Institution: University of Liverpool		
Unit of Assessment: Chemistry		
Title of case study: Enabling the Lucite ALPHA Process for the sustainable production of methyl methacrylate (MMA)		
Period when the underpinning research was undertaken: 2000 – 2019		
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:**
Jonathan Iggo	Reader	Jan 1986 - present
Brian Heaton	Grant Professor of Inorganic Chemistry Emeritus Professor	1985 – 2005 2005 – present
Robin Whyman	Reader in Inorganic Chemistry Honorary Fellow	1991 – 2007 2007 – present
John Satherley	Lecturer in Physical Chemistry	1992 – 2018
Period when the claimed impact occurred: 01/08/13 – 30/12/20		
Is this case study continued from a case study submitted in 2014? Yes		

1. Summary of the impact

Methyl methacrylate (MMA) is the monomer used to produce polymers such as Perspex or plexiglass, and acrylic resins that are used widely across construction, medical and optical applications. The annual market value of MMA is ca. $8 billion p.a.

Research at the University of Liverpool enabled the commercialization of a new process for MMA production, called ALPHA. ALPHA plants now provide 10% of world MMA production capacity. This has led to economic and environmental impacts including:

- The production of 1.6 Mtonne of MMA at ALPHA plants during the REF period with an estimated value of >$3 billion to Lucite International.
- The construction of a 2nd ALPHA plant ($360 M investment) with a capacity of 250,000 tonne p.a. in 2018
- Reduced energy consumption and lower CO_2 emissions leading to 40% lower operating costs for ALPHA produced MMA (vs. conventional MMA plants)
- Elimination of toxic (HCN) and corrosive (c.H_2SO_4) feedstocks and solid wastes associated with the conventional process that Alpha technology is displacing.

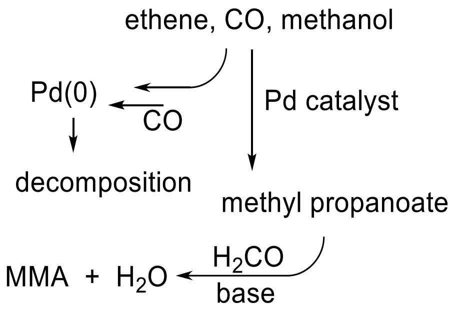
2. Underpinning research

The ALPHA process for MMA production uses a homogeneous Pd catalyst that was filed for patent by Lucite International (then ICI/Ineos Acrylics) in 1999. The catalyst enables the selective carbonylation of ethene in methanol to yield methyl propanoate, which can then undergo a condensation reaction with formaldehyde to yield MMA, scheme 1. Prior to the work of Iggo, Heaton and Whyman this precious metal catalyst was too unstable for commercial exploitation, rapidly decomposing under the operating conditions used [5.1]. Turnover numbers (TONs) of only a few thousand occurred before irreversible decomposition [3.1, 5.1, 5.2]. A high value precious metal catalyst only becomes viable if it has sufficient lifetime and productivity.

The Liverpool team delivered two programmes of underpinning research that overcame this critical limitation resulting in turnover numbers increasing to >10^7 and enabling the ALPHA process to be commercially viable and to be employed at scale.

(i) Identification of operating conditions that delivered orders of magnitude increase in TON (> 10^7) through mechanistic research: To achieve the improvement in catalyst stability required to make the process commercially viable, the Liverpool team and Lucite International studied the mechanism of the Pd ALPHA catalyst. This collaboration continues to this day [5.1], but the underpinning research that enabled commercialisation of the process was reported in a series of joint Liverpool-Lucite publications between 2000-2004 [3.2-3.5].

Lucite ALPHA Process



Scheme 1 The Lucite ALPHA process eliminates hydrogen cyanide and concentrated sulfuric acid from MMA manufacture. Commercialization was prevented by the short lifetime and low productivity of the catalyst, a problem solved by Iggo *et al.'s* mechanistic studies.

Using the unique high pressure NMR bubble column developed by Iggo at the University of Liverpool [3.5] it was possible to carry out *in-situ* studies of the ALPHA mechanism. The ability to monitor the working catalyst under realistic conditions led to the identification of the reaction intermediates responsible for activity and the conditions under which these could be stabilized. In a 2002 study the Liverpool team used NMR spectroscopy to identify the main catalyst decomposition pathway, poisoning of the palladium hydride intermediate by carbon monoxide [3.2, 3.4]. The unstable Pd species formed, rapidly aggregated forming irrecoverable metal particles giving rise to the commercially un-viable TON [5.2]. This led the collaborative team to develop CO-lean operating conditions that resulted in several orders of magnitude increase in catalyst TON, to a value $>10^7$. As carbon monoxide is a substrate for the desired reaction these operating conditions are counter-intuitive without knowledge of the reaction and catalyst decomposition mechanisms [5.1, 5.2].

