Institution: Queen's University, Belfast

Unit of Assessment: 8

Title of case study: Mercury capture technology for the global petroleum industry

1. Summary of the impact (indicative maximum 100 words)

Queen's University's Ionic Liquids Laboratory (QUILL) has developed an ionic liquid technology for removing mercury, a toxic, corrosive contaminant naturally present in hydrocarbon reserves, with the national oil and gas company Petroliam Nasional Berhad (PETRONAS).The technology has been successfully installed in 1- and 15-ton units in two PETRONAS gas processing plants in Malaysia. The process, marketed as HycaPure Hg™, captures all mercury species present in natural gas and has up to 3 times higher capacity than competing state-of-the-art commercial alternatives. This technology represents a significant improvement towards ensuring the health and safety of workers, process plant and the environment.

2. Underpinning research (indicative maximum 500 words)

QUILL was the first research centre to focus on the development of ionic liquids (liquid salts) and is now recognised as the world-leader in new applications, notably in green chemistry. We drew on our expertise to design an entirely new ionic liquid based approach to remove mercury from natural gas supplies, a feat that has much broader applications. The underpinning research has been performed since the formation of QUILL in 1999 to now. Over this period of time a significant understanding of the controlling features of ionic liquids was determined from a fundamental perspective. This included the phase behaviour of ionic liquids and the effect of anion and cation structure as well as new synthetic methods for the production of low cost ionic liquids and the effect of impurities (halide and water, for example) on physicochemical properties of the materials (references 1-5 *in section 3*). Due to the large number of ionic liquid systems possible, predictive methods for the determination of both chemical interactions and physical property determination were also formulated (references 4 and 5 *in section 3*). Using this understanding and a knowledge of the requirements of the challenge – notably the need to extract inorganic, organic, and elemental forms of mercury from natural gas streams on an industrial scale, and the need for rapid capture kinetics in order to protect down-stream facilities from spikes in mercury content, Seddon, Nockemann and Holbrey led the team which targeted the design, synthesis and testing of ionic liquid materials at laboratory scale. Following the initial screening, the Queen's team successfully incorporated the active ionic liquids into porous solids without leaching. Finally, the composition of the solid-supported ionic liquid (SSIL) was optimised as a direct retrofit to existing mercury scrubbers with no added investment required (reference 6 *in section 3*). In partnership with PETRONAS, the optimised SSIL was scaled-up and validated at pilot scale and subsequently scaled up to 15 tons of adsorbent providing the first commercial charge to treat natural gas at an on shore PETRONAS gas processing plant.

3. References to the research (indicative maximum of six references) * signify the references which best indicate the quality of the underpinning research

Key references from the investigators, demonstrating the strength and depth of fundamental research underpinning the design, understanding and application of ionic liquid materials.

1. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids, KR Seddon, A Stark, MJ Torres, Pure Appl. Chem., 2000, 72, 2275, DOI:

10.1351/pac200072122275. This is a key paper which demonstrated to the ionic liquid research community the importance of understanding and maintaining knowledge of the purity of ionic liquid systems.

2. The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals, JD Holbrey, KR Seddon, J. Chem. Soc., Dalton Trans., 1999, 2133, DOI: 10.1039/a902818h. This fundamental study demonstrates the effects of systematic structural changes on the thermophysical properties of ionic liquid systems.

3. Efficient, halide free synthesis of new, low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions, JD Holbrey, WM Reichert, RP Swatloski, GA Broker, WR Pitner, KR Seddon, RD Rogers, Green Chem., 2002, 4, 407, DOI: 10.1039/b204469b. New ionic liquids were described prepared using simple, clean and halide-free syntheses.

*4. Desulfurisation of oils using ionic liquids: selection of cationic and anionic components to enhance extraction efficiency, JD Holbrey, I Lopez-Martin, G Rothenberg, KR Seddon, G Silvero, X Zheng, Green Chem., 2008, 10, 87, DOI: 10.1039/b710651c. The paper applied analysis of structure-activity relationships to determine the ‘best’ cations to use in the design of ionic liquids for desulfurisation of diesel fuel.

