Institution: Queen's University Belfast		
Unit of Assessment: 8		
Title of case study: Replacement of hydrogen fluoride (HF) by ionic liquids in the alkylation of gasoline- increasing the efficiency and safety of global clean fuel production		
Period when the underpinning research was undertaken: 2005 - 2015		
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:**
Kenneth R. Seddon	**Professor, Director of Queen's University Ionic Liquids Laboratory 1999 - 2018 (QUILL)**	**1993 – 2018**
Małgorzata Swadzba-Kwasny	**Senior Lecturer, Director of QUILL 2018 – present**	**2015 – present**
Period when the claimed impact occurred: 2013- 2020		
Is this case study continued from a case study submitted in 2014? N		

1. Summary of the impact

QUILL (QUB) provided long-term research expertise and support for Chevron's development of ISOALKY™ Technology, replacing the conventional catalyst for the production of alkylate gasoline, hydrofluoric acid (HF), with an ionic liquid. HF is an extremely corrosive and poisonous volatile liquid, making the safe plant operation demanding and costly. The non-volatile acidic ionic liquid used in ISOALKY™ is inherently safer and easier to contain, making the process cheaper and safer, in addition to yielding high quality fuel. The first full-scale plant (580t per day) is now operating, and the Chevron/Honeywell UOP partnership (the ISOALKY Alliance) has already licensed the technology to other producers.

2. Underpinning research

Ionic liquids are salts that are liquid below 100 °C, and often at ambient temperature. Developed in the 1970-80s as exotic electrolytes, three decades later they have been tested around the globe in a myriad of applications, including solvents for biomass, liquid catalysts, extracting agents and lubricants. This fundamental change in perception of ionic liquids is often credited to *Professor Kenneth R. Seddon* (Chair of Inorganic Chemistry at QUB 1993-2018†), who envisaged that the curious electrolytes could be used as exciting new media for industrially relevant chemistry (Holbrey, Welton, *Green Chem*, 2018, **20**, 776). As a vehicle to realise that vision, in 1999 Seddon co-founded QUILL (Queen's University Ionic Liquid Laboratories), an industry-university partnership based on the National Science Foundation's Industry-University Cooperative Research Centre (IUCRC) model. Supported by an Industrial Advisory Board of 17 companies (including Chevron, then represented by Dr Tom Harris), QUILL was set up to explore the potential of ionic liquids in industrial applications, with Seddon as the Director and leader in the field (*viz.* landmark review with 4,000 citations: Plechkova, Seddon, *Applications of ionic liquids in the chemical industry*, Chem. Soc. Rev., 2008, 37, 123).

Seddon authored over 400 peer-reviewed papers, which amassed +42k citations (H-index 88), was listed as the most cited chemist in the UK for 2000-2010 (Times Higher Education Supplement, 10 Feb 2011), and in 2015 was awarded an OBE for his services to chemistry.

Despite his death in January 2018, the QUILL Research Centre he established associates 18 academics, whose groups actively pursue research in the field of advanced liquid materials. ISOALKY^{TM} technology relies on catalysis with a Lewis acidic ionic liquid, containing chloroaluminate anions as the Lewis acidic species; QUILL activities directly relevant to this technology were initially led by *Professor Seddon*, then by *Dr Swadźba-Kwaśny* (current Director of QUILL). Research by QUILL and its national and international collaborators covers all aspects of ionic liquids studies, from fundamental investigations on physical properties, inorganic chemistry in/of ionic liquids, through spectroscopic and catalytic studies, fundamental chemistry related to catalyst regeneration and recycle. It was this breadth of expertise that enabled QUILL to support Chevron at all stages of ISOALKY^{TM} development.

Based on interactions with QUILL, Chevron initiated an in-house research programme, scoping out the most promising technologies that could benefit from the implementation of ionic liquids, which led to the selection of alkylate gasoline production.

When Chevron focused on the alkylation technology, QUILL provided expertise, training and unique instruments to Chevron researchers, in order to measure physical properties of the ionic liquid catalyst. These data were indispensable for chemical engineering models of the prospective ISOALKY^{TM} process. In the early 2000s, the engineering use of ionic liquids was very novel, and this kind of data was scarcely available and difficult to measure – particularly in this case where the IL was extremely sensitive to atmospheric moisture.

Finally, the impact of impurities and the solubility of ionic liquids (especially chloride species associated with corrosion) in the solvent systems used in the alkylation reactor (liquid phase) was also not well understood. QUILL has been the key pool for industrial knowledge on ionic liquids, preparing ionic liquids in pure form and having the know-how to study speciation and construct phase diagrams with confidence. It is this level of expertise that is needed when developing a commercial plant, as Chevron have been able to do for the ISOALKY^{TM} technology.

Specific research innovations related to the development of ISOALKY^{TM} are detailed below.

