Mercury Removal From Gas Streams Using New Solid Adsorbents

PETRONAS in Collaboration with Queens University, Belfast

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Presentation Outline

- Background on PETRONAS and QUB
- Mercury and Its Removal Technologies
- Ionic Liquids – what are they
- New Process Using Ionic Liquids for Mercury Removal
- Summary
PETRONAS Corporate Information

Fully integrated multinational oil and gas corporation involved in Exploration & Production, Gas and Oil Processing, Petrochemicals, Shipping and Retailing

- Crude oil and natural gas production is 2.1 million BOE per day

FORTUNE 500 ACHIEVEMENTS

12% Return On Assets

23% Return On Revenues

USD 77 Bil. Revenue

USD 17 Bil. Profit
PETRONAS Integrated O&G Company

- **EXPLORATION & PRODUCTION**
- **OIL**
- **REFINING**
- **CONDENSATES**
- **PROCESSING**
- **LIQUEFACTION**
- **AROMATICS**

- **CRUDE OIL**
- **MARKETING FACILITIES**
- **PETROLEUM PRODUCTS**
- **PETROCHEMICAL**
- **LPG**
- **SALES GAS**
- **FERTILISERS**
- **LNG**
Mercury has been discovered in the hydrocarbon stream delivered by PETRONAS to the Gas Processing Plant (GPP) in Kerteh, Terengganu, Malaysia.

As mercury removal is becoming more challenging, there is a need to find a more robust, new technology to reduce the content of mercury to a much lower level.
Fact: Mercury is present in our oil and gas reservoir

<table>
<thead>
<tr>
<th>Location</th>
<th>Mercury Concentration</th>
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<tbody>
<tr>
<td></td>
<td>Gas (µg m⁻³)</td>
</tr>
<tr>
<td>Europe</td>
<td>100 - 150</td>
</tr>
<tr>
<td>South America</td>
<td>50 - 120</td>
</tr>
<tr>
<td>Gulf of Thailand</td>
<td>100 - 400</td>
</tr>
<tr>
<td>Africa</td>
<td>80 - 100</td>
</tr>
<tr>
<td>Gulf of Mexico USA</td>
<td>0.02 - 0.4</td>
</tr>
<tr>
<td>Overthrust Belt USA</td>
<td>5 - 15</td>
</tr>
<tr>
<td>North Africa</td>
<td>50 - 80</td>
</tr>
<tr>
<td>Malaysia</td>
<td>1 - 200</td>
</tr>
<tr>
<td>Indonesia</td>
<td>200 - 300</td>
</tr>
</tbody>
</table>

Estimated levels of Mercury in natural gas and condensate from around the globe.


The effect of mercury is threatening to the oil and gas industry and hence mitigation programme has been developed.

- Geological contaminant could adversely affect the safety and integrity of a processing plant.
- Accumulation in the process units can cause HSE issues for workers.
- Potential threats:
  - Liquid metal brittle corrosion especially on the aluminum cold box
  - Deactivation of certain catalyst units
  - Products contamination

Mercury Mitigation Plan
- Periodic monitoring – facilities and personnel
- Enforcement of Mercury Operating and Safety Procedures
- Installation of Mercury Removal Facilities
- Decontamination & Disposal Procedures
Commercially Available Mercury Removal Technologies (MRT)

- Current commercial MRT uses supported sulphides, halides and silver as active materials.
- MRT can be used to treat gas, liquid hydrocarbon and water streams.
- Depending on the applications, the targeted mercury levels at MRT outlets are:
  - 0.1 μg/m³ for gas stream
  - 5 μg/l for liquid stream

Current Issues with MRT:
- Determination of the actual mercury concentration due to fluctuation in the content of mercury.
- Issues in sampling, sample treatment and analysis.
- MRT’s capability to remove all types of mercury species.
- Robustness of the MRT system when other contaminants are present in the feed.
PETRONAS in collaboration with QUB through QUILL as world leaders in Ionic Liquids R&D