(ii) Enabling scale-up by experimental verification of thermodynamic models: Following the identification of optimised operating conditions it was possible to deploy the ALPHA technology. However, the first ALPHA plant required a 30,000 fold scale-up of the reactor size. To enable the safe commissioning of the plant and the correct specification of equipment it was vital that experimental data was provided to validate the thermodynamic models used in the plant design. In follow-on studies that focused on enabling process scale–up, Iggo and Satherley used the Liverpool high-pressure NMR bubble column [3.5] to study the four-component mixture CO-ethene-MeOH-methyl propanoate, a system that was previously un-reported, to provide the essential vapour-liquid-equilibrium data to the Lucite design team.[5.1, 5.2] This underpinning research was carried out in 2004 following the award of funding to Iggo and Satherley from Lucite (project title: In situ measurement of gas concentrations in working mini-reactors, £69,030).

Continued development of the ALPHA process: In total Lucite has co-sponsored 2 PDRA's, 5 PhD students and provided equipment and funding of >£500k to Iggo demonstrating the importance placed by the company on this mechanistic research. Alongside the two key programmes of work outlined above Iggo has worked with Lucite on multiple further projects to further improve the ALPHA process. Projects include work between 2010-2017 to improve the second stage of the ALPHA process, the condensation of methyl propanoate with formaldehyde. This has led to the discovery of a new catalyst for the 2nd step of the ALPHA process (condensation reaction) and the filing of two patent families by Lucite with Iggo named as an inventor [3.6]. Most recently in 2019 Iggo established a work programme with Lucite's Wilton R&D team using *in situ* NMR to identify the role of different feedstock impurities on catalyst stability and TON and so define the feedstock quality and grade requirements [5.1].

The vital roles of the Liverpool team in bringing the ALPHA process to market is detailed by Lucite in a letter to Iggo, and summarised by the statement from the Business Research Director "*I am pleased to be able to confirm the critical role played by the collaborative studies between Heaton, Whyman and yourself at Liverpool University and Lucite in enabling the successful commercialization of the ALPHA process*." [5.1]

3. References to the research

3.1. Eastham, G. R. *et al.* Synthesis and spectroscopic characterisation of all the intermediates in the Pd-catalysed methoxycarbonylation of ethene. *Chem. Commun.*, 609-610, doi.org/10.1039/B001110J (2000). [72 citations]

3.2. Clegg, W. *et al.* Characterization and dynamics of $[Pd(L\text{-}L)H(solv)]^+$, $[Pd(L\text{-}L)(CH_2CH_3)]^+$, and$[Pd(L\text{-}L)(C(O)Et)(THF)]^+$ ($L\text{-}L=1,2\text{-}(CH_2PBu_2^t)_2C_6H_4$): Key intermediates in the catalytic methoxycarbonylation of ethene to methylpropanoate. *Organometallics* **21**, 1832-1840, doi:10.1021/om010938g (2002). [104 citations]

3.3. Liu, J. K., *et al.* The complete delineation of the initiation, propagation, and termination steps of the carbomethoxy cycle for the carboalkoxylation of ethene by Pd-diphosphane catalysts. *Angew. Chem.-Int. Ed.* **43**, 90-94, doi:10.1002/anie.200352369 (2004). [40 citations]

3.4. Wolowska, J. *et al.* The effect of mechanistic pathway on activity in the Pd and Pt catalysed methoxycarbonylation of ethene. *Chem. Commun.*, 2784-2785, doi:10.1039/b208450c (2002). [11 citations]

3.5. Torres, A. *et al.* High-Pressure In Situ NMR Methods for the Study of Reaction Kinetics in Homogeneous Catalysis. *ACS Catalysis* **2**, 2281-2289, doi:10.1021/cs300439n (2012). [12 citations]

3.6. Eastham, G. R. et al., A process for the production of ethylenically unsaturated carboxylic acids or esters, WO2016166525 (A1), (2016)

4. Details of the impact

ALPHA plants produce high purity MMA using a process that has a lower energy intensity and avoids the use of toxic and highly corrosive reagents. This has allowed it to rapidly displace incumbent processes; ALPHA plants currently provide 10% of the world MMA supply and this is expected to rise to 17% by 2023 [5.1]. The global MMA market is *ca.* $7-8 billion p.a. [5.1, 5.3]. This has given rise to substantial economic and environmental benefits.

