Institution: Queen's University Belfast		
Unit of Assessment: 8		
Title of case study: Building on the success of mercury capture to drive change in the petroleum industry		
Period when the underpinning research was undertaken: Jan 2000 – Dec 2013		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Prof John Holbrey	**Professor of Green Chemistry**	**1996-2001, 2005-2020**
Prof Kenneth R. Seddon	**Professor of Inorganic Chemistry**	**1993-2018**
Period when the claimed impact occurred: Aug 2013 – Oct 2020		
Is this case study continued from a case study submitted in 2014? Y		

1. Summary of the impact

The previous Impact Case Study described how a collaboration between PETRONAS (the national oil and gas company of Malaysia) and the Queen's University Ionic Liquids Laboratory (QUILL) led to development of a new technology (HycaPure™) to remove mercury contaminants from natural gas.The first commercial scale pilot Hycapure™ system was launched 2012. Significant impact in the current REF period has arisen from the roll out of this technology and its use on an industrial scale. By 2017, thirteen full industrial Hycapure™ systems had been installed in PETRONAS processing plants. This constitutes a huge processing capacity, a single processing train for dry natural gas will typically process >2,500,000t per year. In addition, the impact of this work on the company has been much broader, the ongoing research links between QUILL and Petronas have provided a mechanism for the company to begin to move the focus of their research away from traditional oil and gas, as evidenced by their new GBP2,400,000 joint programme on innovative low carbon technologies.

2. Underpinning research

QUILL was the first research centre to focus on the development of ionic liquids (liquid salts) and their applications in green chemistry. It carries out fundamental studies on the design and performance of ionic liquids, as well as their application in industrial processes.
The centre has a strong background in understanding structure-property relationships in ionic liquids from a fundamental perspective which forms the basis for controlling and exploiting them. Examples of work published 2000- (see references *1-4 below*) illustrate the breadth and depth of the expertise in the QUILL. These are seminal papers in the field and cover areas that include synthetic methods[1], determination of liquid structure[2], influence of impurities on physical properties[3] and application for desulfurisation of fuels[4].
This expertise has allowed entirely new ionic liquid-based approaches to remove mercury from natural gas and condensate supplies to be developed. This is a considerable challenge since it requires complex mixtures of inorganic, organic, and elemental forms of mercury to be extracted from natural gas and liquid hydrocarbon streams on an industrial scale, and must be sufficiently rapid to protect down-stream facilities from spikes in mercury content.

The previous Impact Case study (REF2014) described how Seddon and Holbrey led a team that designed, synthesised and tested materials based on active ionic liquids incorporated into porous solids for the treatment of contaminated gas streams at laboratory scale. The composition of these solid-supported ionic liquids (SSIL, later named HycaPure™) was optimised so that they could be used as a direct retrofit to existing mercury scrubbers with no added investment required. In partnership with PETRONAS, the optimised SSIL was scaled up and validated at pilot scale and subsequently scaled up to 15t of adsorbent, providing the first commercial charge to treat natural gas at an on-shore PETRONAS gas processing plant which was launched in 2012 (see Figure 1). The technology is protected by a series of patents the most relevant of which was filed by QUB in 2011[5]. An overview of the inorganic chemistry underpinning this technology was first described in the open literature in 2015[6].

Figure 1: Team at the plant (top left), material coated with Hycapure (bottom left), and two Mercury Removal vessels loaded with 15t SSIL installed at onshore and offshore facilities (middle, right).

There is strong ongoing engagement between QUILL and PETRONAS, for example use of the Diamond Light Source *in operando* extended X-ray absorption fine structure spectroscopy, to confirm the mechanism of mercury capture in the SSIL materials, which revealed evidence for secondary reaction that provides an unanticipated doubling of the scrubbers' working capacity,[7]

Seddon and Holbrey subsequently used the experience gained jointly between QUILL and PETRONAS developing the ionic liquid dry gas mercury removal technology (described above) to explore how the challenges with wet gas and liquid hydrocarbon condensate streams could be addressed. This work was carried out by two PETRONAS employees M. Bin Mohamed Raml and M. Bin Rafeen as part of their PhD research at QUB.

3. References to the research

1. 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 (cited 462 times, WoS, March 2021). An exemplar of how new ionic liquids can be prepared using simple, clean and halide-free syntheses and fully characterised to enable their use.
2. Small angle neutron diffraction from 1,3-dimethylimidazolium chloride, **C Hardacre**, **JD. Holbrey**, **SEJ McMath**, DT Bowron, and AK Soper, *J. Chem. Phys.*, 2003, 118, 272, DOI: 10.1063/1.1523917 (cited 416 times, WoS, March 2021). Underpinning atomistic studies, this work in collaboration with the disordered materials group at ISIS RAL, was the first to demonstrate how neutron scattering could be used to directly visualise ionic liquid structure linking atomic and bulk properties.

