hydrate plugs were discovered to form mostly after shut-in and restart of pipelines and wells in the last two decades.
Clathrates of nature gas, commonly called gas hydrates, are ice-like compounds and have crystalline structures that are formed with the proper combination of small guest molecules, such as methane, ethane, propane, carbon dioxide, and hydrogen sulfide, which are trapped in cavities of a hydrogen-bonded water framework.
What is Gas Hydrate?

1. recovering global warming gases, such as CO\(_2\) and H\(_2\)S from flue gas
2. recovering methane from low-concentration coal mine methane
3. recovering organic contaminants from gaseous or aqueous mixtures

**INDUSTRIAL APPLICATION**

**Gas mixture separation**

- Volumetric proportions between water and gas in a methane hydrate
  
<table>
<thead>
<tr>
<th>Gas</th>
<th>Water</th>
<th>Hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>164 m(^3)</td>
<td>0.8 m(^3)</td>
<td>1 m(^3)</td>
</tr>
</tbody>
</table>

**Storage and transportation**
CHEMICAL HYDRATE INHIBITION

Thermodynamic Hydrate Inhibitors
- High volumes (10-60 wt%)
- Toxic/hazardous
- Environmentally harmful
- Robust & effective
- Well understood
- Predictable

Kinetic Hydrate Inhibitors
- Low volumes (<1wt %)
- Non-toxic
- Environmentally friendly
- Time dependency
- Limited exp. In oil system
- No predictive models

Anti-agglomerants
- Low volumes (<1wt %)
- Non-toxic
- Environmentally friendly
- Time dependency
- Limited experience
- No predictive models
Hydrate Research Project Objectives

• Commissioning Micro bench top reactor as a typical hydrate cell
• Acquiring HLVE data for two types of QNG mixture
• Investigate the thermodynamic and kinetic performance of Choline Chloride.
• Comparing the performance of Choline Chloride with Classical thermodynamic inhibitor “Methanol” obtained using HydraFLASH software
• Studding the influence of memory effect on induction time
in late 2012 micro bench top reactor was commissioned after it was redesigned to act as a hydrate cell and calibrated using pure Ch₄ and CO₂ to verify its performance and efficiency before it was used in gathering QNG-S1 hydrate equilibrium points.
Micro Bench Top Reactor

- **Micro bench top reactor modification**
  - **Re-designing the heating system**
    - Movable Heater → Heater Aluminum Block
  - **Re-designing heating & cooling system**
    - Internal heating system → External water bath heating system
  - **Re-designing experimental set-up connection**
    - Rubber Tubing → Metal Tubing

---

**Diagram Elements:**
- **Reaction Cell**
- **Hydrate Cell**
Autoclave is a typical hydrate cell. It is mainly used to visualize the whole hydrate formation/dissociation process. It was used in gathering QNG-S1 hydrate equilibrium points.
RC-5 is a typical hydrate cell. It contains 5 test cell that can run simultaneously. It is used in this study to test ionic liquid performance form thermodynamic and kinetic points of view.
Hydrate Equilibrium Predicting Software

**HydraFlash** software is utilized to provide an initial estimation HLVE data using different models such as standard equation of state. In this work cubic plus association equation of state (CPA) was applied because it has better performs for components that can form hydrogen bonds such as water and methanol.

![HydraFlash Software Interface](image1)

![Hydrate Equilibrium Results](image2)

![Hydrate Dissociation Pressure vs. Temperature](image3)
Hydrate Equilibrium Study

Thermodynamic point of view

- Hydrate Liquid vapor equilibrium

Kinetic point of view

- Induction time
Hydrate Liquid vapor equilibrium (HLVE) curve

Hydrate Equilibrium Study

Hydrogen bond between water molecule and van der Waals interaction forces between gas and water molecule were broken.
PROCEDURE
Induction time is obtained using pressure-time relationship.