Pathways to impact for Lucite ALPHA process

Catalyst decomposition prevents commercialization of environmentally friendly new process

↓

Liverpool research gives essential insight into the stability of reaction intermediates and catalyst decay processes

↓

Insight gained directs Lucite to adopt counter-intuitive CO-lean operating conditions

↓

Enhanced catalyst stability increases catalyst productivity and lifetime (TON)

↓

Enables commercialization of new, environmentally friendly MMA production process

The ALPHA process only became commercially viable following research at the University of Liverpool, which led to a step-change in the turnover number of the carbonylation catalyst. A letter of support from the Business Research Director (Strategic Projects Group) of Lucite confirms that prior to the work of Iggo and colleagues the catalyst was not economically viable and confirms the crucial role played by the research at the University of Liverpool in developing the counter-intuitive operating conditions that enabled commercial deployment of, and remain critical to the success of, the ALPHA process. "*Prior to the initiation of our collaboration, we had uneconomically low catalyst turnover numbers. Between 2000 and 2008 the work at Liverpool gave essential insight into the mechanism of the reaction and catalyst decomposition, which provided crucial direction to Lucite's internal lab, pilot plant and technical development activities and led directly to the adoption of unexpected, counter-intuitive operating conditions that gave the step change in catalyst turnover number that is an essential element of the commercial success of the ALPHA process. The counter-intuitive operating conditions developed are used in, and remain critical to, the operation of all ALPHA plants*" [5.1, 5.2]. The UoL research was thus decisive in the launch of and remains critical to the commercial success of the Lucite process.

The team at the University of Liverpool also provided important experimental data for the scale up of the reaction to the plant level: "*the Liverpool team (2002-2009) provided key physical property data that was used during plant design and scale up. The experimental solubility data from the work of yourself and Dr Satherley was used to verify the thermodynamic models employed in the design of the first ALPHA plant.*" [5.1]

The support letter from Lucite International clearly demonstrates that without the underpinning research at Liverpool the ALPHA process would not have been a commercial success.

Fig. 1 ALPHA 2, the world's largest MMA plant, came on stream in Al Jubail, Saudi Arabia in 2018.

Economic Impact of ALPHA: The first ALPHA plant opened in 2008 in Singapore with a capacity of 130,000 tonne p.a. of MMA and was the basis of the REF 2014 impact case. This plant has remained operational also generating economic impact through this REF period through product sales. In a major expansion of the impact during this REF period, in 2018 the second ALPHA plant came on stream in Saudi Arabia following an investment of $360M, in the form of a joint venture between Mitsubishi Chemical (current owners of Lucite) and the Saudi Basic Industries Corporation (SABIC) [5.4, 5.5]. The second ALPHA plant (250,000 tonne p.a.) is the world's largest MMA plant and is the global cost leader (cheapest to run as of 2018), [5.4, 5.5]. The Lucite letter confirms that "*ALPHA 2 represents a $360m investment, and it also uses the operating conditions developed as a result of the Liverpool teams' research".* [5.1] Furthermore, Lucite confirm in their support letter and in public statements that a third 350,000 tonne p.a ALPHA plant using the operating conditions discovered by Iggo and colleagues is planned for the USA [5.1, 5.5]. In total, Lucite state in writing that, ALPHA plants have produced 1.6 Mtonne of MMA during the REF period [5.1], the value of which is estimated to be >$3 billion based on an average cost and freight price of $2000 pmt (over the assessment period [5.3]).

The ALPHA process offers significant economic advantages when compared to conventional acetone cyanohydrin (ACH) plants through the generation of a particularly high purity MMA which is suitable for high value applications such as those where transmission of visible light is critical (LED/LCD displays, surface coatings) and medical applications (dental and implant cements). [5.6] Iggo continues to work with the Lucite team in Wilton which remains the research and support site for ALPHA, anchoring high value jobs and activities in the UK [5.1].

Environmental Impact: By making the ALPHA process commercially viable, and through research assisting the plant design process, the University of Liverpool team has enabled significant environmental benefits.

ALPHA MMA production is rapidly displacing the established ACH process and is key to Lucite achieving its target of a 20% reduction in environmental emissions and to achieve zero waste to landfill [5.1, 5.7, 5.8]. As well as using available, relatively low-cost feedstocks/solvents (ethylene, carbon monoxide, methanol and formaldehyde), ALPHA chemistry eliminates the use of hydrogen cyanide, a highly toxic chemical. Conventional ACH plants require ~30 ktonne p.a. of highly toxic hydrogen cyanide (for an ACH plant of 150 ktonne pa.) leading to strict controls which dictate plant and reactor design, waste treatment and operating procedures [5.9, 5.10].

