Institution: University of Glasgow (UofG)		
Unit of Assessment: UoA8 Chemistry		
Title of case study: Enhanced heat recovery, catalyst conditioning and feedstock flexibility in industrial scale phosgene synthesis		
Period when the underpinning research was undertaken: 2002−2020		
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:**
David Lennon	Professor of Physical Chemistry	1995−present
John Winfield	Professor of Inorganic Chemistry	1965−2005
Period when the claimed impact occurred: 2016−2020		
Is this case study continued from a case study submitted in 2014? N		

1. Summary of the impact

Working in collaboration with Huntsman Polyurethanes, UofG researchers have developed a new reaction model that comprehensively describes phosgene synthesis catalysis over an activated carbon catalyst. This knowledge has allowed continued improvements in plant operational practice to improve the feedstream management in the phosgene synthesis process and refine their catalyst activation and heat recovery strategies across their Rotterdam (Netherlands), Caojing (China) and Geismar (USA) manufacturing facilities. The open-source publication of research outputs from the UofG/Huntsman collaboration has restricted competing companies from patenting large blocks of process operations with direct connections to Huntsman's phosgene synthesis operations.

2. Underpinning research

UofG research led by Prof. Lennon (physical chemistry) and Prof. Winfield (inorganic chemistry) has advanced the fundamental understanding of the physico-chemical processes required for the industrial scale production of methylene diphenyl diisocyanate (MDI, $OCNC_6H_4CH_2C_6H_4NCO$), a component in the production of polyurethanes.

Despite its industrial pertinence, there have been few publications over the last 70 years in the open literature on phosgene synthesis catalysis connected with large-scale chemical manufacturing operations. This is, in part, due to the difficulty in safely handling of hazardous chlorinated materials such as chlorine (Cl), hydrogen chloride and phosgene. For over 18 years, the industrial/academic partnership between UofG research and Huntsman Polyurethanes sought to address these deficiencies, advancing capability directly relevant to this area of commercial endeavour. Phosgene is generally manufactured on-site as a precursor in the MDI process chain, to minimise hazards associated with the storage and transportation of this highly toxic gas.

This underpinning phase of the collaborative venture includes (i) investigating issues connected with Cl recovery within an MDI process chain [3.1] and (ii) an examination of unfavourable consequences of over-phosgenation of intermediates encountered within the MDI process chain [3.2].

For the latter body of work, the industrialists assisted the academic team by sharing 'best practice' in phosgene safe-handling procedures. In 2011 this culminated in the Huntsman's investment as a founding partner in the School of Chemistry's Chemical Process Fundamentals Laboratory (CPFL), a facility designed to investigate various areas of technical chemistry. In 2012 a phosgene synthesis catalysis facility was commissioned by Huntsman within the CPFL.

A series of three publications from the CPFL has led to a new awareness in phosgene synthesis. The first paper describes a series of laboratory procedures for analysing candidate phosgene synthesis catalysts, including protocols adopted for the safe handling of this hazardous reaction system [3.3]. The second paper considers such topics as activation energy, reaction profile and mass balance relationships. The work also determines the rate law for phosgene synthesis over the selected substrate [3.4]. The third paper examines adsorption and desorption characteristics of reagents and product [3.5]. Together this work by UofG has developed (in collaboration with

Huntsman Polyurethanes) a new reaction model that comprehensively describes how CO and Cl_2 combine over activated carbon to produce phosgene at high selectivity, in an industrial process environment. This model is the backbone of the Impact Case Study.

The mechanism proposed shows dissociatively adsorbed dichlorine resides in two sites; one site supports phosgene formation (via a ballistic collision with CO), whilst the other does not. Thus, a degree of Cl is retained at the catalyst surface that does not directly engage in phosgene production. This matter is confirmed by mass balance measurements, a parameter rarely encountered in halogen-themed heterogeneous catalysis. Moreover, building on this heightened awareness of phosgene synthesis, a subsequent paper demonstrated how Br_2, a common impurity in the Cl_2 feedstream, can significantly modify the surface chemistry of phosgene synthesis over activated carbon in an industrial setting [5.3].