Induction time = catastrophic pressure drop time – HLVE point time
Micro bench top reactor was calibrated using methane and carbon dioxide. A small deviation of less than 2 °C was observed compared with past research and theoretical calculation methods.
### Qatar natural gas mixture (QNG-S1)

**HLVE curves obtained using Micro Bench Top Reactor**

<table>
<thead>
<tr>
<th>No.</th>
<th>Component</th>
<th>QNG-S1 mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane</td>
<td>0.84990</td>
</tr>
<tr>
<td>2</td>
<td>Ethane</td>
<td>0.05529</td>
</tr>
<tr>
<td>3</td>
<td>Propane</td>
<td>0.02008</td>
</tr>
<tr>
<td>4</td>
<td>2-methylpropane</td>
<td>0.00401</td>
</tr>
<tr>
<td>5</td>
<td>Butane</td>
<td>0.00585</td>
</tr>
<tr>
<td>6</td>
<td>2-methylbutane</td>
<td>0.00169</td>
</tr>
<tr>
<td>7</td>
<td>Pentane</td>
<td>0.00147</td>
</tr>
<tr>
<td>8</td>
<td>Octane</td>
<td>0.00152</td>
</tr>
<tr>
<td>9</td>
<td>Toluene</td>
<td>0.00090</td>
</tr>
<tr>
<td>10</td>
<td>Methylcyclopentane</td>
<td>0.00102</td>
</tr>
<tr>
<td>11</td>
<td>Nitrogen</td>
<td>0.03496</td>
</tr>
<tr>
<td>12</td>
<td>Carbon Dioxide</td>
<td>0.02331</td>
</tr>
</tbody>
</table>

#### Mixture Gas Hydrate Equilibrium

**Graph**

- **Experiment Loop 1**
- **Experiment Loop 2**
- **SG Method: Plain - QNG-S1**
- **HLVE-HydrFLASH - Plain - QNG-S1**

**Axes**

- **Temperature (°C)**
- **Pressure (bar)**
Mixture Gas Hydrate Equilibrium

High-pressure Autoclave

- The measured HLVE shows a good agreement with HydraFLASH and gas gravity method.
- Autoclave vs. Micro bench top reactor shows a deviation less than 1 °C, which confirm the success of building hydrate cell from reaction cell.
Choline Chloride performance (1 wt% vs. 5 wt%)

- 1 wt.%: **up to 1.0 °C** for Autoclave
  **up to 1.8 °C** for Micro bench
- 5 wt.%: **up to 2.0 °C** for Autoclave
  **up to 2.7 °C** for Micro bench

Choline Chloride performance vs. Methanol

- 1 wt.%: **up to 1.0 °C** for ChCl
  **up to 2.8 °C** for MEOH
- 5 wt.%: **up to 2.0 °C** for ChCl
  **up to 4.4 °C** for MEOH
Ionic Liquid and Induction Time Effect

Effect of choline chloride on induction time

Induction time increased for higher concentration from 1.75 h for 1 wt. % to 2.15 h for 5 wt. % at starting pressure of 60 bar.
Gas Hydrate Summary

Commissioning of micro bench top reactor as a typical hydrate cell with deviation of 2 °C from theoretical and less than 1 °C from autoclave.

Obtaining HLVE curve of a typical QNG-S1, A frontier academic achievement in Qatar.

ChCl has proved to have a dual function, as it was able to shift HLVE curve up to 2 °C with 5 wt.% and prolong induction time by 22 %.

Memory effect can be eliminated by applying Isothermal heating step up to 30 °C.

ChCl is not as efficient as Methanol, but when the amount of inhibitor used, toxicity levels and corrosion effects are considered ionic liquids still are good candidates.

