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Methyl methacrylate production processes: a comparative analysis of alternatives using life cycle assessment methodology

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ABSTRACT

Green chemistry is part of the chemical industry's response to calls for improved environmental responsibility. It is also one of the industry's several paths to redemption from its erstwhile infamous reputation as one of the most polluting sectors. We studied the impacts of implementing some of these principles on the production of methyl methacrylate (MMA), the monomer of the PMMA popularly known as acrylic glass. This study used Life Cycle Assessment (LCA) methodology to compare the potential environmental impacts of three different approaches to the production of MMA. Two of these are established industrial pathways: acetocyanohydrin process (ACH-MMA) and Alpha Lucite process (AL-MMA), which represent the conventional and a fast-rising industrial route respectively, while the third, in-situ formaldehyde process (inFAL-MMA) is a lab-based process. The scenarios were evaluated using Cumulative Energy Demand (CED) and the ReCiPe 2016 impact assessment methods. The results obtained highlighted some hotspots that can benefit from process improvements and careful material and energy source selection. It also underscored that AL-MMA can record significant improvements in environmental performance by reducing overall resource intensity of the process. inFAL-MMA synthesis was adjudged to be the most evolved of the three alternatives with respect to the green chemistry principles, hence the study sought to investigate possible environmental gains attributable to this. Some limitations of the methodology uncovered during the study necessitated the use of an additional tool for further assessment the potential risk. Thus, the GREEN MOTION^{TM} was adopted to examine this relationship. Overall, the study established hotspots and areas for process improvements in the scenarios examined. It also confirmed the importance of the different factors like data

quality, degree of process optimisation, energy source and others on the results that can be obtained in a life cycle assessment.

INTRODUCTION

The sustainable development goals have become the ultimate driving force for most of the innovative efforts across several industries today including the chemical industry. Bontempi et al.[1] investigated the direct link between sustainable materials and the sustainable development goals,[2] and they concluded that the solutions to the major global challenges cannot exist outside of new innovative and more sustainable components. Substitute or alternative materials are however not going to be completely novel as they do not necessarily originate from new supply chains which can be made to be sustainable by default. Sustainability efforts therefore needs to be heavy on process improvement which encompasses the critical work of overhauling the existing supply chains and manufacturing approaches to ensure that the nascent promise of sustainability can be realised.

For the chemical industry, process improvement is a daunting task given the complexity of the supply chain and the cost of changing established and successful production approaches.[3] The introduction of the 12 green chemistry principles[4] is one of the first response of the chemical sector to calls for higher levels of environmental responsibility in its activities. They can be and have indeed been used both as a template for the adoption of green chemistry as a concept as well as evaluate the greenness of existing processes.[5] The calls for process improvement are also largely driven by the need to lower the environmental impacts of chemical processes, so an assessment of the status quo is key to understand the extent and concentration of undesirable environmental impacts in a usually complex chain of events. Life Cycle Assessment (LCA)[6-8] has emerged as a widely used methodology for evaluating environmental impacts across the entire chain of a processes involved in industrial chemical production from raw material extraction to disposal after end of life.[9,10.]

Poly methyl methacrylate (PMMA) popularly known as acrylic, acrylic glass or plexiglass is one of the versatile materials that have emerged in recent years.[11] It also found wide applications in response to the corona virus pandemic through its use in the production of barriers and shields for limiting direct contacts.[12] The importance of this polymer however transcends being a physical wall against the free flow of pathogen carrying elements of nature. PMMA is an optically clear (transparent) thermoplastic, and it is widely used as a substitute for glass, because it shows high impact strength, is lightweight, shatter-resistant, weather resistant, scratch resistant and exhibits favourable processing conditions.[13] PMMA has promising applications in several industries which include architecture and construction, automotive, electronics, design and arts, medical and health, visual communications and several others.[13]

The EU recognises the potentials of PMMA as an important material and therefore has an active strategy in place to increase the production of this polymer on the continent.[14] To achieve this, a much-coveted property of PMMA different from its versatility and technical abilities is being explored. This polymer is capable of undergoing depolymerisation to produce its monomer, methyl methacrylate (MMA) without an associated loss in purity and quality.[18] Depending on the depolymerisation technique employed, multiple cycles of depolymerisation-reuse can be achieved with the maintenance of high purity standards. At a time when plastic wastes are a major concern, with an estimated 75-199 Mt of plastics in the oceans and an expected amount of 53 Mt/year in 2030[19], PMMA offers an impeccable recycling and reuse properties which makes it very attractive for the circular economy agenda of the EU and indeed throughout the world.[15-17] Therefore, having a material with this level of reuse capabilities is significant to circular economy objective and the EU has funded the MMA two projects which is aimed at constructing a novel and fast growing PMMA recycling value chain based on the production of second-generation MMA from post-consumer and post-industrial PMMA based products.[20,21]

Process improvement for a polymer like PMMA starts from its monomer, MMA, which undergoes polymerisation through different techniques. MMA synthesis is the most significant aspect of the final polymer production, hence more environmentally sustainable monomer essentially translates to greening PMMA. MMA, the methyl ester of methacrylic acid, is a specialty monomer and key building block for acrylic polymers with PMMA being the most notable product consuming more than 70% of the entire monomer produced.[22,23] MMA can also be co-polymerised with other substances in the productions of resins and polymers with versatile characteristics. One example of such a co-polymer is methyl methacrylate-butadiene-styrene (MBS), commonly used as a modifier for PVC.[22-24] The unique properties of PMMA have made it one of the most sought-after materials in the recent times and this has translated to greater demand for MMA. As at 2019, the global demand for MMA reached 3.8 million tonnes, worldwide production volume is expected to increase steadily over the years to reach 5.7 million tonnes by 2028.[18,25] Despite not being a commodity chemical per se, there are several MMA manufacturing plants distributed all over the world with sizes ranging from 1,500 to 360,000 metric tons per year.[26] Asia-Pacific is the main market in which China ranks first for production and consumption.[27]

Despite the evolution of the industrial production process for MMA over the years, very little work has been carried out to assess the emerging approaches and process based on sustainability and environmental impacts. Mostly condensed in the evaluation of at early design stage. Sugiyama[28,29] and co-workers have proposed a multi-criteria framework for early design of MMA considering 17 synthesis pathways to select the route with the best multi-objective performances, and to produce an optimized process flowsheet. This activity model integrates environmental, health and safety (EHS) evaluation with technical and economic considerations. Later Banimostafa et al.[30] evaluated the adoption of a method based on principal component analysis (PCA) for the selection of the better synthetic path for MMA (and 4-(2-methoxyethyl)-phenol). The PCA-based method was demonstrated to identify the most promising chemical routes as well as the most important evaluation categories. Andraos[31] proposed an evaluation of 18 industrial routes to MMA by a combined usage of green metrics (such as atom economy, reaction mass efficiency and process mass intensity), the reaction yield, the energy input, the benign index for waste materials, the safety-hazard index for waste materials, and safety-hazard index for input materials. It represents a robust piece of work focused on material and energy consumptions, environmental and safety impact. Song et. al[32], applied a framework of safety performance index (ISPI), which consists of chemical hazard index (flammability, explosiveness, toxicity, and reactivity) and process hazard index by unit (temperature, pressure, inventory). This was applied for evaluating inherent safety of chemical process and design to six MMA production routes. The framework is on chemical properties, process data, and chemical accident databases. The results are then compared with existing methods and experts' rankings by using three risk-rules, which are related to the experts' opinions and the tendency of decision makers. So far none LCA analyses were performed with the aim of simulating and sharing the inventories for other MMA routes rather the traditional from acetone cyanohydrin. In addition, as far as we know, no other sustainability assessment was performed on other MMA pathways able to avoid the usage of formaldehyde by producing it in-situ. The focus of this research on using LCA to investigate the progression of process improvement efforts with regards to MMA production is therefore timely as we believe it can provide the necessary foundation for further works on promoting the sustainability of one of the most popular and useful materials.

CHEMICAL BACKGROUND

The first industrial production of MMA dates to the 1930s[33], a time when very little attention was paid to environmental impacts and sustainability considerations in the design of chemical processes. So, ordinarily, the traditional process developed at this time called the acetone cyanohydrin (ACH) process becomes lacking when held to the present day's standards of more sustainable chemical process design. However, the advent of the green chemistry era has been a significant impetus to drive the much-needed turnaround in these industrial processes. The quest to "green" the industrial MMA production process has been a progressive journey. Armed with the growing understanding of the twelve principles and in true commitment to process improvement, different approaches have emerged by targeting the problematic areas identified in the traditional ACH process. In this study, we applied the LCA methodology to evaluate the possible benefits in terms of environmental impacts that can be attributed to this type of progressive implementation of the industrial production of MMA based on green chemistry principles. Below a full description of the main pathways selected for comparison is reported.

The Acetocyanohydrin process (ACH process)

The acetocyanohydrin process (ACH-MMA) starts with acetone and hydrogen cyanide to produce MMA after three major reaction steps (Scheme 1, a).[34] The first step proceeds at a mild temperature of around 40 °C with selectivity and yield greater than 90%. Excess sulphuric acid is introduced to treat the intermediate at temperatures between 80-140 °C. The final step involves treatment of the second intermediate with methanol (MeOH) to produce MMA with a selectivity of 77% and $(NH_4)HSO_4$ (ammonium bisulphate) as by product. With an overall yield in the range of 80-90% based on acetone cyanohydrin, the ACH route is a desirable process in terms of pure performance. It also starts off with significant economic advantage by using feedstocks that are by-products of industrial processes (acetone and hydrogen cyanide).

The high performance of this process is however overshadowed by undesirable realities like the use of toxic HCN and excess H_2SO_4. An estimated 1.6 kg of sulphuric acid is required to produce 1 kg of MMA because the acid acts as both a reagent and solvent for the reaction.[34] Away from the feedstocks, the route also produces a large quantity of inorganic waste in the form of $(NH_4)HSO_4$: 1.2 kg is produced for every kilogram of MMA.[27,34] A process like this with hazardous reagents, producing large amounts of inorganic waste and depending entirely on fossil feedstock is not consistent with the emerging era of incorporating green chemistry in industrial chemical processes and offers valid grounds for process improvement and innovation.