*5. Small angle neutron diffraction from 1,3-dimethylimidazolium chloride, C. Hardacre, J. D. Holbrey, S. E. J. McMath, D. T. Bowron, and A. K. Soper, J. Chem. Phys., 2003, 118, 272, DOI: 10.1063/1.1523917. This paper was the first to demonstrate the use of neutron scattering (using STFC large-scale facilities at ISIS) to directly visualise ionic liquid structure. This allows us to uniquely link bulk properties of ionic liquid systems with their behaviour at the atomic level.

The materials that form the basis of the HycaPure™ technology are proprietary knowledge and form a suite of 4 patents the most relevant being:

*6. Process for removing metals from hydrocarbons, M. Abai, M. Atkins, K. Y. Cheun, J. D. Holbrey, P. Nockemann, K. R. Seddon, G. Srinivasan, Y. Zou, World Patent Application PCT/WO 2012/046057 A2

4. Details of the impact (indicative maximum 750 words)

QUB and PETRONAS in a unique partnership have developed a novel mercury removal technology HycaPure Hg™ based on ionic liquids which offers advantaged performance and flexibility to treat a full range mercury types and gas composition (Figure 1). The first full-scale HycaPure Hg™ units containing 1 and 15 tons of absorbent were installed at a PETRONAS gas processing plant in Malaysia in Oct 2011 and have been successfully producing ethane for PETCHEM and sales-quality gas since commissioning (references 1-4 *in section 5*). The mercury content has been consistently below the legal safe limits, with no excursions. The new technology has a number of benefits over the competing commercial systems, e.g. the kinetics of mercury absorption are 10-20 times faster, allowing the operating plant to cope with large spikes of mercury with no risk to the downstream plant, and the mercury absorption capacities of the new materials are 2-3 times better on a volume/volume (reactor) basis. The new system is a direct retrofit to commercial plants and installs without any additional costs or modification to procedures (see PETRONAS’ Technology Products and Technical Solutions literature).

A typical medium-sized mercury removal unit contains around 15 tons of material, and costs in the order of US$180,000 per fill. By comparison, the increased absorption capacity of HycaPure Hg™ materials represents a potential cost saving of over 20% per vessel, and with a market size running into hundreds of thousands of tons, this new technology is not only efficient but highly competitive.

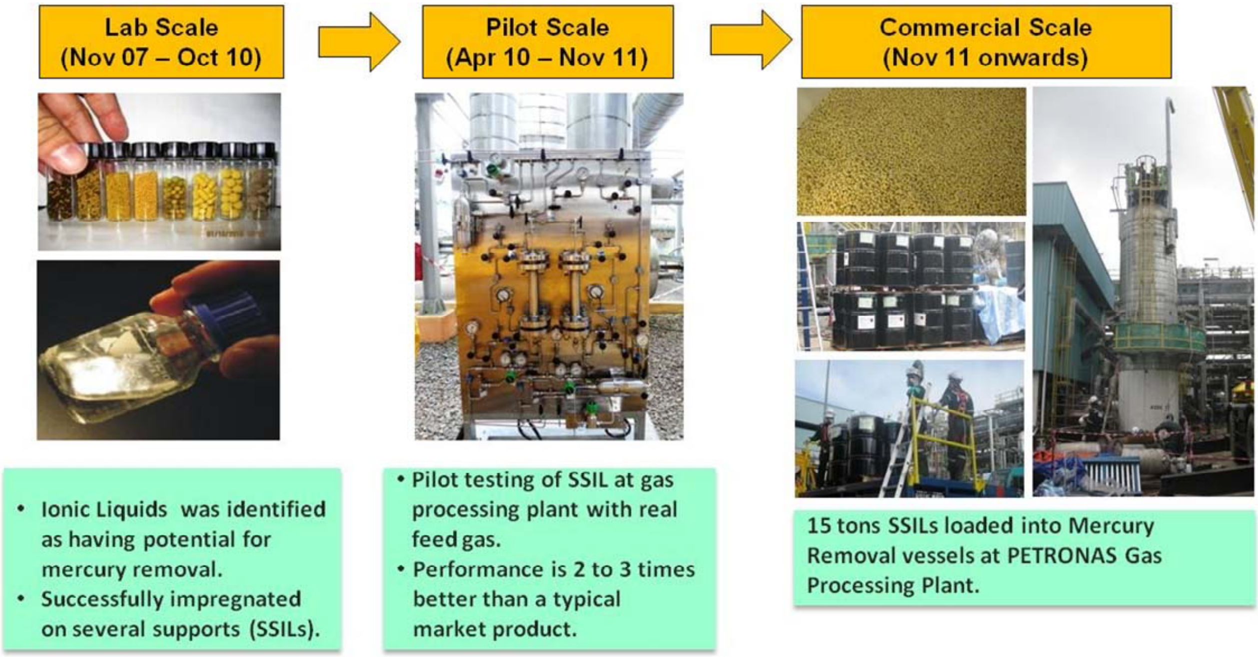

Figure 1 Development of the mercury capture technology for natural gas clean up in conjunction with PETRONAS