HydraFlash is good for initial estimation of HLVE condition, however, deviations up to 5% was observed for QNG-S1. This might be due to the insufficient level of programming for any arbitrary complex multi-component gas mixture.
Environmental Related Issues

$\text{CO}_2$ Capture
Power Generation

Sources as they apply to 24 hour

- Coal: 12 hours
- Natural Gas: 5 hours
- Nuclear: 5 hours
- Hydropower: 1.5 hours
- Wind: 18 minutes
- Petroleum: 16 minutes
- Biomass: 9 minutes
- Geothermal: 5 minutes
- Solar: 21 seconds

Coal	 Natural Gas	 Nuclear	 Hydropower	 Wind	 Petroleum	 Biomass	 Geothermal	 Solar
Global energy use accounts for over 85% of the 37 Gt of CO$_2$ released to the atmosphere annually.
Then, what happens?...

Science warns of a 450 ppm upper limit. Emissions are rising at over 2 ppm per year.
**CAPTURE**

$\text{CO}_2$ is captured from large emission sources, including:
- Coal-fired power plants,
- Oil and gas operations (including oil sands upgraders and refineries),
- Other industrial activities such as chemical, fertilizer and cement.

**STORAGE**

$\text{CO}_2$ is injected at a depth of 1 – 5 kilometres into deep underground rock formations where it is permanently stored. A barrier of impermeable rock and natural chemical interactions ensures long-term storage.

Geological formations used for storage include:
- Depleted oil or gas reservoirs
- Saline Formations
- Coal seams

*Not to scale*
Cost – Learning Curve

Learning Curve Example
Flue Gas Desulphurization

Problem(s)?

“If you are looking for a nice academic/industrial/environmental problem to work on, CO₂ capture is a great one!”

*Paul Alisivatos & Michelle Buchanan*
CO$_2$ Capture Perspective

Various Opinions: *Politicians vs. Academicians*

A Politician's definition of “Clean Energy”
Grand Challenges of the 21st Century

**Environment**

- **Greenhouse gases**
  - CO₂ levels will reach ~500 ppm by 2050 (460 ppm is the point of no return)
  - Ocean floor has more carbon (in CH₄) than all fossil fuels combined

**Sustainability**

- **Accessible technologies**
  - Lack of accessible and sustainable technologies
  - Higher energy prices
  - Expensive infrastructure maintenance

+ Energy
+ Water
Where is the problem?

**Big Picture of the CO2 Cycle**
human activity vs. nature activity

**A modern day example**
Dissecting a fossil fuel power plant

Permissible exhaust fume: CO2, H2O, N2, O2

- Target CO2 capture locations:
  - Post combustion
  - Pre combustion

- Solving one problem shall not produce another problem

- Thermodynamically appreciable solutions
Current Status

**Pre-combustion**

http://millicentmedia.com/

**Oxy-Fuel**

http://millicentmedia.com/

**Post-combustion**

http://www.ico2n.com/
Chemical Engineers are conservative: Amine Process

- Gas-liquid interface controls kinetic studies of structure and dynamics
- Can complex fluids be employed?

- Can the non-ideal solution behavior in mixtures be predicted and exploited?
- Can chemically / thermally stable materials be designed with high and reversible reactivity and specificity? Ionic Liquids...

Membranes

Polymer membranes are used in many gas separation applications such as:

- Natural gas treatment (removal of CO$_2$ before the natural gas can be passed to the pipeline)
- Hydrogen isolation and recovery
- Air separation as oxygen enrichment from air (medical devices)
- Nitrogen enrichment from air (used as a protecting atmosphere for oxygen sensitive compounds)
Membranes

• Separation based on selective permeation of targeted gas:
  – Selectivity based on relative solubility and diffusivity in membrane
  – Selectivity is not 100%
• **Trade-off on selectivity and permeability** (need to have both)
• Change in **pressure needed to drive separation**
• Can new materials be designed with nano-scale structures to enhance transport and selectivity?
• How can chemical and physical properties be used to design new membrane materials for **enhanced performance**?

Robeson Plot

Schematic presentation of the trade-off between permeability and selectivity with the 1991 and 2008 Robeson upper bounds.