Several chemical companies have taken up the challenge of innovating around the limitations of this high performing process over the years. Mitsubishi Gas Chemical Company introduced the new ACH route[34,35] that avoids the use of sulphuric acid thus eliminating the production of ammonium bisulphate and the need for its further treatment for acid regeneration. Although this improved route is more atom efficient than the original and less toxic, it introduces an additional step to the initial pathway, and this makes it to be at an economic disadvantage. Production routes based on four carbon molecules were the next innovation in this space. Starting with C_4 molecules as feedstock is slightly advantageous with respect to atom economy considerations. With C_2 and C_3 feedstocks, a new carbon frame must be formed by adding one or two carbon atoms using C_1 compounds such as CO, HCHO or HCN whereas with C_4 feedstocks, like isobutene or tert-butanol, the carbon skeleton is used as is. Isobutene oxidation (Scheme 1, ***b***) is one of the C_4 strategies which proceeds in two steps with the production of methacrolein intermediate which can be further oxidized to methacrylic acid (MAA). While the first stage can reach high selectivity towards the methacrolein, the conversion of methacrolein intermediate to MAA remains a challenge due to catalyst limitations.[27]

Isobutene ammoxidation (Scheme 1, ***c***) is another C_4 conversion commercialised by Asahi Chemicals based on the existing knowledge of the SOHIO (Standard Oil of Ohio) process which produces acrylonitrile through the ammoxidation of propene. Asahi Chemicals found that methacrylonitrile could be produced in the same fashion starting with isobutene and they developed a catalyst by modifying the already established system used for acrylonitrile.[33] The reaction faces similar problems to those with the classic ACH process with the formation of $(NH_4)HSO_4$ waste and the use of ammonia which is not incorporated into the final product.[36]

Direct oxidative esterification (Scheme 1, ***d***) is another C_4 route by Asahi Kasei Corporation (AKC) that avoids the input of ammonia and sulphuric acid and their corresponding waste products.[36] However, it also proceeds through a methacrolein intermediate that needs to be further oxidized to MAA, a process that has already being established to be challenging with respect to catalyst formulations. AKC however developed a catalyst system based on Pd-Pb supported on core-shell structured $AuNiO_x$ nanoparticles that has proven to be effective. The performance of the Au/NiO_x at the industrial scale was verified in a 100 kt per year MMA plant in 2008 and the technology is still in use.[27,37]

Another popular approach to the production of MMA starts with a two-carbon feedstock which will require additional carbon sources to build the required carbon skeleton in MMA. The C_2 routes primarily use ethylene. Ethylene is mostly converted into an intermediate molecule with three carbon atoms, notably propionaldehyde, propionic acid, or methyl propionate. This intermediate is thereafter typically reacted with formaldehyde (FAL) to form either methacrolein, MAA or MMA depending on the reaction conditions (***e***). BASF goes the ethylene to propionaldehyde pathway before subsequent condensation with FAL.[38] However, the reaction happens in four steps which makes commercialisation tedious. The route is also heavily dependent on peculiar circumstances at BASF during its development and reproducibility has been a challenge. Evonik Industries also developed their C_2 based MMA process, called the LiMA (Leading in Methacrylates) technology,[39,40] which goes through a methacrolein intermediate. The oxidative esterification of methacrolein has been a critical point for a lot of the innovations around MMA production and Evonik was able to make significant inroad with the LiMA catalyst formulation which has been said to be making phenomenal strides where others before it stumbled. The LiMA has been successfully piloted and a 250,000 tonnes plant is expected to launch in 2023.[41]

The Alpha Lucite process and its lab-scale improvement (one-pot synthesis)

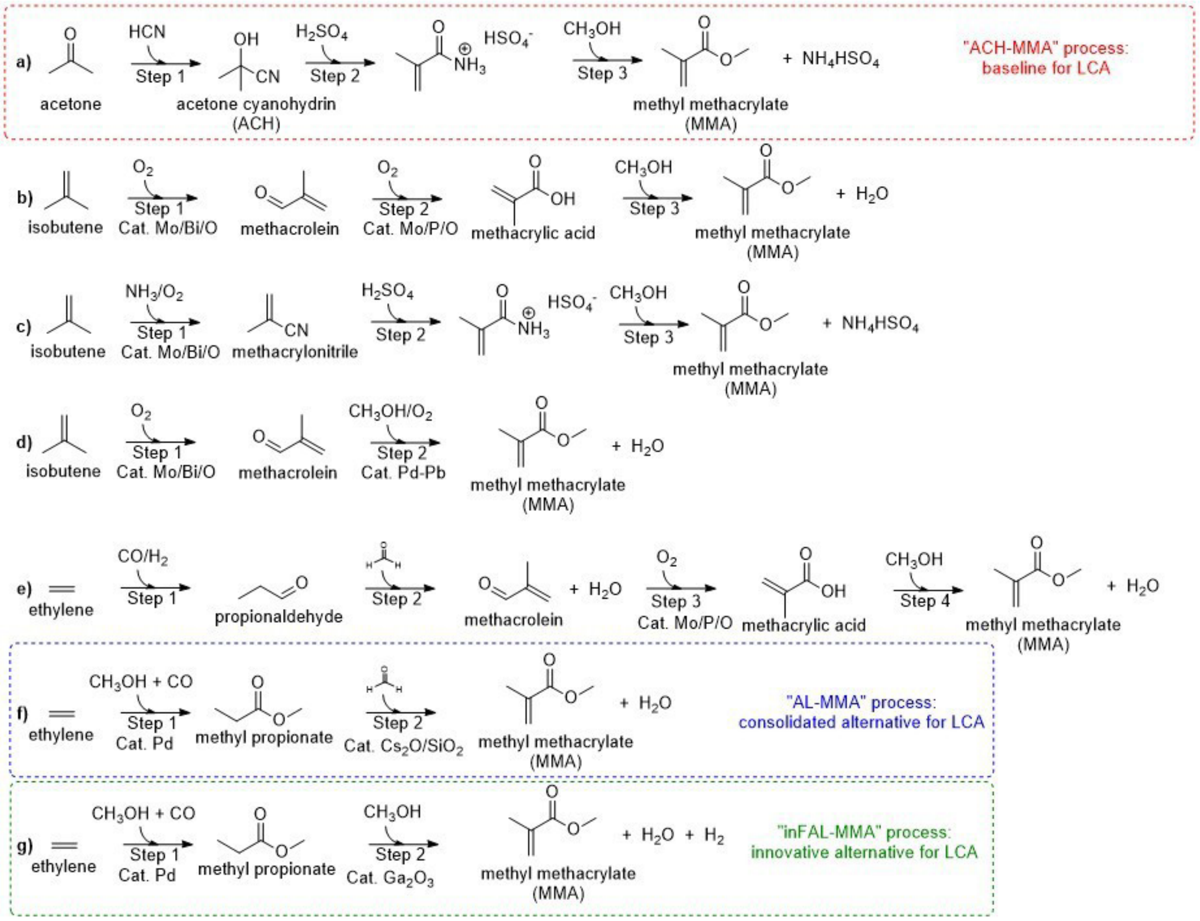
The Alpha Lucite route to MMA (AL-MMA) is a C_2 process developed by Lucite International which is now a company under the Mitsubishi group.[42] This route bypasses the common approach with methacrolein intermediate whose conversion to MAA has been plagued by catalyst limitations. It starts with ethylene and proceeds in two steps which makes it an ideal process for commercialisation. The Alpha Lucite (AL) process (Scheme 1, ***f***) is discussed in further details in the following sections. The first step involves a carbonylation of ethene with carbon monoxide coupled with esterification with methanol to build the required four carbon skeleton base. The methyl propionate (MeP) intermediate formed subsequently undergoes condensation with formaldehyde (FAL) to produce MMA. The two-step setup of the Alpha Lucite process (AL-MMA) gives it an economic edge over several other processes with longer chain of reactions. The overall industrial setup has also been optimally designed to promote process integration and on-site synthesis of inputs like FAL. The use of anhydrous formaldehyde during the second stage is essential to obtain best results, this however introduces a dehydration stage with additional energy implications. The first step of the reaction produces no by-products, with high atom economy of nearly 100%. The second step produces small amounts of heavy, relatively involatile compounds which can lead to the coking of the catalyst thereby reducing catalytic activity and selectivity.

Compared with the traditional ACH process, the AL process seems have significant advantages. Among these, the elimination of the use of hydrogen cyanide and sulphuric acid is consistent with green chemistry principles (n° 2, 3 and 5). Therefore, the Lucite technology has also witnessed significant commercial success and it is arguably the fastest growing MMA production technology. The first plant was commissioned in Singapore in 2008, it has a production capacity of 120,000 tonnes per annum and is said to be 30-40% cheaper to build and run than conventional systems.[43] Ten years later in 2018, the Saudi Methacrylates Company (SAMAC), another plant based on the Lucite technology with a production capacity of 250,000 tonnes per year of MMA monomer and 40,000 tonnes per year of PMMA commenced operations.[44] Another larger plant is scheduled to be commissioned in 2025, this time in the USA, with a proposed production capacity of 350,000 tonnes.[45]

Despite these positive figures, the AL process has some drawbacks, such as the low yields of the second step (27%) and hence multiple production cycle must be carried out to reach higher productivity levels.[46,47] There are also the issues about the production of undesirable by-products like metal complexes of methyl methacrylate which cannot be converted to any of the reaction intermediate or final product. Finally, the needs for use and store anhydrous FAL which results in elevated energy requirements for the distillation and ultimately, operation costs. If compared with the combination of HCN and H_2SO_4 of the ACH process, FAL itself has a lower hazard profile. However, it possesses inherent harmful properties and therefore been classified as belonging to the group 1 carcinogen, so there are existing concerns around its handling and storage.[48] The use of toxic substances contravenes the principle of a benign-by-design chemical industry and society.[49-51] Therefore, this naturally presents an opportunity to improve the process, make it safer and more sustainable from an environmental point of view.

Also, the AL process for the dehydration of formalin to obtain anhydrous FAL is prone to easy polymerisation of paraformaldehyde giving insoluble polyoxymethylenes, which can lead to severe fouling of transfer lines. The development of an alternative process in which anhydrous formaldehyde is produced in situ would provide a simplification over the current process. It eliminates the presence of FAL in the upstream stages of the process and in the outlet stream as the FAL formed in situ is completely converted.

Methanol has already been used as an *in-situ* source of formaldehyde (Scheme 1, g "in-situ formaldehyde process, so-called inFAL-MMA"), the most important examples, applied at industrial scale, rely on the methylation of phenolic substrates in continuous-flow, gas-phase reactors.[52-54] While it has been shown to be a good hydrogen source in hydrocarbonylation reactions with concomitant formation of FAL, the formaldehyde is converted to methyl formate. Methanol oxidation also coproduces water which as explained earlier is detrimental to coupling of FAL with methyl propionate to form MMA. Water also favours the hydrolysis of MeP into propionic acid and carboxylic acids, which are more reactive and can follow other parasitic pathways. The oxidation of dimethoxy methane offers another route for the *in-situ* generation of FAL but this reaction also produces water and by virtue of being an oxidation is more susceptible to low selectivity due to unselective oxidations. Methanol dehydrogenation therefore remains the best choice for *in-situ* generation of FAL for MMA production. As with many industrial chemical processes, the key to obtaining the best result for this reaction rests with the catalyst choice. Few catalysts have been investigated at laboratory for this reaction. Among these, we selected the Gallium oxide catalyst system prepared by De Maron et al. [55] as a basis for simulation.