Furthermore, during conventional ACH MMA synthesis sulphuric acid is used in very large quantities; a 150 ktonne p.a. ACH plant produces at least 360 ktonne p.a. of spent sulphuric acid waste that needs to be recovered/recycled [5.7]. ALPHA plants do not use sulphuric acid thus avoiding the need for the energy intensive acid recovery processes. This combined with the very high selectivity of the ALPHA stage 1 process (>99.9%), which minimises purification steps, lowers energy inputs, lowers emissions and leads to a 40% reduction in running costs [5.1, 5.5, 5.9].

The ALPHA process also has excellent atom efficiency, it generates virtually no waste/by products other than water [5.1]. In contrast, the ACH process produces 1.2 tonnes of ammonium bisulfate co-product per tonne of MMA [5.10] which must be pyrolysed to SO_2 for conversion to sulfuric acid, a highly energy intensive process, or sold as (low value) fertilizer.

Finally, ALPHA provides a pathway to generate sustainable polymers. ALPHA's feedstocks such as ethylene, carbon monoxide and methanol are ideal candidates to derive from biomass.

Unusually for a plastic, pMMA can also be returned in high yield to its monomer and MMA to develop a circular MMA economy and Lucite is actively pursuing this strategy.

The impact of the Alpha process has been recognised by many awards [5.6]
The Lucite ALPHA™ Process is one of very few, successful, large scale, industrial process using a homogeneous palladium catalyst to be developed and come on stream in the last 30 years and is protected by 50 patent families totalling over 650 patents and has been recognized as follows:
2009 The Biennial Kirkpatrick Chemical Engineering Award - Winner
2009 Chemical Industry Association Innovation Award - Winner
2009 ICIS Innovations Awards - Short-listed for Best Product Innovation
2010 The Royal Academy of Engineering MacRobert Award – Finalist
2016 RSC Applied Catalysis Award to Dr David Johnson, retired Business Research Associate, Lucite International, who led the Lucite team responsible for developing ALPHA

5. Sources to corroborate the impact

5.1. Business Research Director, Strategic Projects Group, Lucite International. Letter corroborating Liverpool's impact on the successful commercialization of the process, (2020).
5.2. Research Associate (rtd), Lucite International. Letter corroborating Liverpool's impact on the successful commercialization of the process, the decomposition pathway of catalyst and the environmental impact of the ALPHA Process (2013).
5.3. Hymer-Borica, Acrylic World Newsletter (2020); Persistence Market Research, https://www.persistencemarketresearch.com/market-research/methyl-methacrylate-market.asp (2019). Market reports, corroborating economic value of MMA.
5.4. IHS Markit (2012) https://ihsmarkit.com/products/chemical-technology-pep-methyl-methacrylate-11e.html; Market report confirming ALPHA has lowest fixed capital and operating costs.
5.5. Lucite International, https://blog.luciteinternational.com/alpha-3-the-journey-to-world-class-mma-production/ (2020) Web page corroborating environmental benefits of ALPHA technology and ALPHA2 (2018) and ALPHA3 (expected full operation 2025).
5.6. Lucite, https://www.luciteinternational.com/monomers-emea-manufacturing-alpha-technology-15/ Web page outlining ALPHA production facilities and impact, product purity and applications (2020).
5.7. DKL Engineering (2002) http://www.sulphuric-acid.com/techmanual/AcidRegen/mma.htm Web page outlining quantity and reprocessing of sulphuric acid wastes from ACH plants.
5.8. " Lucite, "Sustainability - 2050 vision "https://www.luciteinternational.com/responsibility-sustainability-191/#2050-vision Web page outlining Lucite's aims to reduce reduce enrgy usage, eliminate waste and environmental emissions. See also ref 5.1
5.9. Harris, B. "Acrylics for the future". *Ingenia online* (2010), Article confirming challenges Lucite faced I developing ALPHA https://www.ingenia.org.uk/Ingenia/Articles/3ab65b97-7930-452a-b3a3-bbd5147f41a4.
5.10. Darabi Mahboub *et al,* Catalysis for the synthesis of methacrylic acid and methyl methacrylate, *Chem. Soc. Rev.*, **47**, 7703-7738. DOI:10.1039/C8CS00117K (2018). Independent review of MMA manufacturing processes