Mixed Matrix Membranes
Adsorbents: High Temperature & High Pressure

ChemSusChem 2009, 2, 796 – 854

Angew. Chem., 2010, 49, 6058 – 6082
Tunable Properties

- Continuous innovation in control of:
  - Pore structure/ connectivity
  - Dimensionality and symmetry
  - Adsorbate site interactions

- Porous solid adsorbent material can be designed to be highly size- and shape-selective.
Atilhan Group

COFs
MOFs
Zeolites
DLH
Amines
Ionic Liquids
Urea
MCO₃
Prussian Blue

Department of Chemical Engineering
Rubotherm ® Magnetic Suspension Balance Assembly Atilhan Lab, Qatar University

Rubotherm ® Gmbh
Magnetic Suspension Sorption Apparatus (top-left)
Magnetic Suspension Thermal Analyzer (bottom-left – Gas Processing Center, Qatar University)
Rubotherm® Magnetic Suspension Balance (MSB). Photos of the magnetic suspension assembly, sample container basket, measuring cell and the magnetic coupling housing.
High Pressure Sorption Apparatus
Magnetic suspension sorption apparatus screenshots at, (a) vacuum and, (b) under pressure measurement.
Schematics of magnetic suspension sorption apparatus operating principle. (A) sample loaded to measuring basket in high pressure cell; (B) Measurement point 1 (MP1) – magnetic coupling is on and mass of the sample is measured; (C) Measurement point 2 (MP2) – in–situ density of the adsorbed gas is measured.
High Pressure Sorption Apparatus

• Adsorption data is analyzed and the amount of adsorbed gas on the sample is calculated by using the equation below:

\[ W + W_{buoy,sample} + W_{buoy,sink} = m_{ads} + m_{sample} + m_{sink} \]

where:
- \( W \) = Signal read by the instrument
- \( W_{buoy,sample} = V_{sample} * d_{gas} \) = Buoyancy correction due to the sample
- \( V_{sample} \) = Volume of the sample
- \( V_{sample} = V_{total} - V_{pore} \)
- \( d_{gas} \) = Density of the gas
- \( W_{buoy,sink} = V_{sinker} * d_{gas} \) = Buoyancy correction due to the sinker
- \( V_{sinker} \) = Volume of the sinker
- \( m_{ads} \) = Surface excess mass of the CO\(_2\)
- \( m_{sample} \) = Mass of the sample
- \( m_{sink} \) = Mass of the sinker

• \( d_{gas} \) is measured \textit{in situ} and the mass of empty sinker is measured at several pressures of helium to determine the buoyancy caused by the sinker (\( W_{buoy,sink} \)). Volume of the sinker (\( V_{sinker} \)) is calculated from the slope of weight vs. density plot obtained from this measurement. A blank measurement at vacuum is performed to determine the mass of the sinker (\( m_{sink} \)).
TEE Lab

Laboratory general view
Atilhan Lab, Qatar University

Bruker ® D2 Phaser XRD
Bruker ® Vertex 80 Far+Near FTIR
Perkin Elmer ®, GC-MS
Organic Engineering for Effective CO\textsubscript{2} Capture: Amidoximes I

Amidoxime functionality

The lowest energy structures of the (a) CO\textsubscript{2}-AAO and (b) CO\textsubscript{2}-methyl-MEA complexes with comparable binding energies (BE).