Scheme 1: synthetic pathways to MMA. a) Three-step acetocyanohydrin route to MMA (ACH process); b) isobutene oxidation to MMA; c) isobutene ammoxidation to MMA; d) oxidative esterification of isobutene to MMA; e) from ethylene to MMA (Evonik's LiMA process); f) Alpha Lucite process for MMA production; g) one-step synthesis of MMA from methyl propionate and methanol.

MATERIALS AND METHODS

LCA was applied as scientific methodology to address potential environmental sustainability of three of the possible pathways described above, in particular: i) ACH-MMA (baseline), ii) AL-MMA (consolidated alternative) and iii) inFAL-MMA (innovative). LCA is a standardized approach,[6-8] able to simulate the benefits and burdens of products, processes and systems among the entire life cycle (or part thereof). The conceptual framework identifies four stages: goal and scope definition, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation.

The LCA methodology has been utilised for similar studies evaluating the potential environmental impacts associated with industrial chemical production and comparison of the different production approaches based on their level of impacts. Mostly all the sectors are covered, fossil-based industry,[56,57] bio-based fuels and chemicals,[58-61] pharmaceuticals[62] and the synthesis of new catalytic system from earth abundant metals.[63-65]. Studies presented above along with several others established the suitability of the LCA methodology for pinpointing areas where different approaches to the production of chemical compounds excel in terms of environmental performance and the possible areas where process improvement efforts should be concentrated to drive significant environmental gains.

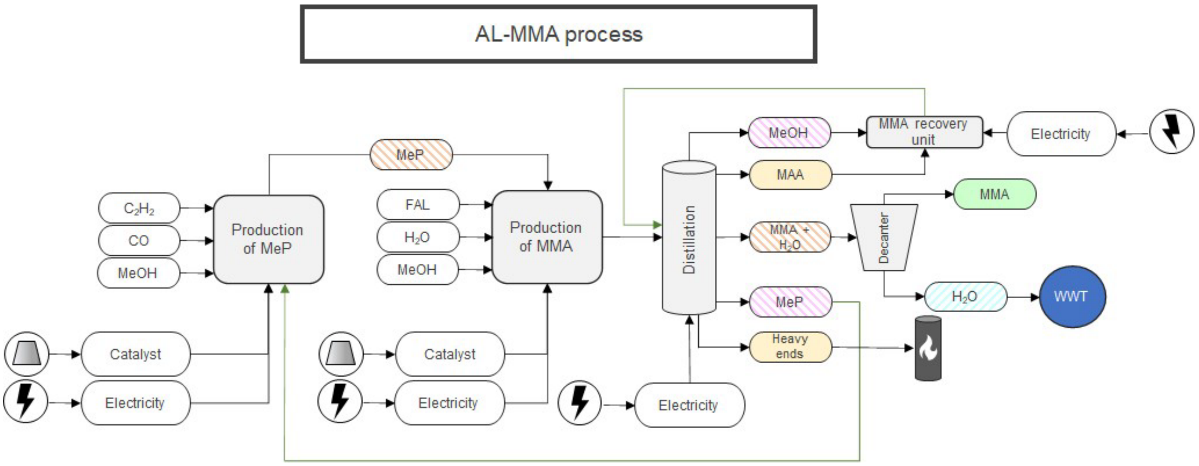
The overarching goal of this study is to see if there are indeed environmental benefits that can be attributed to the adoption of some green chemistry principle as a process improvement strategy. Specifically, we set out to establish the possibility of recording commensurate reduction in the environmental impacts attributable to MMA due to the substitution of toxic feedstocks (HCN and H_2SO_4) with seemingly fewer toxic ones (e.g., FAL) in the production process. We went further to identify the complexity of these processes that might not result in an outright gain in environmental performance as might have been envisaged.

A cradle to gate approach was adopted for the study. This system boundary does not include the polymerisation to PMMA since the approach is typically similar across different manufacturers and with significantly lower contribution to the overall process. The EoL was not considered because the versatile nature of PMMA means it can end up in a building, as part of an automobile or an artwork. All these final products have different end of life scenarios and the complexity of modelling any of this is beyond the scope of this work.

The FU of the study was settled to 1 ton of MMA; the mass balances were therefore constructed by calculating the resources needed to produce the reference quantity of MMA for each of the approaches considered. The schematic representation for MMA production according to the two main processes is represented in

. It describes the flow from feedstocks to MMA including the processes involved like catalyst, energy requirements, coproducts, wastes and purification processes. The system boundaries were expanded to accommodate the generation of the co-products (multifunctionality) of the final reaction to MMA. The avoided impacts of their production from traditional pathways were modelled to compensate for the environmental burden of their production that has been assigned 100% to MMA. **Figure S1** in ESI represents the boundaries of the ACH-MMA route. The geographical boundaries of the AL-MMA process were settled in Singapore since the first AL-MMA plant was built there. Equal assumption was carried out for the inFAL-MMA process, basically the same reaction of the AL-MMA with a in loco production of formaldehyde. This is the reason why used the Singapore electricity mix (Electricity, medium voltage {SG}| market for electricity, medium voltage | APOS, U). However, it was not possible to complete the full LCI by using other default processes for Singapore (SG) since the ecoinvent database does not provide the SG scenario for other processes rather than the electricity. Therefore, where necessary we completed the inventory using default ROW and GLO processes. In the case of ACH scenarios, used as a basis for comparison, the default global processes were adopted.

a)



b)

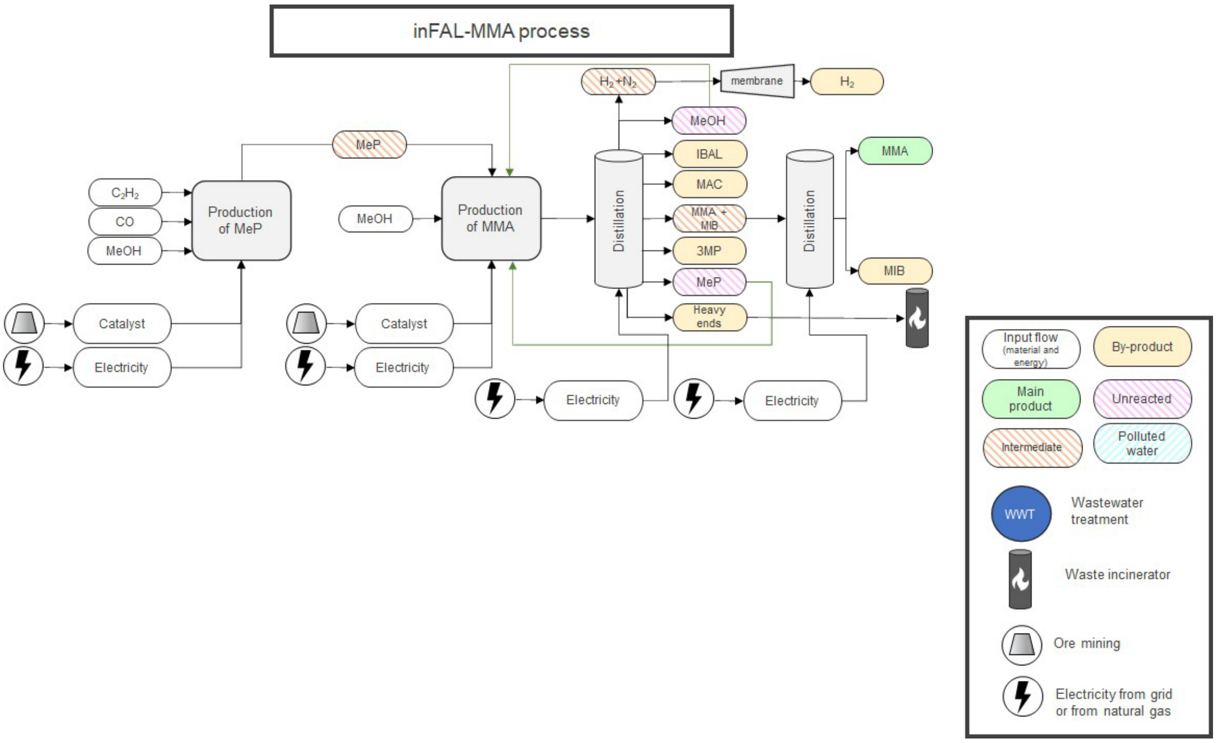


Figure 1 – System boundaries for the methyl methacrylate from; Alpha Lucite process (a) and the in-situ formaldehyde methyl methacrylate process (b).

SimaPro software (v. PhD 9.4) by PRé Consultants[66] was used for the modelling of the inventories, while ecoinvent (3.7)[67,68] and carbon minds (cm.chemicals)[69] databases were used for simulating necessary background information. The datasets in ecoinvent are available in both unit (U) and system (S) processes with the U option grouping individual processes into smaller units, phase or intermediates while the S option report flows as primary resources connected only to the final product. The U option makes contribution analysis and progressive process improvement possible since it reports impacts for each stage or intermediate product, hence it was selected for this analysis, together with the allocation at point of substitution (APOS) models. Despite the fact the consequential approach was adopted for including our by-products in the model, we decided to adopt the APOS model to have more conservative results (i.e., potentially higher burdens). In fact, the application of a consequential approach on the entire supply chains (given by the adoption of the CONSEQ ecoinvent processes) would allow more benefits from potential substitution of material/energy within the entire supply chain. However, there is no assurance the consequential approach is really respected along the chain, since we have no direct control on it, we proceed with a more conservative way. The cm.chemical database is a specialised database for the environmental assessment of plastics and chemicals. Large scale LCI datasets covering about a thousand chemicals in different geographical regions are available with this database. It is also possible to see different LCI datasets to produce a single chemical based on specific production technologies.