3. 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**, 2275-2287 DOI: 10.1351/pac200072122275 (cited 1906 times, WoS, March 2021). Seminal work identifying the influence of common contaminants on the characteristics of ionic liquid fluids defining the protocols for characterisation and reporting of properties.
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 (cited 191 times, WoS, March 2021. A demonstration of the approaches used in QUILL to screen and understand ionic liquid components for extraction processes for industrial separations using structure-activity relationship analysis to design optimised ionic liquids for desulfurisation of diesel fuels.
5. The materials that form the basis of the ionic liquid mercury capture technology are proprietary knowledge and form a suite of 4 patents the most relevant being: Process for removing metals from hydrocarbons, M Abai, M Atkins, KY Cheun, **JD Holbrey**, **P Nockemann**, **KR Seddon**, **G Srinivasan**, **Y Zou**, World Patent Application PCT/WO 2012/046057 A2. Filed 2011, now granted US, Europe, Eurasia and Australia.
6. An ionic liquid process for mercury removal from natural gas, M Abai, MP Atkins, A Hassan, **JD Holbrey**, Y Kuah, **P Nockemann**, **AA Oliferenko**, **NV Plechkova**, **S Rafeen**, AA Rahman, **R Ramli**, SM Shariff, **KR Seddon**, **G Srinivasan** and **Y Zou**, *Dalton Trans.*, 2015, **44**, 8617-8624, DOI:10.1039/c4dt03273j. (cited 62 times, WoS, March 2021). The underpinning chemistry and lab results supporting the mercury removal research are described in this paper, including the link from laboratory to pilot-scale results. This was also covered as a featured news article in *Chemistry World* (http://www.rsc.org/chemistryworld/2015/03/mercury-removal-ionic-liquid-natural-gas).
7. Mercury capture on a supported chlorocuprate(II) ionic liquid adsorbent studied using *operando* synchrotron X-ray absorption spectroscopy, R Boada, G Cibin, **F Coleman**, S Diaz-Moreno, D Gianolio, **C Hardacre**, S Hayama, **JD Holbrey**, **R Ramli**, **KR Seddon**, **G Srinivasan** and **M Swadzba-Kwasny**, *Dalton Trans.*, 2016, 18946-18953, DOI: 10.1039/c6dt03014a. In collaboration between QUB and the STFC Diamond Light Source, *operando* X-ray spectroscopy allowed detailed insights into the reaction mechanism of the ionic liquid mercury capture process.

4. Details of the impact

<u>Background to the problem and context from REF2014</u>

A major challenge in hydrocarbon production is the removal of impurities that pose significant health and safety issues as well as contaminating products. Mercury contamination is a particular problem in natural gas, where the concentration can range from 0.02 μg/m^3 in the Gulf of Mexico to >100 μg/m^3 in the Gulf of Thailand, Malaysia and Indonesia. This can have significant cumulative effects if we consider that plants may processes >5,000t of gas every day. In addition to its well-known problematic health and environmental effects, mercury also damages industrial facilities through corrosion/embrittlement, and 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 previous Impact Case in REF2014 described how the HycaPure™ ionic liquid mercury adsorbent, was developed by PETRONAS and the QUILL Research Centre at Queen's University of Belfast, to address this problem. This technology removes the full range of elemental, inorganic and organic mercury species from gas streams in a single treatment at up to four times the adsorption capacity of conventional adsorbents **[E1]**. A full scale commercial pilot using the technology was launched in February 2012 and was able to demonstrate the technology over the design lifetime of the HycaPure™ mercury removal unit (MRU) charge.

Ongoing Development and Technical Impact within the current REF period
Within the current REF period the successful on-site commercial pilot testing led to transition to full plant implementation. This was based on data which showed that after 3 years continuous operation of the first full system (launched 2012) the mercury concentrations from the outlet gas stream remained low, the system met all the plant specifications and the HycaPure™ material achieved its design lifetime of up to three times that of previous commercial alternatives (such as sulfur-impregnated activated carbon). This potential long operating lifetime was identified in early stage laboratory screening (described in reference 4) and was sustained through pilot testing and into full-scale implementation. This is one of the commercial advantages of the Hycapure™ system, since each fill costs *ca.* USD180,000 **[E2].**

Since the technology demonstrated robust performance in PETRONAS' dry gas processing plants, work was carried out to extend the technology so that it could also be with other more challenging streams. PETRONAS researchers have now successfully designed variants with different fundamental ionic liquid cores, based on the underpinning research conducted at QUILL, and supported by further collaborative work initiated over the period 2012-2017 during which time two PETRONAS staff undertook PhD research at QUILL and QUILL PDRAs undertook secondments with PETRONAS, facilitating knowledge transfer and training. In the FY2014, two advanced plants using more advanced Hycapure™ approaches were commissioned in Malaysia for treatment of other feed materials, one at the Onshore Gas Terminal in Kerteh for liquid condensate and the other for wet gas at the liquid natural gas facility in Bintulu **[E3]**.