Chemical structures of the amidoximes studied in this work
Amidoximes I - CO₂ capture data

(a) & (b) CO₂ adsorption isotherms (mmol g⁻¹) for AAO (---), TPAO (-----) and TQAO (-----) at 43°C and 70°C

(c) & (d) CO₂ adsorption isotherms (mmol m⁻²) for PAO (---) and Activated Charcoal Norit RB3 (-----) at 43°C and 70°C

... Amdioximes II

Atilhan, RSC Adv., 2013, 3, 17203
... Amdioximes II – CO₂ Capture Data
Porous Organic Polymers
Cyanuric Organic Polymers/Frameworks: COPs or COFs
High pressure (200 bar) CO₂ and low pressure N₂ adsorptions for COPs and well-known porous materials, MOF-5 and Activated Carbon. CO₂ adsorption (filled symbol) – desorption (open symbol) isotherms at (A) 318 K, (B) 328 K, (C) 338 K.
Characterization

Thermal stability and recyclability of COPs. (a) TGA of COPs in air. **Inset**: BET surface area change upon boiling COPs in H₂O (100 °C) for 1 day, 3 days and 1 week. (b) Low pressure (1 bar) CO₂ adsorption capacities of COPs were unchanged over boiling in H₂O. (c) Multi-cycle study of high pressure CO₂ adsorption capacity for COP-1 at 318 K up to 200 bar. After each compression, system was depressurized to vacuum and allowed to be degassed completely.
Selectivity: CO$_2$/H$_2$

<table>
<thead>
<tr>
<th>CO$_2$/H$_2$</th>
<th>30 bar</th>
<th>100 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>COP-1</td>
<td>465</td>
<td>1,031</td>
</tr>
<tr>
<td>COP-2</td>
<td>&gt;2,231</td>
<td>&gt;10,480</td>
</tr>
</tbody>
</table>

$H_2$ at 298 K

a

Quantity adsorbed / mg.g$^{-1}$

Pressure / bar
# Comparison: Surface Area / CO₂ capture / Cost

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (_{\text{BET}}) (\text{m}^2\text{.g}^{-1})</th>
<th>Total CO₂ (\text{P in bar})</th>
<th>Total CO₂ (\text{T in K})</th>
<th>Materials cost (\text{$kg}^{-1}\text{CO}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COP-1</td>
<td>168</td>
<td>5,616</td>
<td>200</td>
<td>318</td>
</tr>
<tr>
<td>COP-2</td>
<td>158</td>
<td>2,086</td>
<td>200</td>
<td>318</td>
</tr>
<tr>
<td>PPN-4</td>
<td>6,461</td>
<td>2,121</td>
<td>50</td>
<td>298</td>
</tr>
<tr>
<td>PAF-1</td>
<td>5,600</td>
<td>1,585</td>
<td>40</td>
<td>298</td>
</tr>
<tr>
<td>COF-102</td>
<td>3,620</td>
<td>1,200</td>
<td>55</td>
<td>298</td>
</tr>
<tr>
<td>HCP-1</td>
<td>1,646</td>
<td>585</td>
<td>30</td>
<td>298</td>
</tr>
<tr>
<td>BILP-1</td>
<td>1,172</td>
<td>130</td>
<td>1</td>
<td>298</td>
</tr>
<tr>
<td>POF1B</td>
<td>917</td>
<td>92</td>
<td>1</td>
<td>298</td>
</tr>
<tr>
<td>MEA</td>
<td>N/A</td>
<td>117</td>
<td>24</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>1</td>
<td>298</td>
</tr>
</tbody>
</table>
Sulfur bridged COPs

COP-3
SA_BET: 413 m² g⁻¹
CO₂: 3294 mg g⁻¹; CO₂/N₂: 151

1,3,5-benzenetrithiol

COP-4
SA_BET: 54 m² g⁻¹
CO₂: 33 mg g⁻¹; CO₂/N₂: 24.7

1,4-benzenedithiol

COP-5
SA_BET: 75 m² g⁻¹
CO₂: 24 mg g⁻¹; CO₂/N₂: 18.1

Biphenyl-4,4'-dithiol

Cyanuric chloride

COP-6
SA_BET: 15 m² g⁻¹
CO₂: 20 mg g⁻¹; CO₂/N₂: 65.8

4,4'-thiobisbenzenethiol

COP-3
Characterization

Solid state (a) CP/MAS $^{13}$C–NMR spectra, (b) $^1$H–NMR spectra and relative assignments of the respective structures, (c) FTIR spectra for COP–3 and (d) Thermogravimetric analysis for COP–3 in air and nitrogen.
(a) High pressure CO\textsubscript{2} adsorptions for COP–3 measure at 318, 328 and 338 K up to 200 bar. CO\textsubscript{2} adsorption (filled symbols)–desorption (open symbols). Theoretical simulated isotherms (dashed lines) show similar shapes and temperature dependency as experimental isotherms.