Uncertainty analysis

The Monte Carlo analysis was selected as the statistical method to run the uncertainty analysis. This approach is welcomed by the LCA community, thanks to its versatility. Early applications were on the building and construction sector,[70-72] right now it represents a consolidated approach within the chemical sector. The method adopts an algorithm capable of producing a series of random numbers, within the uncertainty value of every input and output taken into account in the scenarios created, for which it assumes a lognormal distribution, with a confidence interval of 95%. The pedigree matrix developed by Weidema and Wesnæs[73] was used to assess the quality of the input data in order to determine their respective uncertainty values. This quality assessment matrix was applied to the entire dataset of the scenarios ACH-MMA$_{\text{ECO-GLO}}$, AL-MMA and inFAL-MMA. The scores obtained were further used to determine the uncertainty factor and finally calculate the corresponding standard deviation (SD) for the lognormal distribution according to the **Equation 1** in ESI. Monte

Carlo simulation was carried with an iteration of 10,000 runs at a significance level $\alpha = 0.05$. Two sets of comparisons were made.

Life cycle inventories (LCI)

The inventories for the AL-MMA and inFAL-MMA scenarios were computed starting from reported reaction efficiency data. They are detailed below and in ESI. In the case of the AL-MMA process the first step is the methoxycarbonylation of ethylene to methyl propionate which involves a carbonylation reaction coupled with esterification. The catalyst developed by Lucite for this step is based on palladium biphosphine and the step is carried out in a continuous-stirred tank reactor under moderate conditions. The catalyst displays enzyme-like selectivity of >99.98% to MeP. The mass balance for the synthesis of methyl propionate is shown in **Table S1**. The second step of the AL-MMA process is the actual production of MMA which involves the condensation of the MeP produced in the first step with formaldehyde in the gas phase. It therefore became necessary to find additional strategies to balance the system by incorporating avoided impacts or possible environmental gains for the other products. Full mass balance for this process with complete lists of by products is reported in **Table S2**. MAA is one of the products identified in the AL-MMA process and it is a carboxylic acid which can esterified to with MeOH to produce MMA. The process for producing MMA from MAA was modelled according to the work of Moraru et al.[74] as showing in **Table S4** and it was incorporated into the system to improve the efficiency of the whole system. Further details are collected in ESI.

In the case of the inFAL-MMA scenario, the LCI was computed from the journal article that documented the outcome on the research focused on identifying different catalyst compositions that can promote the *in-situ* dehydrogenation of MeOH to FAL.[55] The first step is like that earlier discussed for the AL-MMA as (methoxycarbonylation of ethylene to MeP). The second step however uses MeOH instead of FAL and the catalytic system that showed the best results for the inFAL-MMA is the gallium oxide.[55] The FAL in the AL-MMA process is typically synthesised through the oxidative dehydrogenation of MeOH followed by other process steps. The direct MeOH process is therefore an innovative move following the principles of green chemistry by reducing the overall number of steps, as well as the avoided handling and usage of a hazardous reagent (FAL). In addition to MMA, this route also produces several other products which is not surprising considering that data source is a journal article focused on estimating the ability of different catalyst combinations to achieve the desired objectives. The complete mass balance for this process is shown in **Table S5**. In the same manner it was done for AL-MMA, the avoided impacts of all the other products of the inFAL-MMA process were modelled and incorporated into the system in terms of avoided dedicated synthesis.

The data source for computing the MB for the synthesis of MeP is a 2011 patent assigned to Lucite International UK Limited.[75], while another Lucite patent published in 2016 was used[76] for AL-MMA. Further details about the inFAL-MMA route, as well as the energy requirements and catalyst amount are collected in ESI.

The catalyst system for AL-MMA is based on caesium and zirconium on a silica support with a composition of 0.93wt Zr, 6.35wt Cs with the balance being silica. Data reported in patent[75] showed that 3g of catalyst was used to produce about 15g of MMA, scaling up to the FU of this study using linear proportion will result in a staggering amount of catalyst. The catalyst system for inFAL-MMA is a Gallium oxide from the study[55] earlier referenced. Although the LCI data sources included catalyst compositions and amount, but it was difficult to estimate the quantity of catalyst required for scaling up these processes. Moraru et al.[74] modelled the esterification of MAA to MMA, to produce 2,324 kg of MMA, the catalyst requirement for this process was used as the basis for computation of the quantity of catalyst in conjunction with established peer reviewed catalyst modelling procedure[77]. The procedure consists in including the quantity of metals consumed per catalytic system starting from the stoichiometric amount of the formula.

The LCI for ACH-MMA was adopted from existing cm.chemicals and ecoinvent databases and the scenarios from these dataset are labelled as ACH-MMA$_{CMC}$ and ACH-MMA$_{ECO}$ respectively. In the case of ecoinvent “Methyl methacrylate {RoW}| market for methyl methacrylate | APOS, U” was selected. The LCI dataset for this product was reported to have been derived from the Eco-profiles of the European plastics industry (PlasticsEurope).[66] The inventory comprises of long list of all the individual flows from cradle to gate without any grouping or classification into sub or unit processes embedded in the overall system unit. For the cm.chemicals scenario “Methyl methacrylate {GLO}| technology mix, cyanohydrin route” was selected. The LCI dataset for the process was described to have been obtained by modelling all relevant production steps based on representative data on the production technology used in individual plants along the supply chain. The cm.chemicals methodology is explained further in the database document.[69] As with ecoinvent, the inventory also comprises of long list of all the individual flows with no grouping into sub-processes. It is expected that some variability will be recorded in the ACH-MMA from these two databases based on the differences in how they were derived. For this analysis, the results obtained with the ecoinvent databases will be discussed since it has links to industry players.

Life cycle impact assessment

The strategy adopted for the LCIA in this study is to have two different comparative assessment setups: ACH-MMA vs AL-MMA and AL-MMA vs inFAL-MMA. AL-MMA occupies a central spot in these setups as the designated fast rising industrial alternative. These two setups therefore allow for comparison with the conventional industrial route and a distinct second comparison with the lab-based process which has been adjudged to be a greener version of the AL-MMA.

LCIA was carried out by using both single and multi-impact assessment methods. The Cumulative Energy Demand (CED, v.1.11) is a resource-oriented, single-issue indicator that evaluates the direct and indirect energy consumed during the extraction, manufacturing, and disposal of the raw and auxiliary materials.[78] It essentially gives an indication of depletion of both renewable and non-renewable resources that can be attributed to a system by expressing the consumption in terms of energy equivalent (GJ eq). There are several other environmental impacts beyond resources depletion that must be evaluated for a holistic assessment. The ReCiPe2016 method (v.1.07) being a multi-issue approach provides the needed tools for this. With the 18 problem-oriented (*midpoint*) categories that can be further grouped into three major damage-oriented (*endpoint*) categories, ReCiPe2016 method covers a wide range of environmental issues that are consistent with the goal of this study.[79,80] The Midpoint (H) v.1.07 measures impact by focusing on single environmental problems and the results are reported across 18 problem-oriented categories like global warming potential (GWP); stratospheric ozone depletion (SOD), ionizing radiation (IR); ozone formation, human health (OZ_HH), ozone formation, terrestrial ecosystems (OZ_TE); fine particulate matter formation (FPM); terrestrial acidification (TA); freshwater eutrophication (FWEu); marine eutrophication (Meu); terrestrial ecotoxicity (TEc); freshwater ecotoxicity (FEc); marine ecotoxicity (MEc); human carcinogenic toxicity (HCT); human non-carcinogenic toxicity (HNCT); land use (LU); mineral resource scarcity (MRS); fossil resource scarcity (FRS) and water consumption (WC).

The use of LCA for holistic environmental sustainability assessment of chemical processes faces a crucial limitation in the lack of a risk assessment component. The potential for a hazard occurrence is not built into the LCA tool as it only measures actual flow of materials or discharge. So, to look at the MMA processes through a risk assessment lens, a further tool called GREEN MOTION^{TM} was incorporated into this study. GREEN MOTION^{TM} is a peer-reviewed software[81] able to measure the safety and environmental impacts of products based on 12 principles of green chemistry. It is an open access method able to evaluate the process greenness by the use of seven indicators: i) the nature of the raw material, ii) the type of solvent used, iii) the hazardousness and toxicity potential of the reagents, iv) the reaction conditions (e.g., temperature and pressure), v) the process, vi) the hazardousness and toxicity of the final product and vii) the amount of waste released. It assigns values in the range 0-100% on the base of the grade of completion of each index. Higher is the score achieved and greener is the whole reaction. Despite it was designed primarily for fragrance and flavour products, GREEN MOTION^{TM} was selected as additional methodology to investigate the potential risk associated with the handling of certain chemicals. In fact, it evaluates the potential hazard and toxicity of a reaction based on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) symbols on the reagents used in the product synthesis. The advantages in combining LCA with GREEN MOTION^{TM} in chemical production processes was already discussed in literature.[82]

RESULTS AND DISCUSSION

The first approach to the LCIA is resources consumption. CED is considered a valuable screening indicator of the overall impact of products related with the highest material and energy intensity.[83,84] The extent of the resource requirement is measured across both renewable and non-renewable categories and results are expressed in terms of energy equivalent (GJ eq. in this case). Cumulative scores are shown in **Figure 2 – Resources intensity comparison of AL-MMA with ecoinvent and cm chemical scenarios of ACH-MMA using Cumulative Energy Demand method, version 1.11.Figure 2** and **Figure3.**

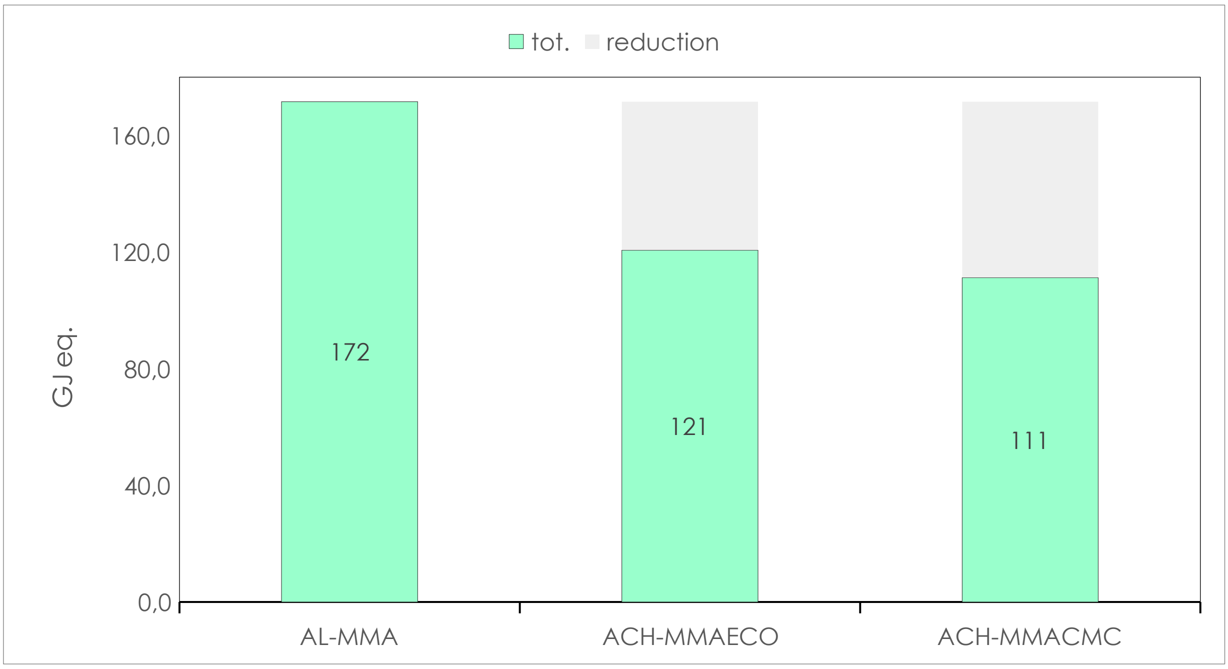


Figure 2 – Resources intensity comparison of AL-MMA with ecoinvent and cm chemical scenarios of ACH-MMA using Cumulative Energy Demand method, version 1.11. Grey bars represent the percentage difference between impacts recorded for the ACH-MMA scenario and AL-MMA.