The Queen’s University of Belfast

- Location: Belfast, Northern Ireland, UK
- Founded in 1846
- Member Russell Group
- Entrepreneurial University of the Year 2009
- 18,500 full and part time students
- 3,500 total staff
- 1,600 teaching and research staff
- 250 buildings, half listed as being of special architectural merit
Chemistry at QUB

- Top UK department in terms of research impact
- *Source*: number 23 in the world and number 1 in the UK (Science Watch©, Thomson Reuters, Sept/Oct 2011)

Prof Ken Seddon and Dr John Holbrey

- Top 2 chemists in UK
- *Source*: Times Higher Education Supplement listing of the world’s 100 Top Chemists of the Past Decade (Feb 2011)
What are, and why use Ionic Liquids?

Liquids composed solely of ions

- Properties, such as little or no measurable vapour pressure, provide impetus for use as solvents and catalysts for green chemistry.

Characteristic properties of most ionic liquids

- Wide liquid ranges (typically over 300 °C)
- High thermal stability
- Non-volatility at room temperature
- Non-flammability of the bulk liquid
- Controllable miscibility with a range of fluids and gasses
- Modifiable solubility and extraction capabilities

Opportunities for process improvement

- Novel materials with unique properties.
- Multifunctional materials offering new approaches (step-change) in process operations.
Integrated R&D concept to commercialisation

R&D

- Design an ionic liquid to capture mercury
  Screen ionic liquids for mercury capture activity and effectiveness

Process Integration

- Integrate within process unit operations
  • Produce solid supported ionic liquids for compatibility with existing process infrastructure
  • Develop rapid screening approaches to cut time to commercialisation

Pilot Plant

- Test at pilot scale
  Design, construct and run slip stream test units early in the development

Deployment

- Deploy on-site
  Teamwork essential at site early in development to facilitate training, smooth integration of novel technology and associated HSE considerations
R&D : Design Ionic Liquids for Mercury Removal from Gas Streams

1. APPRAISE activity - choose between the different IL's and approaches
   - Synthesis and rapid screening of task specific ILs for Hg removal

2. SELECT activity : select the technology for implementation
   - Select the suitable ionic liquid mercury extraction technology for development onto solid support
   - Data for scale-up and preliminary design of IL-based systems for Hg removal, process economics and technology validation.
Ionic Liquids provide a unique active site for capturing Hg

Using Ionic Liquids

- IL incorporates an oxidising moiety
- IL’s have the ability to convert and capture all types of Hg species

Using Solid Supported ionic Liquids (SSILs)

- Prove practicality of ionic liquid reactive extraction processes at scale
- Optimise the system
  - Performance study, robustness and cost
  - Manufacturing – cost reduction and improvement.
  - IP generation

Validate ionic liquids as mercury extractant

Enhance extraction capacity

Deployment for IL/gas scrubbing
Bench Scale Testing of Solid Supported Ionic Liquids (SSILs)

• Bench scale testing to determine:
  – Type of support
  – Adsorption capacity of the SSILs
  – Hg extraction efficiency and kinetics
  – Optimum ionic liquid composition

• Rapid screening to determine breakthrough of mercury on SSIL
Mercury Capture Profile of Solid Supported Ionic Liquids

- The mercury breakthrough for SSIL is 3 times longer than the commercially available sulfur impregnated carbon.

- Laboratory results show considerable improvement in performance compared to the commercial adsorbents evaluated.
Pilot Plant Evaluation at Gas Processing Plant

Pilot plant studies indicate:
- SSIL is performing well under actual plant conditions
- SSIL materials are robust enough to handle the other contaminants present in the feed

Next stage is the commercial trial scheduled for November start up in our PGB plant in Malaysia
Summary

- Ionic liquids offer a method to simultaneously:
  1. Oxidise elemental and organic mercury to inorganic mercury(II) species
  2. Extract inorganic mercury
  3. Capture all mercury species present in the gas

- Solid supported ionic liquids (SSILs) can be retrofitted to existing fixed bed MRUs with no additional CAPEX or modifications to the plant infrastructure
Thank You

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- PETRONAS Management Team (PETRONAS Gas Berhad, Technology and Engineering Division and PETRONAS Research Sdn Bhd)