(b) Effect of boiling in H\textsubscript{2}O on BET surface area and low pressure CO\textsubscript{2} adsorption capacities.
New COPs

2,4,6-trichloro-triazine

Possible linker geometries
What to do with captured CO$_2$?

- Conversion to MeOH or MeOH-derived products
- Chemical transformation of CO$_2$ is not only about mitigating the "side-effects of emissions", rather it’s about recycling of the "carbon".
- Current MeOH synthesis required up to 100 bars (Cu or Zn catalysts)
- Energy efficiency of current tech is almost independent of high pressures as it compensates for lower reactor volumes (construction cost) and chemical plant footprint cost. ([Journal of Supercritical Fluids, 78, 2013])
- Leads to safe handling of H as it will be required less amounts.
- Boost the catalytic activity ([Journal of Catalysis, 309, 2014])
- CCS pipeline transportation
More...

3,3'-Diaminobenzidine

Nitrilotriacetic acid

3,3'-Diaminobenzidine

Trimesic acid

AD-2

AD-6

Adsorption
Desorption

Quantity Adsorbed (mol/L STP)

Relative pressure (P/Po)

Quantity adsorbed (mol/g)

Relative pressure (P/Po)
More... Membrane Separation

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Sample Code</th>
<th>Concentration (wt%)</th>
<th>Polysulfone (wt%)</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>[P4441][formate]</td>
<td>SLESEM-02</td>
<td>0.10</td>
<td>20.0</td>
<td>SEM (surface &amp; cross-sec)</td>
</tr>
<tr>
<td></td>
<td>SLESEM-03</td>
<td>0.25</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-04</td>
<td>0.50</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-05</td>
<td>0.75</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-06</td>
<td>1.00</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>[DIP-C3mim][NTf2]</td>
<td>SLESEM-07</td>
<td>0.01</td>
<td>20.0</td>
<td>SEM (surface &amp; cross-sec)</td>
</tr>
<tr>
<td></td>
<td>SLESEM-08</td>
<td>0.05</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-09</td>
<td>0.10</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-10</td>
<td>0.25</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-11</td>
<td>0.50</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>[C.3mim][NTf2]</td>
<td>SLESEM-12</td>
<td>0.01</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-13</td>
<td>0.05</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-14</td>
<td>0.10</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-15</td>
<td>0.25</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-16</td>
<td>0.50</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>[N4441][formate]</td>
<td>SLESEM-17</td>
<td>0.01</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-18</td>
<td>0.05</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-19</td>
<td>0.10</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-20</td>
<td>0.25</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SLESEM-21</td>
<td>0.50</td>
<td>20.0</td>
<td></td>
</tr>
</tbody>
</table>

![Graph showing CO2/N2 selectivity vs. P (CO2) barrier](image)
High Pressure CO$_2$ Capture: Hydroxy Metal Carbonates

![Graph showing CO$_2$ amount vs. pressure for different compounds]