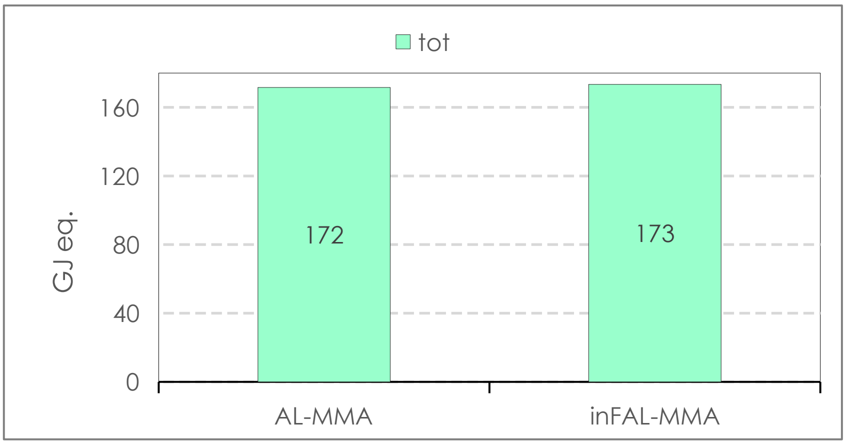


Figure 3 – Resources intensity comparison of AL-MMA with inFAL-MMA using Cumulative Energy Demand method, version 1.11. Results showing similar total resources requirements (energy and materials) for both scenarios.

The CED therefore gives a quick insight to the overall resource and energy consumption (also embodied) of the different pathways to MMA. In the direct comparison with the two different scenarios of the ACH-MMA, AL-MMA has the highest resource requirements (+30-35%). Both pathways are fossil-based so the substances consumed are primarily non-renewable in the fossil sub-category (**Table S6-S7**), so the negligible contribution of renewables to the overall is in line with expectations. The difference in the CED of both processes stems from the absolute fossil resource consumption and results in **Table S7** shows that AL-MMA consumes significantly more (+32-36% on the fossil category). An analysis on the network of processes and material consumption within the supply chains of both processes is presented as Sankey-based diagrams (**Figure S2** and **Figure S3**) and it confirms that both processes rely heavily on petroleum products and natural gas for the synthesis of fossil-based precursor and also for the electrical energy entirely based on natural gas.

In the direct comparison of AL-MMA and inFAL-MMA (Figure 3 and **Table S8**), scores show that both routes have a similar resource intensity profile. This may not be surprising considering that they are similar process differing only in the substitution of formaldehyde with methanol with the direct usage of MeOH resulting in lower number of cumulative reaction steps, by avoiding the oxidative dehydrogenation step necessary to generate FAL from methanol ($CH_3OH + 0.5\ O_2 \rightarrow CH_2O + H_2O$, with 93% reaction selectivity), and the handling of FAL at plant.

However, given that the inFAL-MMA is a lab-based process which does not benefit from the efficiency and scale up advantages of the industrialized and patented AL-MMA, a deep dive is necessary. Contribution analysis (**Table S9** and **Figure S4**) showed that the process benefitted from modelled avoided impact scenarios which offset a lot of the energy and resource demand. In fact, as described in the inventory section, inFAL-MMA scenario provides the generation of methacrolein, isobutyraldehyde, methyl isobutyrate, methylated 3-pentanone and hydrogen per FU. Without these avoided impacts, the result of the CED evaluation will be about 50% higher than the results obtained.

Table S10 shows the results. Three alternatives were investigated, by comparing the AL-MMA production pathway to two ACH-MMA scenarios (ACH-MMA$_{ECO}$ and ACH-MMA$_{CMC}$ as detailed in the LCI section). AL-MMA recorded the lowest impacts in 6 categories (OZ_HH, FPM, OZ_TE, TA and MEu), as well as highest impacts in GWP, FWEu, FEc, MEc, HCT, HNCT, LU, MRS, and FRS. The ecoinvent scenario for the ACH-MMA recorded the lowest impacts in 9 categories (SOD, IR, FWEu, TEc, FEc, MEc, HNCT, LU, and MRS) and the highest impact in 3 categories (FPM, TA, and WC). Results obtained for MRS and FRS using ReCiPe 2016 midpoint are consistent with those obtained from the CED method as AL-MMA recorded the highest impacts in both assessments which are related to resources and energy consumption. To gain precise insights into the part of the process with the highest contribution to the observed environmental impacts, a contribution analysis was carried out on the modelled AL-MMA process only. From the results reported in **Figure 4** (**Table S12**), EE consumption and the synthesis of the precursor MeP are the most critical hotspots for all the impact categories measured except MRS which is solely attributable to the MMA production step. Impacts recorded under the MRS category is linked to the catalyst system in the AL-MMA step which comprises of both zirconium and caesium metals as active phases in the catalyst composition. This result showed that caesium in particular is responsible for most the bulk of impacts under the MRS (98.6%). The reason is the characterization factor used in the MRS category (kg Cu eq/kg metal), the highest among those of the other metals (**Table S10**). According to the report[80] the characterization factor is based on the absolute surplus ore potential (ASOP) value of the mineral resource. Different from other 18 metals, in the case of Cs and other elements not included in this list the ASOP-value cannot be derived on the basis of empirical cumulative grade-tonnage relationships, and the developers used the price of the mineral resource to estimate its ASOP-value. According to literature,[85] the price of 99.8% (metal basis) caesium ranged between $76.97 and $97.86 per gram in 2022, the highest on market after Rhodium. The reason could be associated to its stocks worldwide in the form of pollucite, estimated to be less than 200 kt. Pollucite, in fact, still represents the principal Cs ore mineral,[85] which contains 5-32% caesium oxide. The mineral is mainly found in association with lithium-rich, lepidolite-bearing or petalite bearing zoned granite pegmatites. Therefore, Cs reserves are estimated based on the occurrence of pollucite, a primary lithium-caesium-rubidium mineral. No reliable data are, therefore, available to determine reserves for specific countries. However, the main commercial source worldwide is in Bernic Lake, Manito (Canada). Nonetheless, ReCiPe 2016 still remains the best analysis method for the MRS category in this case, since it represents the only method which includes the characterization factors for all the minerals here addressed It is however impossible to have a direct comparison with the ACH-MMA catalyst system because the LCI obtained from the database is in the form of system unit (S), basically a list of resources in the form of primary substances without any indication whether the catalyst system is included or not.

Table 1 – Life cycle impact assessment of AL-MMA vs inFAL-MMA at the midpoint level (ReCiPe 2016 v.1.07).

Impact category	**Unit**	**AL-MMA**	**inFAL-MMA**
GWP	kg CO_2 eq	8.74E+03	1.23E+04
SOD	kg CFC11 eq	3.01E-03	4.88E-03
IR	kBq Co-60 eq	1.58E+02	2.62E+02
OZ_HH	kg NOx eq	8.61E+00	1.05E+01
FPM	kg PM2.5 eq	4.07E+00	4.53E+00
OZ_TE	kg NOx eq	8.69E+00	1.00E+01
TA	kg SO_2 eq	9.28E+00	9.06E+00
FWEu	kg P eq	1.93E+00	-1.06E+00
MEu	kg N eq	1.85E-01	3.00E-01
TEc	kg 1,4-DCB	2.73E+03	2.67E+03
FEc	kg 1,4-DCB	1.30E+02	1.78E+02
MEc	kg 1,4-DCB	1.65E+02	2.24E+02
HCT	kg 1,4-DCB	1.81E+02	2.22E+02
HNCT	kg 1,4-DCB	2.09E+03	2.53E+03
LU	m^2a crop eq	4.70E+02	7.66E+02
MRS	kg Cu eq	6.89E+02	8.54E+01
FRS	kg oil eq	3.63E+03	3.63E+03
WC	m^3	2.66E+01	2.56E+01

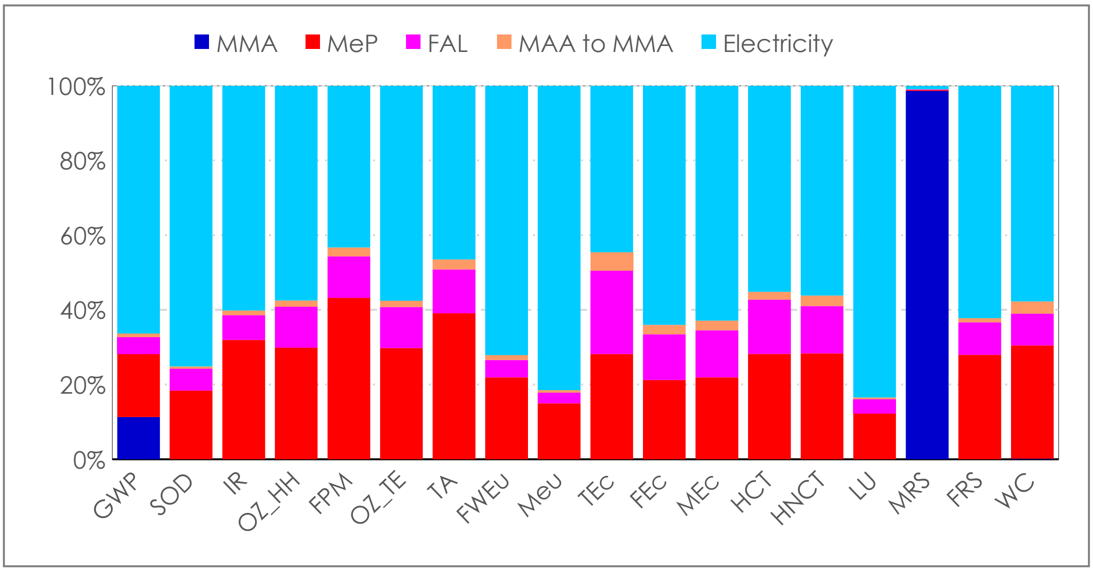


Figure 4 – Analysis of the contributions of the different process component of the AL-MMA process to the impacts recorded using ReCiPe 2016 method, version 1.07, midpoint level. Different colour of bars represents the contribution of each component or flow.