- Experience in predicting and studying physical properties of ionic liquids, including moisture-sensitive systems, such as chloroaluminate ionic liquids, which allowed for obtaining reliable engineering data for the ISOALKY^{TM} process **[R1]**
- Expertise in building phase diagrams of halometallate ionic liquids and relating these to the key physical and chemical characteristics of these systems, including Lewis acidity (which translates to catalytic activity) **[R2]**
- Bottom-up approach to designing new Lewis acidic ionic liquid catalyst, with build-in tunability of physico-chemical properties, combined with low cost and ease of synthesis, therefore acceptable in industrial setting **[R3, R4, R5]**
- Fundamental investigations of speciation of metallate species, using a range of spectroscopic techniques, from in-house spectroscopies (Raman and NMR spectra) to synchrotron-based studies (EXAFS), and relating these properties to catalytic performance **[R2, R3, R6]**
- Vast expertise in reactions catalysed with Lewis acidic ionic liquids, including industrially-relevant aspects of scale-up, catalyst purification and recycling **[R4, R5]**

3. References to the research

[R1] M. Deetlefs, K. R. Seddon and M. Shara, ***Predicting physical properties of ionic liquids***, *Phys Chem Phys*, 2006, **8**, 642. https://doi.org/10.1039/B513453F [336 google scholar citations as of 30th December 2020]

[R2] J. Estager, A. A. Oliferenko, K. R. Seddon and M. Swadźba-Kwaśny, ***Chlorometallate(III) ionic liquids as Lewis acidic catalysts-a quantitative study of acceptor properties,*** *Dalton Trans*, 2010, **39**, 11375. https://doi.org/10.1039/C0DT00895H [53 citations as of 30th December 2020]

[R3] F. Coleman, G. Srinivasan and M. Swadźba-Kwaśny, ***Liquid coordination complexes formed by the heterolytic cleavage of metal halides,*** *Angew. Chem. Int. Ed. Engl.*, 2013, **52**, 12582. https://doi.org/10.1002/anie.201306267 [31 citations as of 30th December 2020]

[R4] H. Q. N. Gunaratne, T. J. Lotz and K. R. Seddon, ***Chloroindate(III) ionic liquids as catalysts for alkylation of phenols and catechol with alkenes***, *New J. Chem.*, 2010, **34**, 1821. https://doi.org/10.1039/C0NJ00301H [13 citations as of 30th December 2020]

[R5] J. Hogg, F. M. Coleman, A. F. Ugalde, M. P. Atkins and M. Swadzba-Kwasny, ***Liquid coordination complexes: a new class of Lewis acids as safer alternatives to BF_3 in synthesis of polyalphaolefins***, *Green Chem*, 2015, **17**, 1831. https://doi.org/10.1039/C4GC02080D [17 citations as of 30th December 2020]

[R6] A. K. Abdul Sada, A. M. Greenway, K. R. Seddon and T. Welton, *Org. Mass Spectrom.*, ***A fast atom bombardment mass spectrometric study of room-temperature 1-ethyl-3-methylimidazolium chloroaluminate(III) ionic liquids. Evidence for the existence of the decachlorotrialuminate(III) anion***, 2005, **28**, 759. https://doi.org/10.1002/oms.1210280706 [62 citations as of 30th December 2020]

4. Details of the impact

Inspired by the possibility of using ionic liquids to address their technological challenges, Chevron joined QUILL in 1999 **[S1]**, initiating in parallel an in-house research programme, dedicated to screening ionic liquids for various applications **[S2]**. The refinery alkylation (process for the production of alkylate gasoline) was identified in 2004 as the most promising target.

Alkylate gasoline is the cleanest and most efficient gasoline blending component (low emissions, high octane number). As far as fossil fuels go, it is both green and economically attractive, with >500 alkylation plants worldwide. The main drawback of the two established technologies for alkylate gasoline production are the catalysts they use: hydrofluoric acid (HF) and sulfuric acid (H_2SO_4). HF is a poisonous liquid with very high vapor pressure, easy to recycle but requiring multiple costly handling precautions. H_2SO_4 is a non-volatile liquid, but its recycling is an energy-demanding, large-scale operation producing significant waste streams **[S2]**.

Although it has been known that chloroaluminate ionic liquids (non-volatile and easy to recycle) can be used as a catalyst for refinery alkylation, identifying the precise catalyst composition, additives and reaction conditions to produce a high-octane gasoline to commercial specifications was a non-trivial task, with a number of operational challenges around catalyst formulation, recycling, and managing corrosion issues. Major oil companies, including Petrochina, Shell, Honeywell UOP and Chevron were all competing to deliver the successful technology **[S3].**