<table>
<thead>
<tr>
<th>compound</th>
<th>corresponding mineral</th>
<th>molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn]</td>
<td>hydrozináte</td>
<td>Zn$_5$(CO$_3$)$_2$(OH)$_6$</td>
</tr>
<tr>
<td>[ZnMg-1]$^a$</td>
<td>hydrozináte</td>
<td>Zn$<em>4$Mg$</em>{0.714}$(CO$_3$)$_2$(OH)$_6$</td>
</tr>
<tr>
<td>[ZnMg-2]$^a$</td>
<td>hydrozináte</td>
<td>Zn$<em>4$Mg$</em>{0.83}$ (CO$_3$)$_2$(OH)$_6$</td>
</tr>
<tr>
<td>[ZnMg-3]$^a$</td>
<td>hydrozináte</td>
<td>Zn$_4$Mg$_1$(CO$_3$)$_2$(OH)$_6$</td>
</tr>
<tr>
<td>[Mg]</td>
<td>hydromagnesite</td>
<td>Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O</td>
</tr>
<tr>
<td>[MgCu]$^a$</td>
<td>mcguinnessite</td>
<td>Mg$<em>{1.5}$Cu$</em>{0.5}$(CO$_3$)(OH)$_2$</td>
</tr>
<tr>
<td>[Cu]</td>
<td>malachite</td>
<td>Cu$_2$(CO$_3$)(OH)$_2$</td>
</tr>
<tr>
<td>[Ni]</td>
<td>nullaginite</td>
<td>Ni$_8$(CO$_3$)$_2$(OH)$_2$</td>
</tr>
<tr>
<td>[Pb]</td>
<td>hydrocerussite</td>
<td>Pb$_2$(CO$_3$)(OH)$_2$</td>
</tr>
</tbody>
</table>

$^a$ The metal content was determined by ICP-OES analysis.

<table>
<thead>
<tr>
<th>compd</th>
<th>CO$_2$ Adsorption (mmol/g) at 43 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P = 35 bar</td>
</tr>
<tr>
<td>Zn$_5$(CO$_3$)$_2$(OH)$_6$</td>
<td>0.31</td>
</tr>
<tr>
<td>Zn$<em>4$Mg$</em>{0.714}$(CO$_3$)$_2$(OH)$_6$</td>
<td>0.28</td>
</tr>
<tr>
<td>Zn$<em>4$Mg$</em>{0.83}$(CO$_3$)$_2$(OH)$_6$</td>
<td>0.33</td>
</tr>
<tr>
<td>Zn$_4$Mg$_1$(CO$_3$)$_2$(OH)$_6$</td>
<td>0.4</td>
</tr>
<tr>
<td>Mg$_5$(CO$_3$)$_4$(OH)$_2$·4H$_2$O</td>
<td>0.61</td>
</tr>
<tr>
<td>Mg$<em>{1.5}$Cu$</em>{0.5}$(CO$_3$)(OH)$_2$</td>
<td>0.74</td>
</tr>
<tr>
<td>Cu$_2$(CO$_3$)(OH)$_2$</td>
<td>0.14</td>
</tr>
<tr>
<td>Ni$_8$(CO$_3$)$_2$(OH)$_2$</td>
<td>0.43</td>
</tr>
<tr>
<td>Pb$_2$(CO$_3$)(OH)$_2$</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*Langmuir, 27, 2011*
CO₂ Adsorption on Mesoporous Commercial MOFs

Free volume in the studied basolites.

Comparison between experimental and predicted (Monte Carlo simulations) adsorption isotherms at as a function of temperature for the studied basolite sorbents. Symbols: filled circles show experimental data, and lines predicted data.

*Microporous and Mesoporous Materials, 175, 2013*
Limits of MOFs

![Image of MOF 5]

**Air Exposure**

**High Pressure**

**Nanoindentation**

![Graphs showing changes in BET surface area and pore size over time](image)

![Graphs showing CO$_2$ adsorption capacity under different conditions](image)

RSC Advances, 3, 2013
Prussian Blue Analogues

Free volume in Co$_3$Fe$_2$ showing the differences between small and large pores. The shape of the available volume in large pores should be remarked.

Comparison between experimental and predicted (Monte Carlo simulations) adsorption isotherms at 318 K for the studied Prussian blue analogues. Symbols: filled circles show experimental data, and lines predicted data.