Overall, by 2017, thirteen HycaPure™ systems had been built and deployed at several Malaysian operating facilities, including PETRONAS' Gas Processing Plants, PETRONAS Chemical Ammonia Sdn Bhd, PETRONAS Chemical Ethylene Sdn Bhd and MLNG **[E4]**. Each of the dry gas processing systems is a large scale installation, with an average of >10t of absorbent per system, this matches the overall scale of the process; each liquid natural gas (LNG) processing line (train) at the MLNG facility typically has a capacity of >2,500,000t per year (the cost of LNG in Feb 2020 is ~ GBP300 / 1t). To provide a context, the overall capacity of the MLNG facility in Bintulu of ~30,000,000t per year makes it one of the largest LNG plants in the world.**[E5]**

It is useful to estimate the amounts of mercury which need to be removed in a typical gas processing unit. This of course depends on the mercury levels of the feed material but in the mercury 'hot-spots' of Southeast Asia and Australia, this can be as much as 100-800 ppb in hydrocarbon condensate and 200-300 $\mu g/m^3$ in natural gas streams at the wellhead. This contrasts with the levels required to meet industry accepted levels for 'sales gas' of $<0.01\ \mu g/m^3$. Assuming 200 $\mu g/m^3$ in the gas stream, a 2,500,000t per year LNG train scrubbing mercury down to the acceptable levels for sale represents >700kg per year of mercury capture per processing train at the gas terminal. This has direct consequence for plant safety and operational security. The effective removal of all mercury forms from natural gas feedstocks combined with the long operational lifetime of MRU scrubber charges has significant advantages in reducing routes to potential mercury contamination by refinery workers which is most likely during confined space entry when working on contaminated equipment. Efficient scrubbing of mercury ensures that all equipment down-stream of the MRU is protected from contamination, while longer life-time of the HycaPure™ charge reduces the frequency of MRU bed replacement and associated risks of exposure to operators during these change-outs.

Awards and recognition

In recognition of the performance characteristics and the team work between PETRONAS and QUILL in research and development, HycaPure™ was named the winner of the Oil and Gas Award at the IChemE Malaysia Award 2016 **[E6]** and was opened for global commercialisation through a marketing licensing agreement between PETRONAS and CLARIANT (a global scale company whose business includes supply of catalysts for various industrial processes) signed in 2014 (see **[E7]**).

Impact on Corporate Research Culture

The impact of this work on the company has been much broader than the large scale implementation of a single technology. This fast-paced and successful research program into mercury capture cemented the collaboration between PETRONAS and QUILL, which has transformed into a long-term partnership with significant, and ongoing, research and training outcomes as described in the testimonial letter from the Head, Technology Research & CEO PETRONAS Research Sdn Bhd. **[E8]**

The initial work programmes developed through the first Research Collaborative Agreement between QUILL and PETRONAS (2007-2012) established a lively bilateral transfer of knowledge and skills through staff exchanges, PDRA appointments and Doctoral training of PETRONAS staff who have received PhD qualifications from QUB and gone on to assume leadership positions within PETRONAS. Notably, the CEO of Petronas Technology Ventures, the Head of Technology Commercialisation Management (PETRONAS Group Research and Technology), and the Head of R&D Gas Sustainability Technology are all QUB graduates, while the CEO of PETRONAS Research is a member of the QUILL Industrial Advisory Board and holds an Honorary doctorate from QUB. These close connections, and the innovation that has been developed through these links, have had an impact within the company by providing a mechanism to move the focus of their research away from traditional oil and gas towards innovative low carbon technologies, as evidenced by their new GBP2,400,000 joint Research Collaboration Agreement with QUILL, signed in March 2020, to "*strengthen PETRONAS' position at the frontier of innovation beyond conventional oil and gas business model*."

5. Sources to corroborate the impact

[E1] PETRONAS 2015 Annual Report – https://www.petronas.com/ws/sites/default/files/2018-08/petronas-annual-report-2015.pdf

[E2] Feature article on this research and the commercialisation process featured in the Royal Society for Chemistry magazine *Chemistry World* - http://www.rsc.org/chemistryworld/2015/03/mercury-removal-ionic-liquid-natural-gas

[E3] PETRONAS 2014 Annual Report – https://www.petronas.com/ws/sites/default/files/2018-08/petronas-annual-report-2014.pdf

[E4] PETRONAS 2017 sustainability Report- https://www.petronas.com/sites/default/files/2018-07/sustainability-report-2017.pdf, Page 36.

[E5] About Liquefied Natural Gas | PETRONAS Global

[E6] Petronas 2016 Annual Report – https://www.petronas.com/ws/sites/default/files/2018-07/petronas-annual-report-2016.pdf

[E7] Clariant Press Release – https://www.pressreleasefinder.com/prdocs/2014/CLAPR783EN0314_Clariant_and_PETRONAS_sign_licensing_collaboration.pdf

[E8] Testimonial letter from Head of Technology Research & CEO PETRONAS Research Sdn Bhd