3. References to the research

3.1 * E.K. Gibson, J. Callison, **J.M. Winfield**, R.H. Carr, A. Eaglesham, A. Sutherland, S.F. Parker and **D. Lennon** (2018). Spectroscopic characterization of model compounds, reactants, and byproducts connected with an isocyanate production chain. *Industrial Engineering and Chemistry Research*, 57 (22) 7355−7362. (doi:10.1021/acs.iecr.8b00853)

3.2 * J. Callison, F. Betzler, K. de Cuba, W. van der Borden, K. van der Velde, R.H. Carr, H.M. Senn, L.J. Farrugia, **J.M. Winfield** and **D. Lennon** (2012). Origin of impurities formed in a polyurethane production chain. Part 2: a route to the formation of coloured impurities. *Industrial and Engineering Chemistry Research*, 51 (34) 11021-11030. (doi: 10.1021/ie300987v)

3.3 * G.E. Rossi, **J.M. Winfield**, C.J. Mitchell, W. van der Borden, K. van der Velde, R.H. Carr and **D. Lennon** (2020). Phosgene formation via carbon monoxide and dichlorine reaction over an activated carbon catalyst: Reaction testing arrangements. *Applied Catalysis A: General*, 594, 117467. (doi:10.1016/j.apcata.2020.117467)

3.4 * G.E. Rossi, **J.M. Winfield**, C.J. Mitchell, N. Meyer, D.H. Jones, R.H. Carr and **D. Lennon** (2020). Phosgene formation via carbon monoxide and dichlorine reaction over an activated carbon catalyst: Reaction kinetics and mass balance relationships. *Applied Catalysis A: General*, 602, 117688. (doi:10.1016/j.apcata.2020.117688)

3.5 * G.E. Rossi, **J.M. Winfield**, N. Meyer, D.H. Jones, R.H. Carr and **D. Lennon*** (2021). *Applied Catalysis A: General*, 609, 117900. (doi: 10.1016/j.apcata.2020.117900)

* = best indicators of quality

4. Details of the impact

Huntsman Polyurethanes is a global leader in MDI-based polyurethanes, serving over 3,000 customers in more than 90 countries, with applications in diverse areas such as construction, automotive components, and insulation. The Company operates world-scale production facilities in the US, The Netherlands and China, reporting a sales revenue for the last 12 months of USD3.5 billion [5.1].

Huntsman's MDI-based polyurethanes *"play a critical role in addressing many of the global megatrends affecting the world today. As the most effective thermal insulant in the market, MDI-based polyurethane is widely used to deliver energy savings solutions in residential and commercial buildings. It is used throughout the cold chain, in refrigerators and cold stores, helping preserve food."* [5.2].

As noted in Section 2, phosgene is generally manufactured on-site as a precursor in the MDI process chain. Due to commercial confidentially, Huntsman are unable to quantify the precise financial benefits to them of the UofG research concerning individual steps in multi-stage overall manufacturing processes of MDI-based polyurethanes [5.1]. They can, however, report on how the company is utilising the knowledge gleaned from the phosgene synthesis catalysis project.

The UofG Model has enabled the Company to improve plant operational practice and feedstream management in the phosgene synthesis process. The open-source publication of research outputs was strategically sought to restrict competing companies from patenting large blocks of process operations with direct connections to Huntsman's phosgene synthesis operations.

1. **Improved management of bromine (Br) and chlorine (Cl) in the phosgene synthesis process**.

Huntsman's large-scale MDI manufacturing facilities consume high volumes of Cl at their Rotterdam (400,000 tonnes per annum; tpa), Caojing (240,000 tpa) and Geismar (500,000 tpa) plants. The UofG Model was applied to evaluate concern related to small quantities of Br_2 in the Cl_2 feedstream. This matter is of importance to the Company because trace contamination of Br can result in unwelcome MDI colouration. Although process patents exist to mitigate against the presence of small quantities of Br_2 in the Cl_2 feedstream of phosgene synthesis units [5.5-5.8], a submitted UofG/Huntsman collaborative publication [5.3] is the only open source and transparent scientific paper that addresses the issue of how the Br_2 affects the surface chemistry of the phosgene synthesis process.