Calculated isodensity surfaces (red surfaces) for CO$_2$ molecules in Mn$_3$Fe$_2$ at 318 K and (a) 1 and (b) 50 bar. Red and green dashed lines show CO$_2$ distribution in small and large pores, respectively.

Microporous and Mesoporous Materials, 162, (1) 2012
**CO₂ Solubility in Ionic Liquids at High Pressures**

**Imidazolium Based Ionic Liquids: Experimental and Simulation Approaches**

Swelling effect on each ionic liquid was calculated and corrected.
1-butyl-3-methylimidazolium hexafluorphosphate, [bmim][PF₆],
1-ethyl-3-methylimidazolium bis[ trifluoromethylsulfonyl]imide, [emim][Tf₂N]
1-butyl-3-methylimidazolium bis[ trifluoromethylsulfonyl]imide, [bmim][Tf₂N]

Isothermal experimental solubility data of CO₂ in the studied ionic liquids.
Swelling corrected for high pressure CO₂ absorption data.

*Fluid Phase Equilibria, 2013, 74-86 (351)*
*Energy Fuels, 2010, 24 (11), pp 5817–5828*
*Energy Fuels, 2010, 24 (9), pp 4989–5001*
In-Situ High Pressure FTIR Analysis for CO2 Capture Chemistry

COP-3 in situ IR analysis to see CO₂ strech locations (preliminary raw data)
A hydrotalcite material promoted with $K_2CO_3$ and $Ga^{+3}$ substitution has three times higher CO$_2$ capture capacity.
Ga substituted Hydrotalcites

\[ x(1-y)\text{Al}^{3+} + xy\text{Ga}^{3+} + \text{Mg}^{2+} + x\text{CO}_3^{2-} + 2\text{OH}^- \rightarrow \text{Mg}_{1-x}M_{xy}\text{Al}_{x(1-y)}(\text{OH})_2(\text{CO}_3)_x\cdot n\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Ga-LDH</th>
<th>(M%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ga5]</td>
<td>5</td>
</tr>
<tr>
<td>[Ga10]</td>
<td>10</td>
</tr>
<tr>
<td>[Ga50]</td>
<td>50</td>
</tr>
<tr>
<td>[Ga100]</td>
<td>100</td>
</tr>
</tbody>
</table>

We studied Ga, La, Ce, Y based HTLC in this project. The results for Ga HTLC are available and presented.

Expected XRD pattern for HTLCs

XRD results for this work
FTIR and TGA Characterization

**H-O-H stretch**  **CO stretch**

**Ga-LDH**

**Expected and experimented IR patterns for HTLCs**

**Experimented TGA patterns**

\[
\text{Mg}_{1-x}\text{Ga}_x\text{(OH)}_2\text{(CO}_3)_x\cdot n\text{H}_2\text{O} \\
\Delta \\
\text{H}_2\text{O(g)} \\
\Delta \\
\text{Mg}_{1-x}\text{Ga}_x\text{(OH)}_2\text{(CO}_3)_x \\
\text{(1-x)MgO + (x)Ga}_2\text{O}_3 \\
\]

196
CO₂ Sorption at high pressures

High pressure CO₂ sorption on experimented Ga-100 HTLC.

[Ba100] adsorbs 8.24 mmol/g of CO₂ at 43°C and 200 bars.

<table>
<thead>
<tr>
<th>BET Surface Area (m²/g)</th>
<th>43.6354</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.172598</td>
</tr>
</tbody>
</table>

Department of Chemical Engineering
CO2 Sorption at high temperatures

High temperature CO$_2$ sorption on experimented HTLCs (Ga-100)

High temperature CO$_2$ sorption contour plot. Most efficient region is 150 °C and 20 bars.
CO$_2$ Sorption Studies: Chemisorption or Physiosorption?
Group...
Theoretical and Experimental Evaluation of Natural Gas Properties & Environmental Issues

Gas and Fuels Research Initiative
Mert Atilhan
Qatar University & TAMUQ
March 26, 2014
Houston, TX