In 2005, a small pilot (**12 litre per day**) using chloroaluminate ionic liquids commenced operation in Chevron's scale-up laboratory. Following encouraging results from the pilot plant, a demo plant (scaled x100, to **1.2t per day**) was constructed in a Chevron refinery, next to a full-scale HF alkylation unit. Operating for 5 years (2010-2015), the plant was fully integrated with all sub-processes and worked on refinery feedstock, generating process data for scale-up design **[S2]**. The realistic operating conditions revealed further challenges, especially reducing the chloride content in the product and reliable operation of the regeneration process. To tackle these issues, in 2012, Chevron appointed *Professor Seddon* as the consultant and intensified using QUILL's expertise for fundamental insight and troubleshooting. In July 2012, following on from a consultancy visit by *Professor Seddon*, a Staff Chemist from Chevron visited QUILL and used the in-house facilities and know-how of *Dr Swadzba-Kwasny* and other researchers to construct the phase diagram of the catalyst, to record a full set of physical property data and to study its speciation. "*Insight from the phase diagram and some speciation studies performed at QUILL were indispensable for the development of the integrated process technology, which was crucial for the long-term success of the ISOAKLY Technology*" as confirmed in the corroborating letter which was provided by a Principal Scientist in Chevron **[S4]**. A patent covering the alkylation process with catalyst regeneration has been granted (US Patent US8987159B2). The work between QUB and Chevron led directly to the impact which is described below.

In 2013 Chevron initiated assessment of the **580t per day** Salt Lake City HF Alkylation Plant, exploring the potential of retrofitting it with the new ISOALKY™ technology, concluded in September 2016 with the positive Final Investment Decision **[S5]**. Following this, the Chevron Staff Chemist visited QUILL again, to obtain key physical properties of the ionic liquid catalyst necessary for the commercial plant design. "*The standout expertise of the research team led by Professor Seddon, and later by Dr Swadzba-Kwasny, has been crucial in supporting the development of this truly innovative technology*" stated the Chevron Principal Scientist **[S4]**. In 2017, construction of the new alkylation unit commenced in the Salt Lake City to retrofit their HF Alkylation Plant with the ISOALKY™ Technology (see photograph below) **[S2, S5]**. Following a large scale 3 year construction process, the retrofitted **580t per day** ISOALKY™ plant started operating in 2021.

Figure 1. (above left) The 1.2t per day ISOALKY™ demonstration plant which operated 2010-15 and (above right) a schematic of the planned retrofit of the full scale process plant.

Credit: Chevron

Figure 2. (above) photograph of construction carried out during the retrofit of the 580t per day ISOALKY™ plant in Salt Lake City, which was completed and started production in January 2021.

In 2016, Honeywell UOP and Chevron formed the ISOALKY Alliance to license the ISOALKY™ Technology to the industry globally **[S6]**. In 2019, Sinochem Hongrun

Petrochemicals became the first petrochemicals manufacturer in China to license ISOALKY™ **[S7, S8]**.

The ISOALKY™ Technology is the first successful new technology in alkylate gasoline production in 75 years, expected to significantly impact the global production of clean fuels in decades to come. The technology was awarded the Platts Global Energy Award for "Breakthrough Solution of the Year" in December, 2017 **[S9]**: "*Judges welcomed it as a "game changer" that solves a big environmental issue for refiners and offers significant market opportunities (…) [with] "immense potential impact" on global production of clean fuels.*"

Compared to conventional acid catalysts (H_2SO_4 and HF), the ISOALKY™ Catalyst exhibits several advantages **[S10]**:

- Non-volatile, ionic liquid catalyst (improvement over HF)
- Smallest catalyst inventory (compared to both processes)
- Integrated on-line regeneration of catalyst (improvement over H_2SO_4)
- Eliminates polymer incineration
- Reduces caustic solution waste
- Major improvement in refinery safety both for individual operators and neighbouring refinery process units

5. Sources to corroborate the impact

[S1] Paper describing launch of QUILL: K. R. Seddon, ***Green Chem.***, 1999,**1**, G58-G59, https://doi.org/10.1039/GC990G58

[S2] Chevron presentation describing the technology: https://web.archive.org/web/20190723074509/http://www.aqmd.gov/docs/default-source/rule-book/Proposed-Rules/1410/chevron-presentation.pdf

[S3] Review describing the use of Lewis acidic ionic liquids for use in industrial alkylation processes: L. C. Brown, J. M. Hogg and M. Swadzba-Kwasny, Topics in Current Chemistry, 2017, 375, 1–40, and references within.

[S4] Testimonial statement from a Principal Scientist in Chevron

[S5] News story describing success of demonstration plant: http://cen.acs.org/articles/94/i39/Chevron-embraces-ionic-liquids.html

[S6] News story describing Honeywell's entry into the ionic liquids alkylation technology: http://www.hydrocarbonprocessing.com/news/2016/09/honeywell-uop-introduces-ionic-liquids-alkylation-technology

[S7] News story covering the building of the Salt Lake City full scale plant: https://cen.acs.org/materials/ionic-liquids/time-ionic-liquids/98/i5

[S8] Coverage of Sinchem-Hongrun Petrochemicals' announcement that they will use ISOALKY™ in China: https://www.honeywell.com/us/en/press/2019/04/sinochem-hongrun-petrochemicals-to-produce-cleaner-burning-fuels-with-honeywells-groundbreaking-alkylation-technology

[S9] Finalists in the Platts Global Energy Award for "Breakthrough Solution of the Year": https://www.spglobal.com/platts/global-energy-awards/finalists/2017

[S10] Video explaining the Honeywell UOP ISOALKYL™ Process solution: https://youtu.be/0ugK3BVW6og