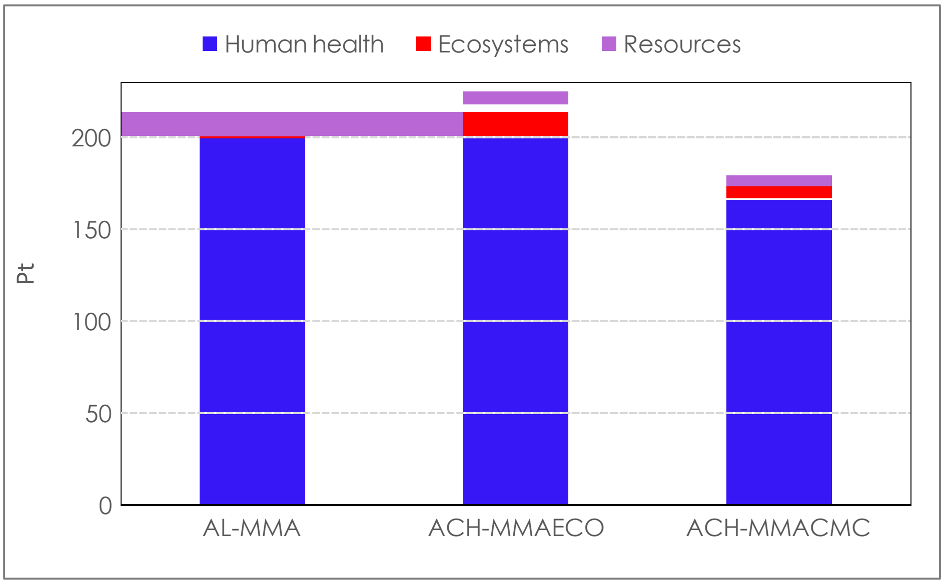


Figure 5 – Single score damage assessment comparison of AL-MMA with both ecoinvent and cm chemicals scenarios of ACH-MMA using ReCiPe 2016 method, version 1.07.

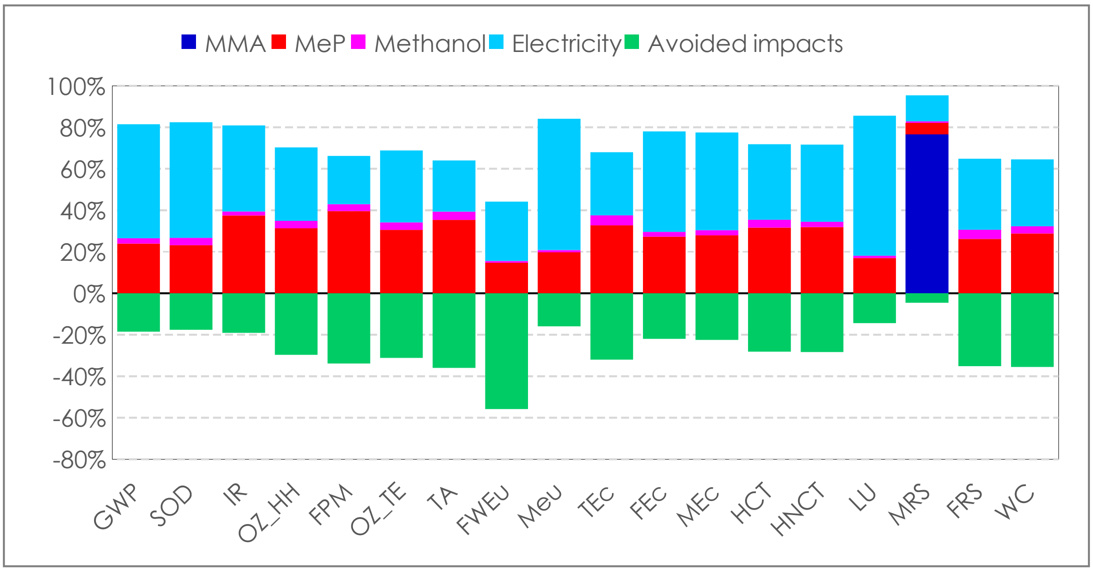


Figure *6* - Analysis of the contributions of the different process component of the inFAL-MMA process to the impacts recorded using ReCiPe 2016 method, version 1.07, midpoint level. Different colour of bars represents the contribution of each component or flow. Green bars represent avoided impacts (negative values).

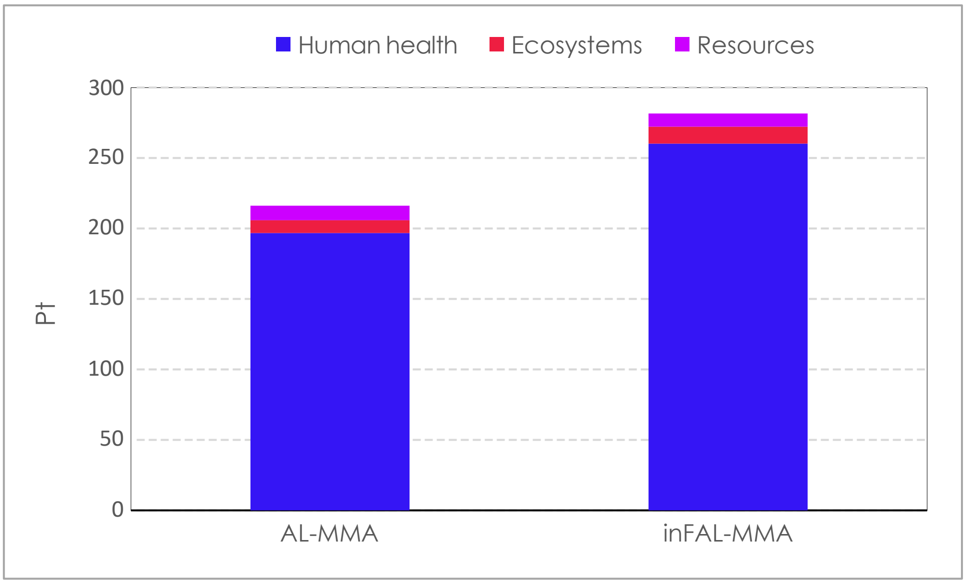


Figure 7 - Single score damage assessment comparison of AL-MMA with inFAL-MMA at endpoint using ReCiPe 2016 method version 1.07.

The perceived toxicity of the ACH-MMA process is one of the driving forces for this study and environmental burden related to this was expected to be prominent in the HCT, HnCT, TEc, FEc, and MEc categories. However, results obtained from the midpoint (**Table S11**) showed that ACH-MMA ecoinvent scenario recorded lower impacts all these categories. Taking the impact assessment with the ReCiPe 2016 method to the damage points level presented as single scores in **Figure 5** however showed that ecoinvent ACH-MMA recorded higher impacts in the broader human health category. It also has higher overall single score suggesting that cumulatively it is more harmful than all other scenarios.

The comparison between the AL-MMA and the inFAL-MMA processes in terms of the ReCiPe 2016 midpoint has showed that both processes have a comparable profile of environmental burdens as shown in **Table 1**. Large differences in burdens are rare and up to 50% difference in impact value are only recorded in 2 of the 18 categories; MRS and FEu. Impacts recorded for AL-MMA is higher than that of inFAL-MMA by more than 80% in the MRS category which confirms the earlier assessment about the importance of the metals in the catalyst composition for the AL-MMA process. The catalyst system for AL-MMA is based on Caesium that, according with ReCiPe 2016, has impacts that are over 100 times higher than Gallium, the active metal in the inFAL-MMA catalyst system. In the FEu category, the innovative scenario recorded negative values implying that, cumulatively, the process is preventing freshwater eutrophication. This is attributable to the modelled avoided impacts scenarios such as the avoidance of natural gas usage due to hydrogen production by the process, as well as the avoidance production of methacrolein, isobutyraldehyde, methylated 3-pentanone and methyl isobutyrate (all recovered from the reaction). GWP category denotes the results achieved by the inFAL-MMA scenario are +28% if compared to those of the AL-MMA. This is not surprising given the higher number of co-products that necessitates the consumption of an extensive amount of electricity for distillation and further recovery as shown in **Figure 6** (**Table S13**).

As stated in the introduction, the inFAL-MMA process was developed at laboratory scale as a valuable option to reduce the potential toxicity of handling and using FAL in the traditional AL-MMA. However, the expected reduction is not immediately apparent with the results obtained at the midpoint (**Table 1**). While inFAL-MMA marginally outperforms AL-MMA in the TEc and FEc categories, with impacts that are 10% and 2% lower respectively, it recorded higher contribution in the other categories related to measuring toxicity and hazard. In HCT and HnCT categories, its burdens are higher by 16% and 21% respectively. Further assessment with the ReCiPe 2016 method at the damage categories with results presented as single scores in **Figure 7** shows that inFAL-MMA has a higher overall single cumulative score. This implies that has higher environmental impacts across all categories. This trend is mostly related to the lower yield of the overall inFAL-MMA route. Higher process efficiency will translate to lesser material consumption which can give the inFAL a significant boost. However, it is important to pointed out the inFAL-MMA is a lab-based pathway, which needs to be optimized before upscaling.

Sensitivity Analysis

According to literature[31] the whole system has a total energy requirement of 1917 kJ/mol MMA produced. As described in the LCI section, in the case of AL-MMA and inFAL-MMA scenarios the energy source was assumed to be covered 100% by EE. Given the significant contribution of the electricity to the observed impacts, a sensitivity analysis was performed by changing the energy source from the average EE mix of Singapore, mainly thermoelectric energy from natural gas (see **Table S14** in ESI),[86] to direct heating with natural gas, burned in combustion furnace located at plant (simulated by Electricity, medium voltage {SG}| market for electricity, medium voltage | APOS, U). For the AL-MMA, total CED seem to be reduced by 35% (**Figure S5**). Similar trend is also recorded with the ReCiPe 2016 (**Figure S7**) except for MRS which remains almost the same buttressing the fact that it is not influenced by energy consumption.