Through a rigorous experimental programme undertaken in the CPFL, the UofG reaction model has been adapted to explain the action of small quantities of Br_2. For the first time, this has shown the Company how the reaction system is modified in the presence of Br_2. The UofG Model highlights a role for BrCl and additionally assesses the relevance of entities such as COBrCl and $COBr_2$ [5.3]. The Company has combined this knowledge with their own pre-existing thermodynamic model (that excludes surface interactions) to rationalise how the Br is partitioning within the large-scale reaction system. This knowledge has enabled Huntsman to improve their adaptability to the source material and produce higher quality MDI through improved management of Br incorporation. It also enables them to mitigate the impact of chlorine-quality variations on unwelcome MDI colouration through manipulation of the temperature gradient at the rear of the reactor [5.8].

2. **Application of UofG model to improve plant operational practice**

The UofG Model in Section 2 comprehensively describes phosgene production over an activated carbon catalyst to produce phosgene at high selectivity in an industrial process environment. Huntsman have applied the UofG model to their thermodynamic model of phosgene production to deliver on-going improvements in plant operational practice concerning two linked actions: (i) the initial catalyst conditioning process and (ii) heat recovery. Phosgene formation is highly exothermic which can lead to increased reaction temperatures in the centre of the catalyst bed. The UofG reaction model has been used to justify why certain Cl pre-treatments lead to more sustained phosgene production and extended catalyst lifetimes. These advancements at the industrial complex have enhanced the ability to maintain sustained maximum Cl conversion. The awareness provided by the academic researchers has assisted Huntsman chemists and chemical engineers in improving operational efficiency at their large-scale phosgene synthesis facilities.

3. Strategic investment in the CPFL by Huntsman.

Huntsman has invested £300,000 in this long-standing academic/industrial partnership to understand the fundamentals of phosgene synthesis and has been fully supportive of publishing research outcomes of in the open literature. This has (i) efficiently disseminated new awareness of a hazardous chemical process *"contributing to cultural change in the whole isocyanate manufacturing sector"* [5.1] and (ii) produced a wide scope of technical material into the public domain. This latter attribute had a business driver; namely, to restrict the Company's competitors from patenting large blocks of process operations with direct connections to Huntsman's global phosgene synthesis operations.

5. Sources to corroborate the impact

5.1 Letter of Support (Huntsman Polyurethanes)
5.2 https://www.huntsman.com/about/polyurethanes
5.3 Phosgene synthesis catalysis: The influence of small quantities of bromine in the chlorine feedstream, G.E. Rossi, **J.M. Winfield**, N. Meyer, D.H. Jones, R.H. Carr and **D. Lennon**, Ind.

Eng. Chem. Res. 2021, 60, 3363−3373. Publication Date:February 18, 2021. https://doi.org/10.1021/acs.iecr.1c00088

5.4 L. Cotarca, C. Lange, K. Meurer, J. Pauluhn, Phosgene, in Ullmann's Encyclopaedia of Industrial Chemistry, Vol. 102, Wiley-VCH, Weinheim 2019.

5.5 E.R. Wright and B.G. Messick, Method for reduction of bromine contamination of chlorine, The Dow Chemical Company, Midland, Mich., USA, US Patent 3,660,261, (May 2, 1972).

5.6 M. Reif, P. van den Abeel, F. Nevejans, H-V. Schwarz, U. Penzel and V. Scharr, Preparation of isocyanates, useful for production of urethane compounds, comprises reaction of amine with phosgene having specified bromine and/or iodine content, BASF SE, Germany, DE 19928741A1 (2000).

5.7 S. Gannon and J. Jacobs, Method for purifying a chlorine supply, BASF SE, Germany, Patent PCT Int. Appl. WO 2011/058069 (2011).

5.8 J.M. van der Leeden, P. Muller, R.H. Carr and A.J. Zeeuw, A process for manufacturing isocyanates and/or polycarbonates, Huntsman International LLC, USA, Patent PCT Int. Appl. WO 2017/194293 (2017).