The potential market for our SSIL technology in the hydrocarbon industry is huge: MRUs are required in almost every gas and oil terminal and refinery/petchem complexes in addition to the produced waters from drilling platforms. Mercury contamination ranges from 0.02 micrograms per cubic metre in the Gulf of Mexico to more than 100 in Europe, South America, Gulf of Thailand, Malaysia and Indonesia. In extreme cases, such as in North Germany, levels can reach 5000 micrograms per cubic metre.

Even 1 ppm of mercury contamination has significant cumulative effects if we consider a typical plant processes 2000 tons every day. In addition to its well-documented health and environment effects, mercury also damages industrial facilities through corrosion, such as embrittlement of aluminium heat exchangers with catastrophic consequences. Hg is also a strong catalyst poison for downstream units.

The current technologies used to remove mercury are chemically-modified activated carbons (with sulphur for gas treatment, and potassium iodide for liquid hydrocarbon treatment) and more expensive technologies, such as silver-impregnated molecular sieves and mixed metal sulphide/oxide scrubbers. But there are issues with these technologies when it comes to efficiency, the removal of all types of mercury species, robustness when other contaminants are present in the feed and the ability to deal with fluctuating mercury levels. The HycaPure Hg™ is proving robust and durable in operation. The technology is being extended to other gas treatment facilties in PETRONAS facilities and licensing/manufacturing partners are planning to launch the product globally in 2014. .

The (anticipated) greater life-time of HycaPure Hg™ scrubbers will lead to lower total volumes of hazardous mercury-contaminated waste for post-unit remediation and reduced frequency of scheduled scrubber replacement, along with reduced occupational exposure to mercury. The issue of mercury exposure was recently recognised by governments in a global, legally-binding treaty to prevent emissions and releases, the Minamata Convention on Mercury.

The impact of this work was recently recognised in the Government's Great British Innovation Vote in March 2013 (reference 5 *in section 5*).

5. Sources to corroborate the impact (indicative maximum of 10 references)

1. The contribution of QUB, through the partnership with PETRONAS, is acknowledged in a letter of corroboration from the Head of Technology Management Department of Technology & Engineering Division, PETRONAS.

2. The PETRONAS Laboratory at the QUILL (Queen's University Ionic Liquids Laboratories) Research Centre was officially opened by The Northern Ireland Assembly Minister for Employment and Learning who recognised it as "an exemplar of industry and academic collaboration, not just for Northern Ireland but for the United Kingdom as a whole." (http://www.northernireland.gov.uk/index/media-centre/newsdepartments/news-del/news-del-april-2008/news-del-170408-minister-opens-new.htm and Petronas 2009 Annual Financial Statement, page 68 (www.petronas.com.my/investor-relations/Documents/annual-report/AnnualReport_FinancialStatement_2009.pdf)"

3. 2011 Annual Financial Statement (www.petronas.com.my/investor-relations/Documents/annual-report/AnnualReport_FinancialStatement_2011.pdf)
Notes the collaboration with QUB and the first commercial commission of HycaPure Hg™ at PETRONAS Gas Bhd (PGB).

4. Strategic presentations describing the technology at the International Gas Union Research Conference (19-21 Oct 2011, Seoul, Korea; http://www.igrc2011.com/programme), EUCHEM 2012 (5-10 Aug 2012, Celtic Manor, Wales; http://www.euchem2012.org/index.php/scientific-programme) and Green Solvents (7-10th October 2012, Boppard, Germany; http://events.dechema.de/events/en/gsfs2012.html).

5. Listed in the Government's Great British Innovation Vote, March 2013
http://www.topbritishinnovations.org/FutureInnovations/IonicLiquid.aspx