Owing to its higher energy consumption, inFAL-MMA showed even greater reduction in impacts across all the selected categories as shown in **Figure S6** and **Figure S8**. CED reduced by 63% and varying levels of mitigation were recorded across the midpoint categories. It is worthy to note that midpoint categories measuring toxicity witnessed significant impact reductions, up to 80% lower in FEc and at least 70% lower in all the others including HCT, HNCT, TEc and MEc.

Given the poor process efficiency of inFAL-MMA process, a further sensitivity analysis was carried out using catalyst selectivity value for the AL-MMAprocess by means 81% compared to 27% for the inFAL-MMA catalytic system. The selectivity was chosen for this sensitivity because inFAL-MMA catalyst achieves a higher conversion compared to AL-MMA catalyst (47.5% to 21.1%), hence where the process falls significantly behind is in the selectivity of the catalyst to MMA. Results in **Table S15** and **Figure S9** show a relatively stable impact in the CED category, which increases cumulatively of <1%. The lack of a huge decrease in impacts recorded despite the over 50% reduction in material consumption is due to the original modelling adopted which expanded the system to account for the avoided impacts of the different by-products. The reason is due to the fact that the increase in the process efficiency allows a reduction in the amount of the inlet substances (MeP and MeOH), followed by a decrease in the quantity of molecules recovered and flagged as "avoided impacts". Therefore, given that the CED is a single-issue method aimed at addressing the direct/embodied consumption of resources and energy flows the two scenarios achieve similar results. Different results are obtained through ReCiPe 2016 which reflects significant reductions in 13 out of the 18 midpoint categories (see **Table S17** and **Figure S10**). The reduction achieves value ≥ -30% for the categories of GWP, SOD, IR, MEu, MEc and LU. For other environmental indicators, like OZ_HH, FPM, OZ_TE, TEc and HNCT, the improvements fall in the range -14% ≤ x ≤ -23%. This trend reflects the potential mitigation in the impacts due to the reduction in the chemical and electricity quantities used as input in the model, which points out a decrease also in other categories not directly linked with the resources depletion but with the damages on human health and ecosystem quality due to their extraction.

Uncertainty Analysis

The first uncertainty analysis (Unc.An._1) between AL-MMA and the ACH-MMA$_{\text{ECO-GLO}}$. The second (Unc.An._2) the AL-MMA was compared with inFAL-MMA. The results of the Monte Carlo analysis are shown as histogram bars for the different impact categories assessed. Figure 8 shows the results of the analysis at midpoint for Unc.An._1. Results earlier obtained are consistent in at least 90% of the Monte Carlo iterations in all but two of the categories, WC and HCT. In the case of Unc.An._2, the simulations return a different level of insight as the probability of obtaining results consistent with the original analysis were lower than 90% in 11 out of the 18 categories as shown in Figure 9. Despite this trend, the robustness of the models created is still confirmed.

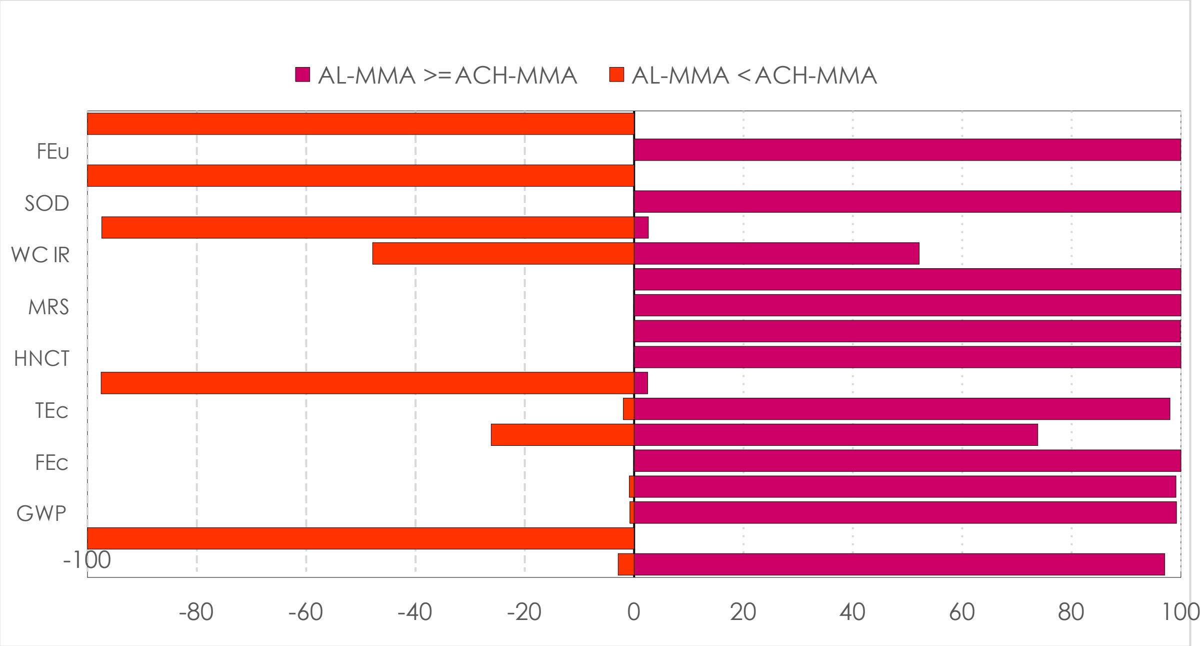


Figure 8 - Unc.An._1 (AL-MMA vs ACH-MMA$_{ECO-GLO}$) at the midpoint level using ReCiPe 2016 v.1.07. Red bars represent the frequency (number of runs) the ACH-MMA$_{ECO-GLO}$ scenario achieves greater impacts rather than the AL-MMA, per category. Purple bars represent the frequency (number of runs) the AL-MMA scenario achieves greater impacts rather than the ACH-MMA$_{ECO-GLO}$, per category.

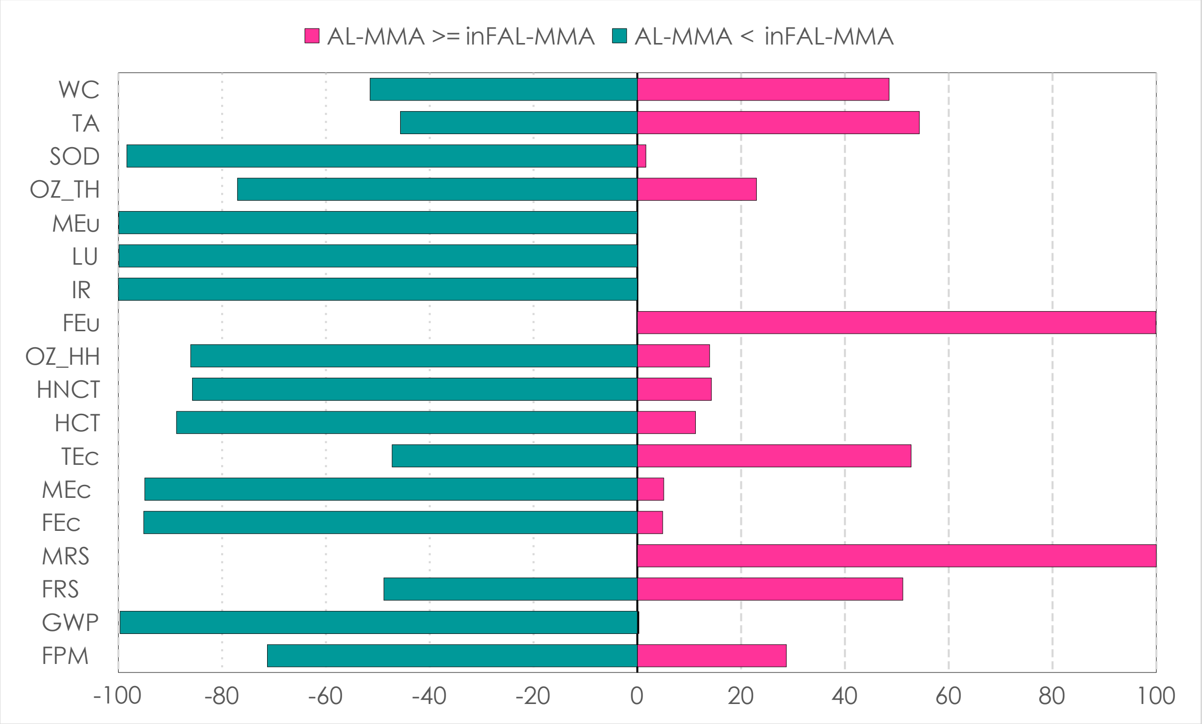


Figure 9 - Unc.An._2 (AL-MMA vs inFAL-MMA) at the midpoint level using ReCiPe 2016 v.1.07. Blue bars represent the frequency (number of runs) the inFAL-MMA scenario

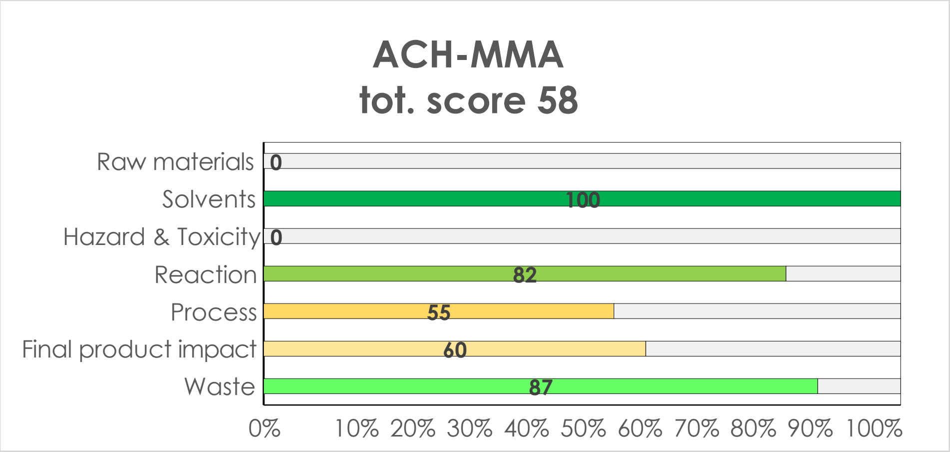
achieves greater impacts rather than the AL-MMA, per category. Pink bars represent the frequency (number of runs) the AL-MMA scenario achieves greater impacts rather than the inFAL-MMA, per category.

GREEN MOTION^{TM} analysis

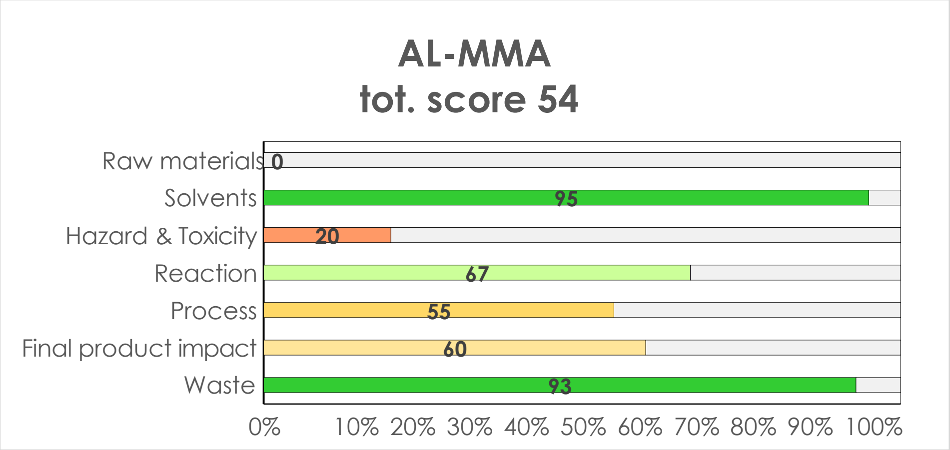
With the mixed results obtained in the categories related to toxicity and hazard assessment, an additional approach to estimate the potential toxicity of the scenarios was explored. A full risk assessment analysis is out the scope of this study, so the GREEN MOTION^{TM} tool was adopted.

This tool was used to compare the three scenarios with a specific focus on the hazard and toxicity. As shown in **Figure 10**, the usage of GREEN MOTION^{TM} allows to point out, first, the difference between the three MMA routes to what it concerns the hazard and toxic indicator. The pathway from ACH achieves the cumulative score of 0%, ranking itself as the worst. This outcome is in line with the nature of the acetone cyanohydrin, substance potentially fatal if swallowed, inhaled or accidentally touched without personal protective equipment. In addition, ACH is a highly flammable liquid and vapour, which may cause serious eye irritation and drowsiness or dizziness.[87] Other interesting outcomes of the tool are the scores obtained for the AL-MMA and inFAL-MMA scenarios. In the first case, the use of FAL as starting reagent contributes to reducing the potential impacts by increasing the index of +20%. However, the formaldehyde is not considered a proper green reagent and the pathway is still far from being labelled as completely safe. On the contrary, the tool highlights the advantages of substitution FAL with its production *in situ* from MeOH. The inFAL-MMA process, even if developed on lab-scale only, achieves +30% versus AL-MMA and + 50% respect to ACH-MMA. Therefore, despite the fact the GREEN MOTION^{TM} evaluation is determined solely based on the GHS labels on reagents and intermediates, the results for inFAL-MMA confirm the route was developed by encompassing the principle of a benign-by-design synthesis that avoids (where possible) the usage of hazardous substances. Other categories included in the GREEN MOTION^{TM} tool include raw materials in which all the three scenarios assessed scored zero because the feedstock used in the synthesis are synthetic materials obtained by chemical process and are also do not contain any renewable carbon content from biobased precursors. In line with green chemistry principles the solvent category assigns higher score to processes in which no solvents are used, and the rating here begins to decline based on the characteristics of solvent including whether they are renewable, safe, or carcinogenic. The reaction category is judged based on parameters of the reactions such as yield, atom economy, number of solvents used, whether it is a protection or deprotection step, distillation step and the duration of the reaction. ACH-MMA with a high yield as mentioned earlier has the best outcome in this category. The "process" indicator focused mainly on the energy consumption of the process assessed through parameters like pressure of the system, source, and duration of heating and/or cooling, presence of a distillation step, and the inclusion of well-known hazardous or energy intensive stages. inFAL-MMA performed best in this category. The "product" index relates to peculiar properties of MMA itself and this is the same for all scenarios. Finally, the "waste" category is derived exclusively from the E-factor metric[88,89] and the AL-MMA pathway performed best. This is because ACH-MMA process is intrinsically more polluting while the catalyst for inFAL-MMA is less efficient than the AL-MMA catalyst.

a)



b)



c)

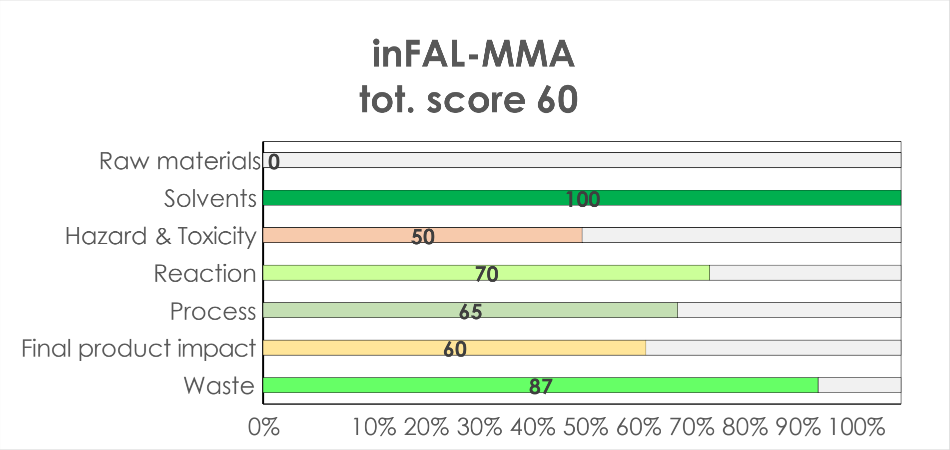


Figure 10 - GREEN MOTION^{TM} evaluation for ACH-MMA (a), AL-MMA (b) and inFAL-MMA (c). Higher is the value (%), greener is the route for each category.

CONCLUSION

This study applied the LCA methodology to evaluate the potential environmental burdens of MMA production for the two prominent industrial production routes ACH-MMA and AL-MMA and a lab scale process (inFAL-MMA) with a view to identify opportunity areas where significant gains can be recorded to reduce impacts. One of the important rationales for this assessment is to see how toxicity of materials and reagents will manifest in the measured impacts. The results obtained in this study with respect to the categories that border on toxicity assessments do not suggest that there are significant gains associated with substituting hazardous materials, such as HCN and related compounds in the ACH-MMA process with carcinogenic FAL or less toxic MeOH in AL-MMA and inFAL-MMA respectively.

The results measured in the toxicity categories leads to the uncovering of a limitation of this study which is strictly related to the LCA methodology. LCA's approach to estimation of potential environmental burdens associated with a process relies on actual flows of substances included within the system boundaries. This means LCA cannot predict the potential risk or impacted related to the usage of a hazardous substance if there is no actual leakage or flow to the environment. Therefore, in order to assess the inherent risk of handling a hazardous substance (e.g., FAL) or the benefits related to its substitution with a safer alternative (e.g., MeOH) an integration with a risk assessment analysis must be contemplated.[90] This limitation is responsible for some of the mixed results recorded where expected scenarios with known propensity for toxic and hazardous occurrence did not necessarily record overwhelmingly higher impacts because there was no actual release of toxic emissions to be assessed. While preliminary assessment was carried with the GREEN MOTION™ tool, the use of a more robust risk and toxicological assessment tool is recommended.

On process improvement, the AL-MMA can benefit from substituting fossil-based ethylene with bio-ethylene to produce methyl propionate and using electrical energy sources that are less dependent on natural gas. These two actions will result in significant gains in the resource consumption category where AL-MMA lagsACH-MMA.

AL-MMA process can also register significant improvement by finding an alternative to caesium in the catalyst composition (not an easy feat) or implementing catalyst recycling.

Implementing these actions can contribute to mitigating the total impact of the AL-MMA in respect to the MRS category where it is distinctively worse off than all other scenarios.

Overall, results of this study suggests that the journey towards the sustainable production of PMMA will be a balancing act of different important process contributions. A synergistic effect will be required from raw material choices to energy sources as well as catalyst composition. inFAL-MMA offers a promising perspective that is hampered by the efficiency of the catalyst system as shown by the results obtained in this study, further catalyst optimisation resulting in better yield can improve the environmental performance of the process.

Supporting Information:

System boundaries for the ACH-MMA scenarios, life cycle inventory descriptions and assumptions, standard deviation evaluation (eq.1), mass balances, results of sensitivity analysis and additional results.

List of abbreviations

ACH	Acetone cyanohydrin
ACH-MMA	Methyl methacrylate from Acetone cyanohydrin process
ACH-MMA$_{CM}$	ACH-MMA modelled from CM Chemicals database for global scenario
ACH-MMA$_{EC}$	ACH-MMA modelled from ecoinvent database for global scenario
AKC	Asahi Kasei Corporation
AL-MMA	Methyl methacrylate from Alpha Lucite process
ASOP	Absolute Surplus Ore Potential
CED	Cumulative energy demand
CMC	CM Chemicals database
DALY	Disability-adjusted life year
EE	Electricity
EU	European Union
FAL	Formaldehyde
FEc	Freshwater ecotoxicity
FPM	Fine particulate matter formation
FRS	Fossil resource scarcity
FWEu	Freshwater eutrophication
GWP	Global warming
HCT	Human carcinogenic toxicity
HNCT	Human non-carcinogenic toxicity
inFAL-MMA	Methyl methacrylate from lab-scale in-situ formaldehyde process
IR	Ionizing radiation
ISO	International Organisation for Standardisation
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LCT	Life Cycle Thinking
LU	Land Use
MAA	Methacrylic acid
MB	Mass Balance
MC	Monte Carlo Simulation
MEc	Marine Ecotoxicity
MeOH	Methanol
MeP	Methyl Propionate
MEu	Marine Eutrophication
MMA	Methyl Methacrylate
MRS	Mineral Resource Scarcity
OZ_HH	Ozone Formation, Human Health
OZ_TE	Ozone Formation, Terrestrial Ecosystems

PMMA	Polymethyl Methacrylate
SOD	Stratospheric Ozone Depletion
Unc.An.	Uncertainty Analysis
TA	Terrestrial Acidification
TEc	Terrestrial Ecotoxicity
WC	Water Consumption

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Several routes exist for the production of MMA; life cycle assessment can compare them in terms of environmental sustainability.